**ANP 204
INTRODUCTION TO AGRICULTURAL BIOCHEMISTRY**

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INTRODUCTION

Introductory Agricultural Biochemistry (ANP 204) is an introduction to the chemistry of nutrients in foods and feedstuffs and their metabolism in living organisms. Food is a vital need of living organisms and its component nutrients are vital for animals in the performance of the following functions:

1. Provision of essential elements for repairing deteriorating cells.
2. Provision of raw materials for synthesis of body tissues in growth.
3. Source of energy for vital processes in the body: growth, work or production.
4. Generation of heat necessary for maintaining body temperature.
5. Provision of raw materials for the production of milk, meat, egg or wool.

The feed nutrients of importance to be studied in this course are carbohydrates, proteins and their component amino acids, nucleic acids and nucleoproteins, lipids, minerals and vitamins. The nature of enzymes and hormones will also be studied. Though they do function in a nutritional capacity, they are proteins that are essential in the maintenance of metabolism in living cells.

These nutrients function in many important physiological processes in the body and their deficiency can result in metabolic disorders in the animal.

COURSE AIM

This course aims to provide information on the chemical nature of the different classes of nutrients in a bid to increase our understanding and appreciation of their roles in chemical and biological processes concerned with the living process.

COURSE OBJECTIVES

At the end of this course, you should be able to understand:

- The chemistry and importance of carbohydrates and their relevance in nutrition.
- The properties of proteins and their various metabolic forms and functions.
- The role of amino acids as building blocks of proteins and only in this form can proteins be absorbed and utilized for maintenance of physical well being.
- The role of nucleic acids and nucleoproteins in genetics, reproduction and transmission of hereditary factors.

- The chemistry of lipids and its importance in physiological processes.
- The roles of minerals and vitamins in the maintenance of homeostatic balance and mediation of metabolic reactions in the skeleton, tissues, body fluids, digestive juices, etc.
- The effects of nutrients deficiencies on the state of health of the living animal.
- The inexhaustible roles of enzymes and hormones in animal metabolism and their modes of operation.

WORKING THROUGH THE COURSE

This course involves that you would spend a lot of time to read. The content of this material is very dense and requires you to spend some time to study it. This accounts for the great effort put into its development in the attempt to make it easy to read and comprehensible. Nevertheless, the effort required of you is tremendous and you are advised to avail yourself of the opportunity of comparing knowledge with your peers.

THE COURSE MATERIALS

You will be provided with the following materials;
Course guide
Study units
In addition, the course comes with a list of recommended textbooks which though are not compulsory for you to acquire, are necessary as supplements to the course material.

STUDY UNITS

The following are the study units contained in this course:

Unit 1: The Chemistry of Carbohydrates
The chemistry of carbohydrates is discussed, considering its definition, importance, general properties, classifications and nomenclature.

Unit 2: Structure, Properties and Classification of Proteins
Owing to the broad nature of proteins, its general characteristics, structure, physical and chemical properties, classifications and functional diversity are studied in this unit.

Unit 3: Amino acids
The chemistry of amino acids as building blocks for the synthesis of proteins, are studied. This includes their classifications, physical and chemical properties and optical characteristics.

Unit 4: Nucleic acids and Nucleoproteins
The chemistry of nucleoproteins as important constituents of chromatins involved in cell division, reproduction and transmission of hereditary factors are studied under the following: definitions, structures, functions, forms and other nitrogenous compounds of metabolic importance.

Unit 5: The Chemistry of Lipids
The definition, importance, classification and structures of some common lipids and fatty acids are discussed.

Unit 6: Minerals in animal nutrition
Essential minerals, their fundamental roles and factors determining their utilization are discussed. Also studied are sources of minerals and minerals supplements as well as specific functions and deficiencies of Calcium (Ca), Phosphorus (P), Magnesium (Mg), Sodium (Na), Potassium (K), Chlorine (Cl), Sulphur (S), Manganese (Mn), Iron (Fe), Copper (Cu) and Zinc (Zn).

Unit 7: The Chemistry of Vitamins, Coenzymes and their functions
Vitamins of importance are studied in depth, highlighting their structural chemistry, functions, synthesis, dietary sources and deficiency symptoms.

Unit 8: The nature, classification and function of enzymes and hormones.
The definition, nature, functions, limiting factors, nomenclature and classification of enzymes and hormones are discussed. Principles of hormonal action and control mechanisms are also discussed and a listing of hormones of the pituitary and hypothalamus, thyroid, calcium metabolism, adrenal cortex, adrenal medulla, gonads, pancreas and gastrointestinal tract and their functions are presented.

TEXTBOOKS
More recent editions of these books are recommended for further reading:
- Chessworth, J.M., Stuchbury, T. and Scaife J.R (2003): Agricultural Biochemistry 4th Edition Published by Chapman and Hull.
- Maynard, L. A., Loosli, J.K, F.H Harold and R.S Warner (1993). Animal Nutrition, 7th Edition. Published by Tata McGraw Hill Publishing Company Limited
- McDonald, P., Edwards, R.A and Greenhalgh, J.F.D (2003): Animal Nutrition, 4th Edition, pp 58-89.Longman Scientific and

Technical and John Wiley and Sons, Inc, New York. ISBN 0-582-40903-9.

- Robert K. Murray, Peter A Mayes, Daryl K. Granner and Victor W. Rodwell (1990) 22nd Edition, pp 547-562. Appleton and Lange, SanMateo, CA/Norfolk, CT.
- Ross J.S. and K.J.W., Wilson (2001). Foundations of Anatomy and Physiology, 8th Ed. London: Churchill Livingstone.
- Zubay, G (1993): Biochemistry, 3rd edition. Published by Wm. C. Brown Publishers.

ASSESSMENT

There are two components of assessment for this course. The Tutor Marked Assignment (TMA), and the end of course examination.

TUTOR- MARKED ASSIGNMENT (TMA)

The TMA is the continuous assessment component of your course. It accounts for 30% of the total score. You will be given 4 TMAs to answer. Three of these must be answered before you are allowed to sit for the end of course examination. The TMAs would be given to you by your facilitator and returned after you have done the assignment.

END OF COURSE EXAMINATION

This examination concludes the assessment for the course. It constitutes 70% of the whole course. You will be informed of the time for the examination. It may or may not coincide with the university semester examination.

We wish you success in this course and hope your appreciation of agricultural biochemistry has been further enhanced by your exposure to this course.

Best wishes.

MAIN COURSE

CONTENT   **PAGE**

MODULE 1

Unit 1   The Chemistry Of Carbohydrates
Unit 2   Structure, Properties and Classification of Proteins
Unit 3   Amino Acids
Unit 4   Nucleic Acids and Nucleoproteins

UNIT 1   THE CHEMISTRY OF CARBOHYDRATES

CONTENTS

1.0   INTRODUCTION

Carbohydrates make up most of the organic structures of all plants. It is as well present to some extent in all animals. Carbohydrates in plants are produced by the process of photosynthesis (the most important chemical reaction in nature). During photosynthesis, radiant energy (solar energy) from the sun is captured by chlorophyll and changed to chemical energy, which in turn supports formation of glucose from carbon dioxide and water. This overall reaction can be represented by the equation below.

$$6CO_2 + 6H_2O \xrightarrow[\text{chlorophyll}]{\text{sunlight}} C_6H_{12}O_6 + 6O_2 \text{ (sugar)}$$
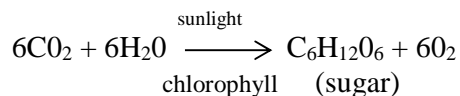
The animal life is basically dependent on the process of photosynthesis.

2.0 OBJECTIVES

At the end of this, you should be able to understand:

- different classes of carbohydrates; and
- their chemical structures and functions.

3.0 MAIN CONTENT

What are Carbohydrates?

Carbohydrates simply put, mean hydrated carbon because many of them can be represented by the simple stoichoimetric formula (CH20)n. This formula is an over-simplification because many carbohydrates (saccharides) are modified, and contain amino, sulphate and phosphate groups.

Generally speaking, carbohydrates are a group of organic compounds that include sugars and related compounds. However, chemically, carbohydrates are polyhydroxy aldehydes and ketones, or substances which yield them (aldehydes and ketones) upon hydrolysis. In this respect, **the group termed carbohydrates includes sugars, starches, cellulose, gums, pectins, saponins, glucosinolates, cyanogenic glucosides, lectins, glycogen, chitin,** etc.

3.1 Importance of Carbohydrates

Carbohydrates are extremely versatile molecules essential to every kind of living organism. Carbohydrates are among the most abundant constituents of plants and animals. They serve the following functions:
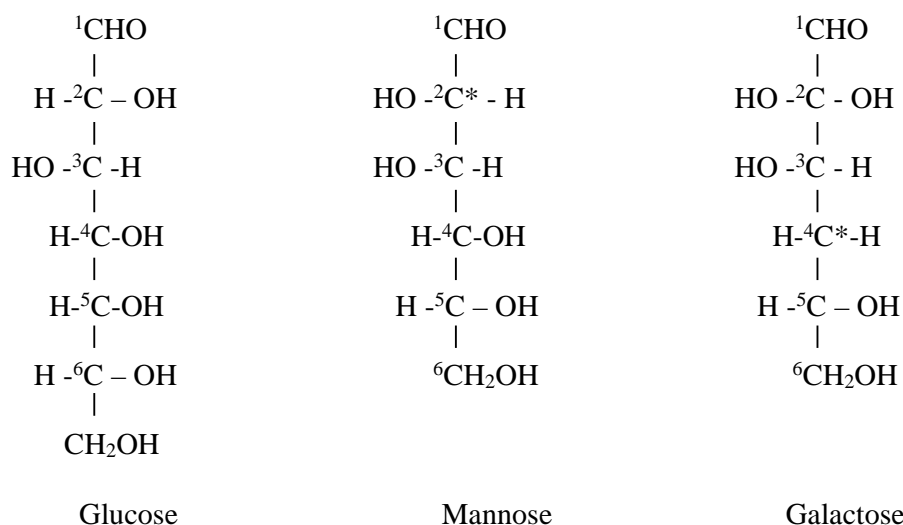
1. As major storehouse of chemical energy for carrying out life processes.

2. They serve as sources of raw materials for chemical synthesis, e.g. milk is synthesised from two kinds of carbohydrates namely, galactose and glucose.

3. They serve as supportive structural components in plants, e.g. cellulose, lignin, hemicellulose, etc.

4.   Carbohydrates are essential in the genetic control of development and growth of living cells. Ribonucleic acid (RNA) and deoxyribonucleic acid (DNA)-the genetic materials contain ribose sugar, a form of carbohydrate.

5.   Some kinds of carbohydrates protect plants against infections, e.g. polyphenolics, saponins, etc.

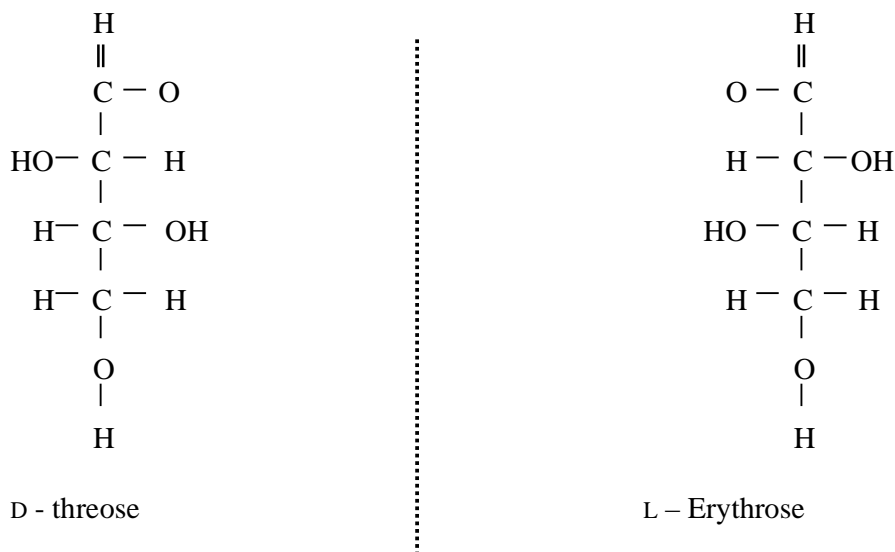## 3.2   Some General Properties of Carbohydrates

Many of the carbohydrates may contain the same number of atoms and the same kind of groups yet behave differently, i.e. same molecular formula but different structural formulae. Example, the C6H12O6 represents sixteen different simple sugars. The different structural formulae are due to different arrangement of the constituent groups of the molecular in space. This phenomenon is called **stereoisomerism** (space isomerism) and these differently arranged sugars are referred as **stereoisomers**.

An illustration of this phenomenon will be given by examining three of the sixteen stereoisomers of C6H12O6. These three stereoisomers are glucose, mannose and galactose.

$$^1CHO \qquad\qquad ^1CHO \qquad\qquad ^1CHO$$
$$|\qquad\qquad\qquad |\qquad\qquad\qquad |$$
$$H - {}^2C - OH \qquad HO - {}^2C^* - H \qquad HO - {}^2C - OH$$
$$|\qquad\qquad\qquad |\qquad\qquad\qquad |$$
$$HO - {}^3C - H \qquad HO - {}^3C - H \qquad HO - {}^3C - H$$
$$|\qquad\qquad\qquad |\qquad\qquad\qquad |$$
$$H - {}^4C - OH \qquad H - {}^4C - OH \qquad H - {}^4C^* - H$$
$$|\qquad\qquad\qquad |\qquad\qquad\qquad |$$
$$H - {}^5C - OH \qquad H - {}^5C - OH \qquad H - {}^5C - OH$$
$$|\qquad\qquad\qquad |\qquad\qquad\qquad |$$
$$H - {}^6C - OH \qquad {}^6CH_2OH \qquad\qquad {}^6CH_2OH$$
$$|$$
$$CH_2OH$$

Glucose   Mannose   Galactose

A closer look at the structures of mannose and galactose will show that they (mannose and galactose) would have assumed the structure of glucose but for a change in the positions of OH group on carbon 2 and 4 for mannose and galactose respectively. The carbon atoms involved are in asterisks. Other structures (stereo isomers) do not exist naturally in nature.

Carbohydrates also exhibit a phenomenon called **enantiomers**. Enantiomers are compounds with the same chemical formula but exist in two forms – one of the forms being a mirror image of the other. This phenomenon is common with monosaccharides because they (monosaccharides) tend to have more than one chiral carbon, which results in their having two types of stereoisomers. An example of this stereoisomer can be illustrated with the monosaccharides, Threose and Erythrose.

```
        H                                    H
        ‖                                    ‖
        C — O                          O — C
        |                                    |
 HO— C — H                        H — C —OH
        |                                    |
    H— C — OH                    HO — C — H
        |                                    |
    H— C — H                       H — C — H
        |                                    |
        O                                    O
        |                                    |
        H                                    H

   D - threose                        L – Erythrose
```

*   d-erythrose and l – erythrose are mixing

The enantiomers for threose and erythrose are arranged according to the manner in which the substituents are arranged about the asymmetric carbon atoms. The naming by l and d (for "dextrorotatory" and "Levorotatory") is according to a convention established by Emil Fisher. The carbohydrates also exhibit the property of **optical activity** and therefore exist as **optical isomers**. When carbohydrates are placed in a **polarimeter; an instrument for studying the interaction of polarized light with optically active substances** (Fig. 1) the resulting light is either circularly polarized to the right or left. When the plane polarized light is rotated clockwise (i.e. to the right) the substance is classified as **dextrorotatory** (d-), but when rotated counterclockwise (anticlockwise-i.e. to the left), the substance is termed **levorotatory** (l-).

However, when equal amount of d and l substances are mixed (DL) together, the resultant **racemic** is optically inactive.
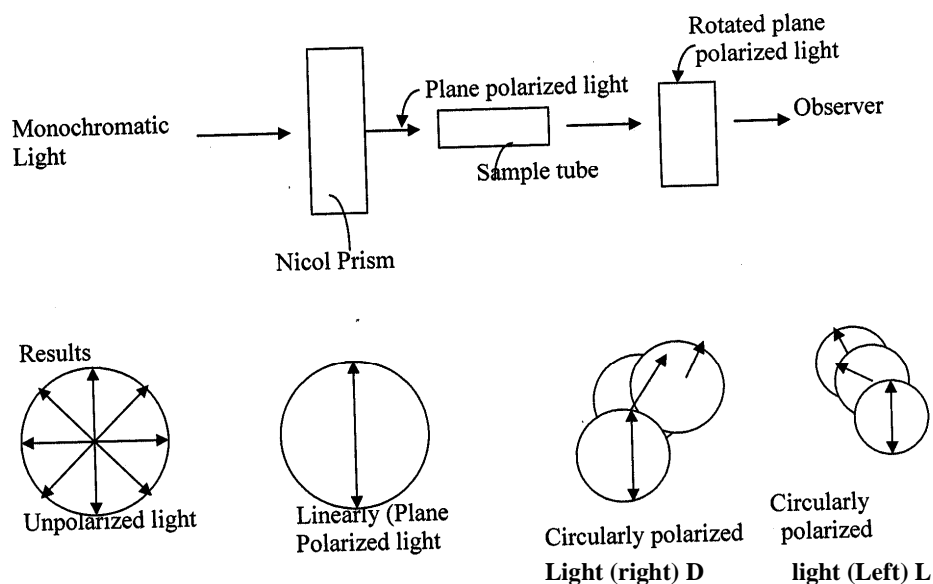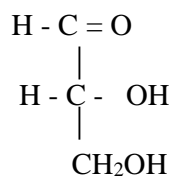
3.3 Classification of Carbohydrates

Carbohydrates are classified into three broad groups, namely:

a)   Monosaccacharides
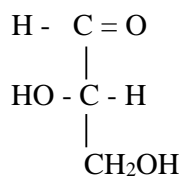b)   Oligosaccahrides
c)   Polysaccharides

We will now take each of these carbohydrates (above) and discuss them in details.

The type of carbonyl group is denoted by the prefix of **aldo**-for an aldehyde and **keto**-for a ketone, e.g. glyceraldehyde is an aldo-triose. The structures of some common monosaccharides are given below.
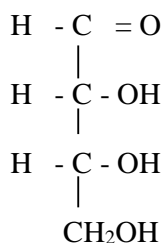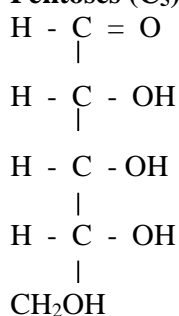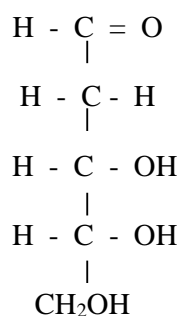
Trioses (C3)

```
H - C = O              H -  C = O
    |                       |
H - C -  OH           HO - C - H
    |                       |
   CH2OH                   CH2OH
```

D-glycerose   L-glycerose

Tetroses (C$_4$)

```
H  - C  = O
       |
H  - C - OH
       |
H  - C - OH
       |
     CH₂OH
```

D-erythrose

Pentoses (C$_5$)

```
H - C = O              H - C = O              H - C = O
    |                      |                      |
H - C - OH             H - C - H              H - C - OH
    |                      |                      |
H - C - OH             H - C - OH             HO - C - H
    |                      |                      |
H - C - OH             H - C - OH             H - C - OH
    |                      |                      |
CH₂OH                  CH₂OH                  CH₂OH
```
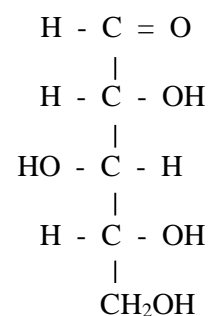
D-ribose (RNA)   2-deoxy-D-ribose (DNA)   D-xylose (hemicellulose)

3.3.1 Monosaccharides

The monosaccharides are also referred to as simple or monomeric sugars. The monosaccharide is the fundamental unit from which all carbohydrates are formed. Monosaccharides are therefore the simplest carbohydrates.
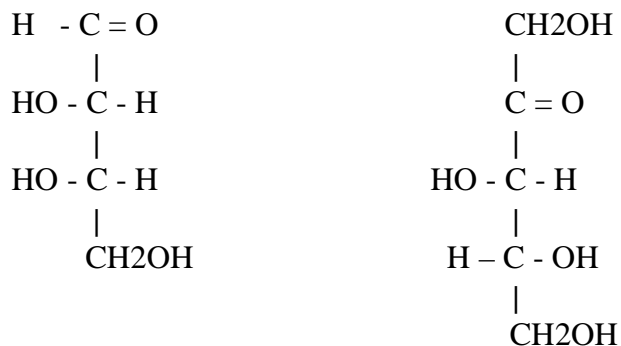
The monosaccharide can be represented by the empirical formular (CH2OH)n when 'n' a whole number is equal or greater than the value 3. The smallest molecules usually regarded as monosaccharides are the trioses with n = 3 (The suffix –ose is commonly used to designate compounds as saccharides).

Monosaccharides containing 2 to 10 carbon atoms have been synthesized, and many occur in nature.

3.3.1.1 Naming of Sugars

The chemical names of sugars and many complex carbohydrates end with the suffix **-ose**. They are also named on a basis of the number of
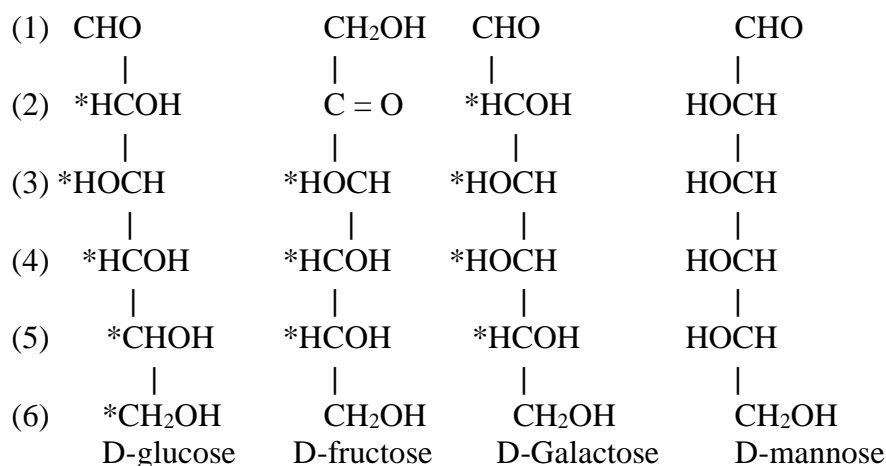
carbon atoms that they contain; tri- for three, and tetra-, petra, hex-, and hept- for 4, 5, 6, and 7, respectively.

```
H   - C = O                          CH2OH
     |                                 |
HO - C - H                            C = O
     |                                 |
HO - C - H                      HO - C - H
   |                                 |
     CH2OH                     H – C - OH
                                     |
                                     CH2OH
```

L – arabinose (Gums)   D-xylulose
                              (Phosphogluconate pathway)

Hexoses (C_6)

```
(1)  CHO              CH₂OH    CHO                 CHO
      |                 |       |                   |
(2)  *HCOH            C = O    *HCOH               HOCH
      |                 |       |                   |
(3) *HOCH            *HOCH    *HOCH               HOCH
      |                 |       |                   |
(4)  *HCOH           *HCOH    *HOCH               HOCH
      |                 |       |                   |
(5)   *CHOH          *HCOH    *HCOH               HOCH
      |                 |       |                   |
(6)   *CH₂OH         CH₂OH    CH₂OH               CH₂OH
    D-glucose      D-fructose   D-Galactose       D-mannose
```

Note that all the hexoses above are aldehydes except fructose which is a ketone. Because of the presence of asymmetric carbon atoms (labeled with an asterisk) a number of stereoisomers are possible.

Some monosaccharides occur in nature while others are synthetic. The hexoses and pentoses are the most important of the simple sugars. The monosaccharides or simple sugars are generally well-crystallined solids, soluble in water, and have a more or less sweet taste.

Pentoses and hexoses with 5 and 6 carbon atoms respectively have the potential to form very stable ring structures via internal **hemiacetal** formation. The bond angles characteristics of carbon and oxygen bonding are such that rings containing fewer than five atoms are strained to some extent, whereas five-or six-numbered rings are easily formed.

In principle, aldotetroses can also form five numbered ring structure, but they rarely do. Hemiacetals with five-membered rings are called **furanoses,** while those hemicacetals with six-membered rings are called **pyranoses** (see figures below). However, we should note that in cases where either five or six-membered rings are possible, the six-membered ring usually predominates. For example, for glucose less than 0.5% of the furanose form exists at equilibrium. Why? Reasons for this are not yet clear, but furanoses and pyranoses are more realistically represented by pentagons or hexagons as in **Hawthorne Convention.** In another way the structures can also be represented as straight chain showing the acetal bonding as described in the **Fisher Projection**.
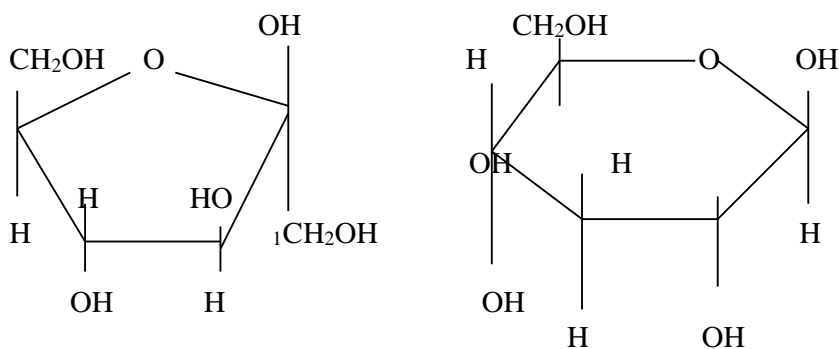
Fructose ($C_6H_{12}O_6$) (Fructofuranose)   β-D-glucose in the pyranose (glucopyranos)

 Ring structures of six carbon atom compounds (Hawthorne convention)
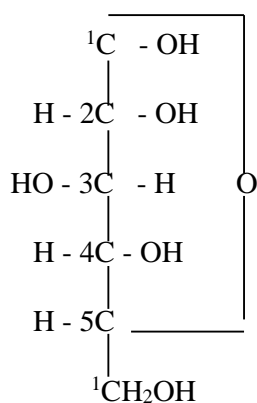
    D – glucose **(Fisher Projection)**

3.3.2 Oligosaccharides

The oligosaccharides contain sugars with 2 – 10 glucose units joined together by glycosidic bonds. The oligosaccharides are therefore formed by the combination (coming together) of 2 or more (maximum

of 10) of the monomers. The monomer sugars may be of same sugars or different monomer sugars. Examples of some common oligosaccharides are mentioned below:

a)   Disaccharides – made up of 2 monomer sugars, e.g. sucrose, maltose, cellobiose.
b)   Trisaccharides – made up of 3 monomer sugars, e.g. raffinose
c)   Tetrasaccharides – made up of 4 monomer sugars, e.g. stachyose
d)   Pentasaccharides – made up of 5 monomer sugars, e.g. verbascose.
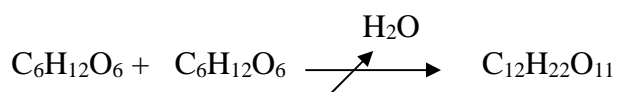
3.3.3 Disaccharides

The simplest and biologically most important oligosaccharides are the **disaccharides**, made up of glycose units, e.g. sucrose, lactose, maltose, cellobiose, gentiobiose. The types of monomer sugars that make up these disaccharides are shown in Table 1.

Table 1   Composition of some Disaccharide Sugars

Disaccharide	Structure
Sucrose	Glucose + Fructose
Lactose	Glucose + Galactose
Trehalose	Glucose + Glucose
Maltose	Glucose + Glucose
Cellobiose	Glucose + Glucose
Gentiobiose	Glucose + Glucose

A look at the table above shows that glucose appeared as a constituent of all the disaccharide. This underscores the importance of glucose as a substance in the nutrition of plants and animals. Secondly, a look at maltose, cellobiose and gentiobiose showed that these disaccharides contain only glucose units. The question now is that how can two glucose units combine to give three different products. This may appear confusing at first. A little explanation is therefore needed at this stage. This will depend firstly on whether the connecting sugars are □ or β type and secondly it will also depend on the points at which the sugars are connected to each other. These points are illustrated by discussing how the disaccharides are formed from two units of monomers.
The disaccharides derive their name from the fact that they are a combination of two molecules of monosaccharides. Their general formulae, C12H22O11 indicates that one molecule of water has been eliminated as the two monosaccharides combined.

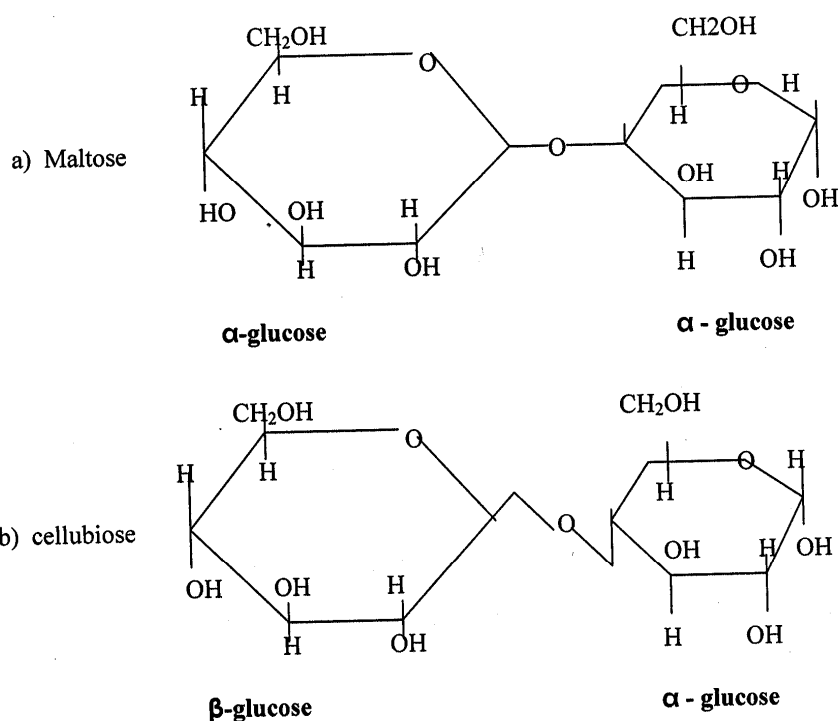$$C_6H_{12}O_6 + C_6H_{12}O_6 \xrightarrow{\quad H_2O \quad} C_{12}H_{22}O_{11}$$
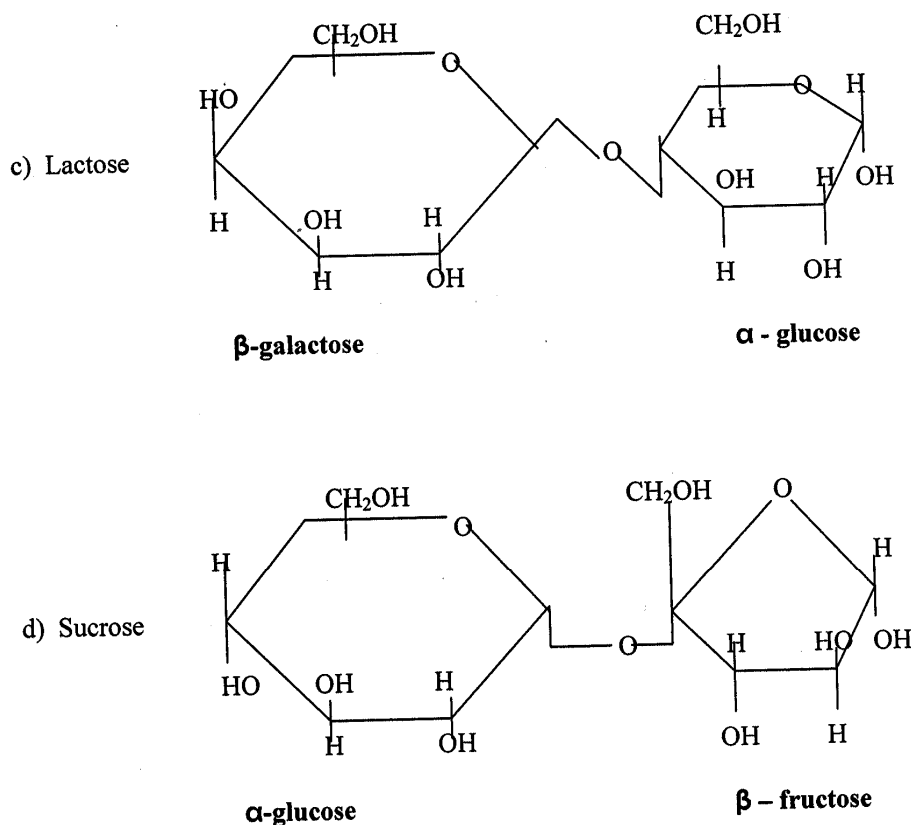
3.3.3.1 Formation of Disaccharides

Two molecules of simple sugars (monomers) are linked together by an acetal to form a disaccharide. The two simple sugars may either be similar or different. The following features therefore distinguish one disaccharide from another.

a)   The two specific sugars involved and their stereo configuration. (Remember the stereoisomerism discussed in 3.3).

b)   The carbons involved in the linkage. Most common linkages are $1\to1$, $1\to2$, $1\to4$ and $1\to6$.

c)   The order (arrangement) of the two monomers.

d)   The anomeric configuration of the hydroxyl group on carbon 1 of each glucose units.

The disaccharide with a bond between the 1 carbon of α – glucose and 4 carbon of another α-glucose is called a **maltose.** The bond is called α – 1, 4 glycosidic link. If however the left hand sugar has been in the β – form before linking then the compound would be a β–linked disaccharide. The compound of this sort which is comparable to maltose is called a **cellobiose**. Lactose, the sugar found in milk resembles cellobiose but the left hand sugar is galactose instead of glucose. The structures of some common disaccharides are shown below.

Common disaccharides

a) Maltose

α-glucose   α - glucose

b) cellubiose

β-glucose   α - glucose

c) Lactose

β-galactose　　　　　　　　　　　**α - glucose**

d) Sucrose

α-glucose　　　　　　　　　　**β – fructose**

Note: With the exception of sucrose, the ring of the right hand glucose unit can open exposing a free aldehyde group and giving reducing properties to the sugars. Also, the disaccharides are soluble in water, though to varying levels.

3.3.3.2 Sucrose (Cane Sugar)

Sucrose is made up of a combination of one molecule of d -glucose and one molecule of d -fructose. It occurs in sugar cane hence the synonym "cause sugar" and also in beets (major sources of commercial sugar). Sucrose also occurs in ripe fruits, in tree sap (maple sugar), and in many fruits and vegetables. Sucrose is dextrorotatory but it is not a reducing sugar as it has no free aldehyde or ketone group. When hydrolyzed by dilute acid or the enzyme sucrose, sucrose splits into two constituents monosaccharides. The resulting sugar is levorotatory. Since the hydrolysis thus results in a change from dextrorotation to levorotation, the process is called **inversion** and the mixture of glucose and fructose is often termed **invert sugar**. Such a process is the way by which honey bees convert sucrose of plant nectar to honey.

3.3.3.3 Maltose (Malt Sugar)

This disaccharide consists of 2 molecules of □ – D – glucose joined together in an α - 1, 4 linkage. The position of H on the number 1 carbon atom molecule (a) is the α position. Note that the number 6 carbon atoms are in configuration. Maltose derives its name from the fact that it is produced commercially from starch by the action of malt, obtained from germination barley which contains a starch hydrolyzing enzyme distaste.

3.3.3.4 Cellobiose

Cellobiose consists of 2 molecules of B – D glucose joined together in a β – 1, 4 linkage. This linkage is the fundamental one for the cellulose molecule and cannot be split by mammalian enzyme. It can be split, however, by microbial and fungal enzymes or acid. Cellobiose does not occur in free form in nature but only as a component of glucose polymers.

3.3.3.5 Lactose (Milk Sugar)

This is the sugar of milk and consists of one molecule of □ – D – glucose and one molecule of β –D- galactose joined in a linkage. This linkage can be separated by the enzymes lactase or by the addition of acid. It is a reducing sugar and is only one-sixth as sweet as sucrose. Lactose is of special interest in nutrition, because it makes up nearly half of the solids of milk and because it does not occur in nature except as a product of the mammary gland.   Having discussed the mono-and disaccharides we shall now focus on the third and last class of carbohydrates – the polysaccharides.

3.3.4 Polysaccharides

The carbohydrates consisting of 10 or more monosaccharide are referred to as **polysaccharides**. They may be considered as condensation of polymers in which the monosaccharides (or their derivatives such as amino sugars and uronic acids) are joined together by glycosidic (acetal) linkages.

Polysaccharides are also called **glycans** and they consist of two types namely **homoglycans** and **heteroglycans.**   Homoglycans are polysaccharides that consist of a single kind of monosaccharide, while heteroglycans consist of more than one kind of monosaccharide.

Polysaccharides consisting mainly of glucose are called **glucans,** while those consisting of fructose, mannose and xylose alone are referred to as fructans, mannans and xylans, respectively.

Examples of homoglycans are starches, cellulose, glycogen, insulin, chitin, etc, while examples of heteroglycans are gum acacia, pectins, alginic acids, mucopolysaccharides (hyaluronic acid, heparin, chondroitin sulphates). Generally speaking, polysaccharides are insoluble in water but upon hydrolysis by acids or enzymes, they are broken down into various intermediate products and finally their constituent monosaccharide units.

In this aspect of this course we shall be concerned with starch, cellulose and glycogen. Other polysaccharides will be discussed in future.

3.3.4.1 Starch

Starch is a storage carbohydrate found in plants. It consists of glucose units. It is therefore a **homoglucan** (remember our earlier discussion on homoglycans). Starch consists of a mixture of 2 different types of molecules, **amylose** and **amylopectin**. Amylose consists of a long chain of glucose units joined by $\alpha - 1, 4$ linkages while amylopectin consists of a mixture of α 1, 4 links with occasional α 1, 6 branches.

The branches occur after about 25 straight α 1, 4 bonds. Starches from different sources vary in the ratio of amylose and amylopectin and in the size of the individual molecules. In general, amylopectin accounts for about 70% of starch.
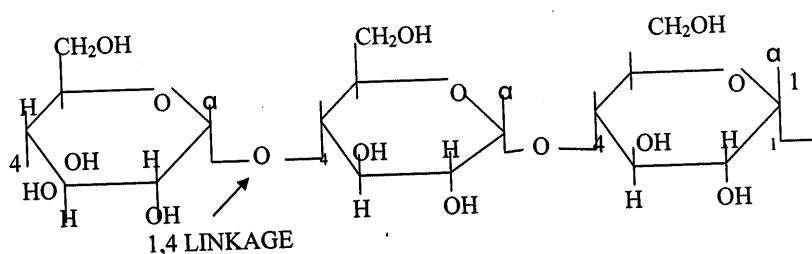
3.3.4.2 Structure of Amylase

The structure above is the glucose units of amylose linked in an unbranched chain. The amylose structure can therefore be considered as an expanded maltose structure with a free sugar group on one end.
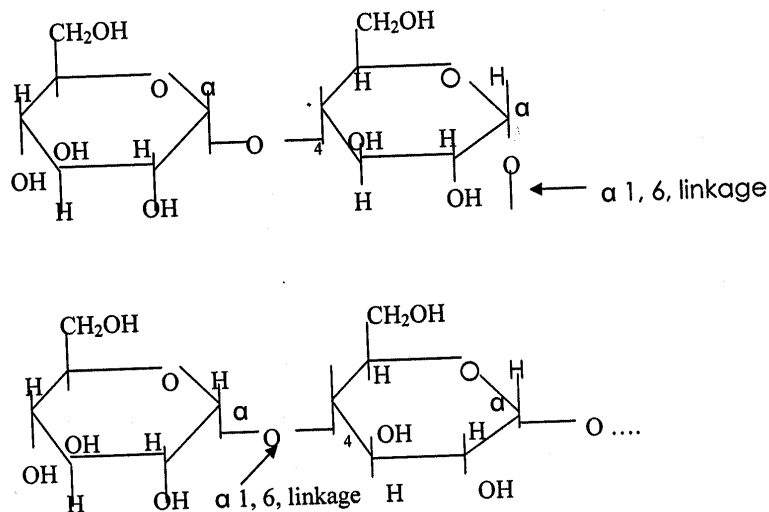
3.3.4.3 Structure of Amylopectin

Amylopectin also contains chains of glucose units like those of maltose, also has branches of these glucose chains linked through the 6 – OH of glucose in the manner as shown in the figure above.

The long chains of amylose roll themselves into a stable helix shape which is held in place by hydrogen bonding. The helix is a tube into which other molecules or atoms can fit. One example of this is the fact that iodine can fit inside the helix and form a blue coloured complex with amylose, a reaction which is often used to detect the presence of starch or iodine. The bluer the colour obtained, the more the amount of amylose component of the starch. Amylose is soluble in hot water while amylopectin is insoluble in hot water.

Starches from different plants when viewed microscopically show difference in shapes and sizes (appearances). This property furnishes the basis for microscopic identification of different types of starches. Some starches show a high degree of hydrogen bonding and such starches are quite resistant to rupture. Tuber starch, such as found in the potato, is extremely resistant and must be cooked before being utilized by species such as pigs or chickens. Starch type in plants is genetically determined. However, starch modification techniques are available and have application in the food industry. Dextrin is an intermediate resulting from the hydrolysis and digestion of starch as well as the action of heat on starch.

3.3.4.4 Cellulose

This is the most abundant substance in the plant kingdom and is a major structural component of plant cell walls. Cellulose is made up of polymerized glucose molecules ranging from 900 – 2, 000 molecules. Cellulose is also a glucan. Chemically, cellulose is a polymer of $\beta – 1, 4$ – linked d – glucose units. As such, the six carbon atoms are in the trans position which results in cellulose being flat, bank-like microfibril. Natural cotton is one of the purest forms of cellulose. Cellulose is not subject to attack by the digestive enzymes of man and other monogastrics; hence it is an important source of bulk in the diets. Contrarily, microbes in the rumen of ruminants can secrete cellulose enzyme which can degrade cellulose.

Cellulose is not soluble in water but soluble in ammonical solution of cupric hydroxide, hydrochloric acid solution of zinc chloride.

3.3.4.5 Glycogen

This is the storage form of carbohydrates in animals and fungal cells. Glycogen is deposited in the liver, which acts as a central energy storage organ in many animals. Glycogen is also abundant in muscle tissue, where it is more immediately available for energy release.

The structure of glycogen is of d-glucose combined with $\alpha - 1, 4$ linkage and an $\alpha - 1, 6$ cross linkage, very similar to that of amylopectin (component of starch moiety) except that the molecules are larger and the cross linkages move frequently (once every 5 or so straight bonds). Glycogen gives a red-brown, red, or at times, violet colour with iodine and which yields d-glucose upon complete hydrolysis.

4.0   CONCLUSION

Carbohydrates make up most of the organic structures of all plants and to some extent in all animals. Carbohydrates are manufactured by process of photosynthesis – the most important chemical reaction in nature.

Chemically carbohydrates are polyhydroxy aldehydes and ketones, or substances which yield aldehydes and ketones upon hydrolysis. The term carbohydrate includes sugars, starches, cellulose, gums, pectins, saponins, glucosinolates, etc.

Functionally, carbohydrates serve as a major storehouse of energy, raw materials for synthesis of milk and also supportive structural components. In addition, carbohydrates are essential in synthesis of

RNA and DNA – the genetic materials. Carbohydrates exhibit stereo isomerism.

5.0   SUMMARY

Carbohydrates are classified into 3 major groups namely; monosaccharides, oligosaccharides and polysaccharides, respectively. The monosaccharides are the simplest forms of sugars and make up oligosaccharides and the polysaccharides. The carbohydrates can be represented by chemical and structural formulae. The structural formulae are either represented in straight chain or in ring forms. This is specially represented by the hexoses (6 – carbon sugars).

The carbohydrates are source of energy for animal nutrition. The monosaccharides and oligosaccharides are efficiently metabolized by simple stomach animals. On the other hand ruminants contain microbes which secrete enzymes capable of degrading cellulose. Glycogen is a polysaccharide found in animal and fungal cells. Glycogen is a storage form of carbohydrate and readily utilized when there is deficiency of energy.

6.0   TUTOR-MARKED ASSIGNMENTS

1.   List the necessary nutrients that are indispensable to farm animals.

2.   Explain the occurrence of protein, carbohydrates, lipids, mineral, vitamins, hormone and enzymes in nature.

7.0   REFERENCES/FURTHER READING

Chewsworth, J.M., Stuchbury, T. and Scaife J.R (1988). Agricultural Biochemistry 1st Edition Published by Chapman and Hull.

Maynard, L. A Loosli, J.K Hintz, H.F and Warner, R.G. (1983). Animal Nutrition (7th Edition). Tata McGraw Hill Publishing Company Limited.

UNIT 2   STRUCTURE, PROPERTIES AND CLASSIFICATION OF PROTEINS

CONTENTS

1.0   INTRODUCTION

Proteins are a group of compounds containing carbon, hydrogen, oxygen, nitrogen (about 16%) and sulphur. In some proteins, phosphorus or iron is present and occasionally may contain iodine, copper and zinc. The approximate average elementary composition of protein is as follows:

Element	Per cent
Carbon	50
Hydrogen	7
Oxygen	23
Nitrogen	16
Sulphur	0-3
Phosphorus	0-3

Other elements may be present in small amounts.

Proteins are found in all living cells in plants and animals, where they are intimately connected with all phases of activity that constitute the life of the cell. Each species has its own specific proteins, and a single organism has many different proteins in its cells and tissues. It follows therefore that a large number of proteins occur in nature. All proteins are made up basically of amino acids and there are 20 standard amino acids in nature. The proteins differ from each other in the number of sequence of these standard amino acids.

2.0   OBJECTIVES

At the end of this unit, students will be able to:

- understand the chemistry of proteins in terms of their structures, properties, classification; and
- importance to plants and animals.

3.0   MAIN CONTENT

Physical and Chemical Properties of Proteins

1.   **Taste:** Pure proteins are generally tasteless, though the predominant taste of protein hydrolysates (proteoses, peptones, peptides, amino acids) is bitter.

2.   **Odour**: Pure proteins are odourless. When heated, they turn brown and char and give off the odour of burning feathers or hair.

3.   **Molecular Weights of Proteins**: Protein molecules are exceedingly complex in structure and are very large. Because of the size of their molecules, proteins belong to the colloidal state of matter.

4.   **Solubility:** All proteins have colloidal properties; they differ in their solubility in water, ranging from insoluble keratin to albumins, which are highly soluble. Soluble proteins can be

precipitated from solution by the addition of certain salts such as sodium chloride or ammonium sulphate. This is a physical effect and the properties of the proteins are not altered. On dilution the proteins can easily be redissolved.
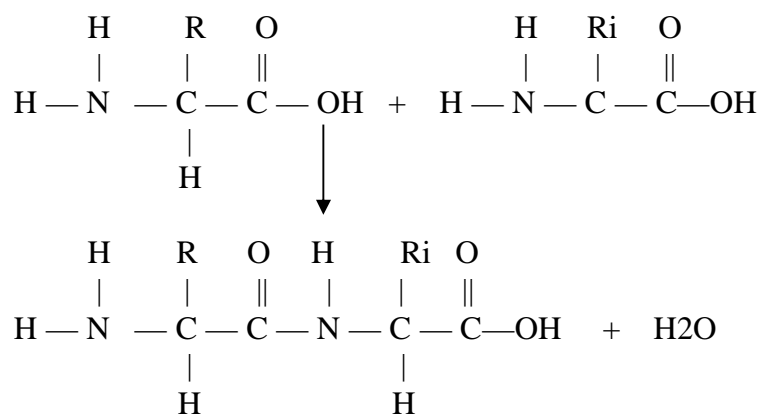
5. All proteins contain a number of free amino and carboxyl groups, either as terminal units or in the side-chain of amino acid residues. Like amino acids, proteins are therefore **amphoteric**. They exhibit characteristic **isoelectric points**, and have **buffering properties**.

6. All proteins can be denatured or changed from their natural state. **Denaturation** has been more accurately defined as '**any non-proteolytic modification of the unique structure of a native protein, giving rise to definite changes in chemical, physical or biological properties**'. Perhaps the best-known example of denaturation is the coagulation of a protein solution, such as egg white, upon heating. Many proteins are **heat-coagulable**. Apart from heat, there are many other agents which can bring about the denaturation of proteins; these include strong acid, alkali, alcohol, acetone, urea, and salts of heavy metals.

3.1 Structure of proteins

The structure of proteins can be considered under four basic headings.

3.1.1 Primary Structure

Proteins are built up from amino acids by means of a linkage between the α-carboxyl of one amino acid and the α-amino group of another acid as shown below.

```
        H     R    O                H    Ri   O
        |     |    ||               |    |    ||
  H — N  — C — C — OH   +   H — N — C — C—OH
              |                           |
              H                           ↓


        H     R    O   H    Ri   O
        |     |    ||   |    |    ||
  H — N  — C — C — N — C — C—OH    +   H2O
              |            |
              H            H
```

This type of linkage is known as the **peptide linkage**; in the example shown a di-peptide has been produced from two amino acids. Large

numbers of amino acids can be joined together by this means, with the elimination of one molecule of water at each linkage, to produce polypeptides. The term 'primary structure' refers to the sequence of amino acids along the polypeptide chains of protein.

3.1.2 Secondary Structure

The secondary structure of proteins refers to the conformation of the change of amino acids resulting from the formation of hydrogen bonds between the imido (NH) and carbonyl groups of adjacent amino acids.
The secondary structure may be regular, in which case the polypeptide chains exist in the form of an α-helix or a β-pleated sheet, or it may be irregular and exist, for example, as a random coil.
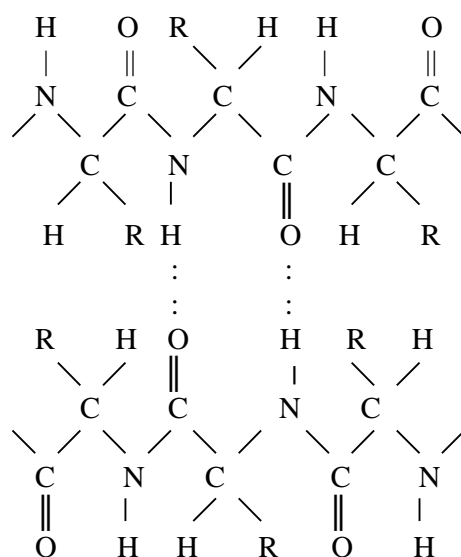
Figure 1   Configuration of Polypeptide Chain doted lines represent possible hydrogen bonds.

3.1.3 Tertiary Structure

The tertiary structure describes how the chains of the secondary structure further interact through the R groups of the amino acid residues. This interaction causes folding and bending of the polypeptide chain, the specific manner of the folding giving each protein its characteristic biological activity.

3.1.4 Quaternary Structure

Proteins possess quaternary structure if they contain more than one poly-peptide chain. The forces that stabilize these aggregates are hydrogen

bonds and electrostatic or salt bonds formed between residues on the surfaces of the polypeptide chains.

3.2 Classification of Proteins

Proteins can be classified on the basis of both physical and chemical properties. The physical properties of most value for classification purposes are those of solubility and heat coagulability. Accordingly, proteins are classified in three main groups of simple, conjugated and derived proteins, and each of these main groups is sub-divided into a number of classes.

3.2.1 Simple proteins

Simple proteins are defined as those proteins, which on hydrolysis yield only amino acids or their derivatives.

3.2.1.1 Albumins

The albumins are soluble in water and coagulated by heat. They are products of both plants and animals. Examples include egg albumin, myosin of muscle, serum albumin of blood, lactalbumin of milk, legumelin of peas and leucosin of wheat. Albumins may be precipitated from solution by saturation with ammonium sulphate.

3.2.1.2 Globulins

The globulins are insoluble in pure water, but they are soluble in dilute neutral solutions of salts, alkali and acids and are heat coagulable. Globulins are precipitated from solution by half saturation with ammonium sulphate. The globulins constitute an important and widely distributed group of animal and plant proteins. Examples include ovoglobulin of egg yolk, serum globulin of blood, phaseolin of beans, legumelin of peas, arachin of peanuts and amandin of almonds.

3.2.1.3 Glutelins

The glutelins are soluble in very dilute acids and alkali but they are insoluble in neutral solvents. They are plant proteins which include gluten of wheat and oryzenin of rice.

3.2.1.4 Prolamins or Alcohol - Soluble Proteins

The prolamins are soluble in 70 to 80% alcohol, but they are insoluble in water, neutral solvents, or absolute alcohol. The prolamins are plant

proteins found principally in seeds. Examples include zein of corn, hordein of barley, and gleadin of wheat.

3.2.1.5 Albuminoids or Scleroproteins

The albuminoids are the least soluble of all the proteins. They are generally insoluble in water, salt solutions, dilute acids and alkali and alcohol. The albuminoids constitute a very diverse group of proteins, the members of which show widely different physical and chemical properties. They are entirely animal proteins and are the chief constituents of the exoskeletal structures such as hair, horn, hoof and nails as well as of supporting and connecting fibrous tissues, and of the organic material of cartilage and bone. Examples include keratins of hair, horn and hoofs, nails, elastin of connective tissue and ligaments, collagen of bones, cartilage and tendons.

3.2.1.6 Histones

The histones are soluble in water and insoluble in dilute ammonia. They are readily soluble in dilute acids and alkali. They are not readily coagulated by heat. Histones are basic proteins. They yield a large proportion of basic amino acids upon hydrolysis. They often precipitate other proteins from solution. The histones being basic usually occur in tissues in salt combination with acidic substances such as heme of hemoglobin and nucleic acids. An example of histones includes globin of hemoglobin.

3.2.1.7 Protamins

The protamins are the simplest of the proteins and may be regarded as large polypeptides. They are strongly basic and yield mainly basic amino acids on hydrolysis, particularly arginine. The proteins are soluble in water, dilute ammonia, acids and alkalis. They are not coagulated by heat. They precipitate other proteins from their solutions like the histones, they usually occur in tissues, in salt combination with acids, particularly with nucleic acid as nucleoproteins.
Protamins, **on the basis of basic amino acid content**, can be sub-divided into 4 groups (a) **monoprotamins**, those which contain only arginine (b) **lysine diprotamins**, those which contain arginine and lysine (c) **histalene diprotamins**, those which contain arginine and histidine; (d) **triprotamins**, those which contain arginine, lysine and histidine.

3.2.2 Conjugated or complex proteins

Conjugated or complex proteins **are composed of simple proteins combined with some non-protein substance.** The non-protein group is referred to as the **prosthetic (addition) group**.

3.2.2.1 Nucleoproteins

The nucleoproteins are composed of simple basic proteins (protamins or histones) in salt combinations with nucleic acids as the prosthetic groups. They are proteins of cell nuclei and apparently are the chief constituents of chromatin. They are most abundant in tissues, both plant and animal, having a large proportion of nuclear material, such as yeast, thymus and other glandular organs. Examples include nucleohistone and nucleoproteins

3.2.2.2 Mucoproteins or mucoids

The mucoproteins are composed of simple proteins combined with mucopolysaccharides such as hyaluronic acid and the chondrotin sulphates. They generally contain rather large amounts of N-acetylated hexosamine (more than 4%) and, in addition, more or less of such substances as uronic acid, sialic acid and monosaccharides. Water-soluble mucoproteins have been obtained from serum, egg white (oyomucoid) and human urine. These water-soluble mucoproteins are not easily denatured by heat or readily precipitated by agents such as picric acid and tri-chloroacetic acid. Their mucopolysaccharides are composed of hexosamine and hexose sugars. Mucoproteins are important constituents of the ground substance of connective tissues. They are present as tendomucoid, osseomucoid and chondroproteins in tendons, bones and cartilage respectively. Insoluble mucoproteins or mucoids have been obtained from egg white, egg chalazae, vitreous humor and sub maxillary glands.

3.2.2.3 Chromoprotein

The chromoproteins are composed of simple proteins united with a coloured prosthetic group. Many proteins of important biological functions belong to this group. The following are examples of chromoproteins

i.   Haemoglobins, respiratory proteins in which the prosthetic group is the iron-containing, porphyrin complex, heme.
ii.   Cytochromes, cellular oxidation-reduction proteins in which the prosthetic group is heme.

iii.   Flavoproteins, cellular oxidation – reduction proteins in which the prosthetic group is riboflavin.
iv.   Visual purple of the retina, a chromoprotein in which the prosthetic group is a carotenoid pigment. There is evidence to indicate that chlorophyll occurs in the chloroplasts in combination with protein constituting a chromoprotein.

3.2.2.4 Phosphoproteins

Phosphoric acid is the prosthetic group of the posphoproteins. (phosphoserine has been isolated from casein and vitellin) Casein of milk and vitellin of egg yolk are the best known phosphoproteins.

3.2.2.5 Lipoproteins

The lipoproteins are formed by combination of protein with a lipid such as lecithin, cephalin, fatty acid, etc. Lipoprotein protein complexes are widely distributed in animal and plant materials. They occur in milk, blood, egg yolk, and chloroplast of plants.
Lipoproteins may be prepared by adding alcoholic solution of lecithin to egg albumin solutions.

3.2.2.6 Metalloproteins

A large group of enzyme proteins contain metallic elements such as Iron, Cobalt, Manganese, Zinc, Copper, Magnesium etc, which are parts of their essential structures. The heme proteins which contain Iron are classified as chromoproteins, which are also metalloproteins.

3.2.3 Derived proteins

This class of proteins, as the name implies, includes those substances derived from simple and conjugated proteins. It is the least well defined of the protein groups. Derived proteins are subdivided into primary derived proteins and secondary derived proteins.

3.2.3.1 Primary derived proteins

These protein derivatives are formed by processes which cause only slight changes in the protein molecule and its properties. There is little or no hydrolytic cleavage of peptide bonds. The primary derived proteins are synonymous with denatured proteins.

i.   **Proteans:** The proteans are insoluble products formed by the incipient action of water, very dilute acids, and enzymes. They are particularly formed from certain globulins, but differ from

globulins in being insoluble in dilute salt solutions. In general, they have the physical characteristics of the naturally occurring glutelins. Examples include myosan from myosin, edestan from edestin, and fibrin from fibrinogen.

ii.   **Metaproteins:** The metaproteins are formed by further action of acids and alkali upon proteins. They are generally soluble in very dilute acids and alkali but insoluble in neutral solvents. Examples include acid and alkali metaproteins such as acid and alkali albuminates.

iii.   **Coagulated proteins:** The coagulated proteins are insoluble products formed by the action of heat or alcohol upon natural proteins. Similar substances may also be formed by action of ultraviolet light, x-rays, very high pressure, and mechanical shaking upon protein solutions at the isoelectric pH. Examples include cooked egg albumin, cooked meat and other proteins, and alcohol-precipitated proteins.

3.2.3.2 Secondary derived proteins

These substances are formed in the progressive hydrolytic cleavage of the peptide unions of protein molecules. They represent a great complexity of molecules of different sizes and amino acid composition. They are roughly grouped into proteoses, peptones, and peptides, according to relative average molecular complexity. Each group is composed of many different substances.

i.   **Proteoses or albumoses:** Proteoses are hydrolytic products of proteins which are soluble in water, are not coagulated by heat, and are precipitated from their solutions by saturation with ammonium sulfate.

ii.   **Peptones:** Peptones are hydrolytic products of simpler structures than the proteoses. They are soluble in water, are not coagulated by heat, and are not precipitated by saturation with ammonium sulfate. They are precipitated by phosphotungstic acid.

iii.   **Peptides:** Peptides are composed of only a relatively few amino acids united through peptide bonds. They are named according to the number of amino acid groups present as di-, tri-, tetra peptides or polypeptides. They are water-soluble, are not coagulated by heat, are not salted out of solution, and are often precipitated by phosphotungstic acid. Various definitely characterized peptides have been isolated from protein hydrolytic products, and many have been synthesized.

The complete hydrolytic decomposition of a natural protein molecule into amino acids generally progresses through successive stages as follows:

protein   →   protean   →   metaproteins →
proteose   →   peptone   → peptides   →   amino acids

The synthesis of proteins by plants and animals consists of a progressive process in which amino acid groups are successively joined by peptide linkages until the molecular size and structure is that of a specific plant or animal protein. On the other hand, in protein catabolism, the proteins of tissues are continually being broken down to amino acids through the various hydrolytic stages. Accordingly, substances belonging to the classes of proteoses, peptones, and peptides are constituents of tissues, though often in very small amounts.

3.3   Protein Denaturation

Most protein molecules retain their biological activity only within a very limited range of temperature and pH. Exposing soluble or globular protein to extremes of pH or temperature for only short periods causes most of them to undergo a physical change called denaturation in which the most visible effect is a decrease in solubility.
Since no covalent bonds in the backbone of the polypeptide chain are broken during this relatively mild treatment, the primary structure remains intact. Most globular proteins undergo denaturation when heated above 60 to 70oC.

Thus, denaturation is a process whereby a globular protein irreversibly unfolds due to the breaking of the bonds which hold it in a globular form.

A common example of protein denaturation is the formation of an insoluble white coagulum when egg white is boiled.
Dissolving protein in alcohol, salts of heavy metals, strong acids or alkali and trichloroacetic acid always result in denaturation.
The most significant consequence of denaturation is that the protein usually loses its characteristic biological activity. For instance, heating usually destroys the catalytic ability of enzymes.

3.4   Functional Diversity of Proteins

Proteins have many different biological functions in living systems.

1.   The main function of food proteins is to provide the major organic structures of the protoplasmic machine, although excess is utilized as a source of energy.
2.   The chemical processes involved in the digestion of foods and also in the utilization or metabolism of foods in tissues are in general catalyzed by substances known as enzymes- which are proteins. The enzymes represent the largest class of protein. Nearly, 2,000 different kinds of enzymes are known, each catalyzing a different kind of chemical reaction.
      Enzymes are highly specific in their function, for instance the enzyme hexokinase catalyses the transfer of a phosphate group from ATP to glucose – the first step in glucose metabolism.

      Another example is cytochrome C which transfers electrons toward molecular oxygen during respiration. Also DNA – polymerase and amino-acid-activating enzymes, participate in the biosynthesis of cell components. Each type of enzyme molecule contains an active site to which its specific substrate is bound during the catalytic cycle. Many enzymes contain a single polypeptide chain, others contain two or more. Some enzymes called regulatory or allosteric enzymes are further specialized to serve a regulatory function in addition to their catalytic activity. Virtually, all enzymes are globular proteins.

3.   Another class of proteins have the function of storing amino acids and using them as building blocks for the growing embryo.

      Examples are; ovalbumin of egg white, casein of milk and gleadin of wheat.

4.   Some proteins have a transport function; they are capable of binding and transporting specific types of molecules via the blood.

      Example include serum albumin which binds free fatty acids tightly and thus serves to transport these molecules between adipose (fatty) tissue and other tissues or organs in vertebrates.

      The lipoprotein of blood plasma transports lipids between the intestine, liver and adipose (fatty) tissues. Haemoglobin of vertebrate erythrocytes transports oxygen from the lungs to the tissues.

Invertebrates have other types of oxygen-carrying protein and molecules such as haemocyanine.

5. Some proteins also serve as essential elements in contractive and motile systems. Actin and myosin are the two major protein elements of the contractile system of skeletal muscle. In muscles, these proteins are arranged in parallel arrays and slide along each other during contraction.

6. Some proteins have a protective or defensive function. The blood protein thrombin and fibrinogen participate in blood clotting and thus prevent the loss of blood from the vascular system of vertebrates, but the most important protective proteins are antibodies or immune-globulins which combine with and neutralize foreign proteins and other substances that happen to gain entrance into the blood or tissues of a given vertebrate.

7. Some proteins are extremely toxic to higher animals in very small amounts. These are called Toxins. They include ricin of the castor bean, gossypol of the cotton seed and haemagglutinins of legumes and certain diseases of both plants and animals are caused by substances called viruses. A few of these have been isolated and purified and have been identified as very complex proteins.

8. Some proteins also function as hormones. Hormones are chemical substances produced in one part of plant or animal's body by ductless (endocrine) glands and produce its effect on distant parts of the body. Much of the integration and regulation of physiological processes in the body is accomplished through these hormones.

   Examples include; Somatotropin (growth hormone) – a hormone of anterior pituitary gland. Insulin – secreted by certain specialized cells of the pancreas. It regulates glucose metabolism and its deficiency in man causes a disease called diabetes mellitus.

9. Another class of proteins serves as structural elements. In vertebrates, the fibrous protein, collagen, is the major extracellular structural protein in connective tissues and bone. Collagen-fibrils, by forming a structural continuum also help to bind a group of cells together to form a tissue.

The other fibrous proteins in vertebrates are elastin of yellow elastic tissue and α-keratin present in skin, feathers, nails, hoofs. Cartilage contains not only collagen but also glycoproteins, which enclose mucous secretions and synovial fluid in the joints of vertebrates with a slippery, lubricating quality.

10.   Besides these major classes of protein, others have unusual functions. Spiders and silkworms secrete a thick solution of the protein fibroin, which quickly solidifies into an insoluble thread of exceptional tensile strength used to form webs or cocoons. The blood of some fishes living in subzero antarctic waters contains a protein that keeps the blood from freezing. This protein is called "Antifreeze protein". Monellin is a sweet-tasting protein found in some fruits. It does not taste sweet when denatured. Unlike sugars it tastes sweet but does not cause fattening. It should be noted that all proteins, including those having intense biological or toxic effects, are built from the same 20 amino acids which by themselves have relatively little biological activity or toxicity.

4.0 CONCLUSION

Proteins possess four basic structures in which they can be identified: these are primary, secondary, tertiary and quaternary structures. Proteins have distinctive characteristics ranging from colloidal, amphoteric and denaturation. They can be classified into simple proteins (albumins, globulins, glutelins, prolamins, albuminoids, histones and protamins), conjugated proteins (nucleoproteins, mucoproteins, chromoproteins, phosphoproteins, lipoprotein, metalloproteins) and derived proteins (primary and secondary derived proteins).

6.0   TUTOR-MARKED ASSIGNMENTS

Q1.   a.   What are proteins?
        b.   List 20 hydrolytic products of protein.
Q2.   a.   Enumerate the structures of proteins.
        b.   Identify the inherent characteristics of proteins
Q3   Based on the hydrolysis products of proteins, describe the three major classes of proteins.

7.0   REFERENCES/FURTHER READING

Dickerson, R.E. and I. Geis (1993). "*Proteins: Structures, Function and Evolution*". Benjamin (Cummings. Menlo Park, Califonia).

Lehninger, A. L. (1992). "*Principles of Biochemistry*". New York: Worth Publ

Linder, M.C. (1991). "*Nutritional Biochemistry and Metabolism*". Elsevier.

McDonald, P., R. A. Edwards and J .F. D. Greenhalgh (1987). *"Animal Nutrition"*.

UNIT 3   AMINO ACIDS

CONTENTS

1.0   INTRODUCTION

Amino acids are the smallest units obtained when complex proteins are broken down in the process of digestion. Chemically, they contain carbon, hydrogen, oxygen, nitrogen and Sulphur

## 2.0   OBJECTIVES

At the end of this study, you will be able to:

- catch a glimpse of amino acids in terms of their structures; and
- properties and indispensability.

3.0   MAIN CONTENT

3.1   Amino acids commonly found in proteins

Amino acids are produced when proteins are hydrolyzed by enzymes, acids or alkalis. They are required as building blocks for the synthesis of the proteins of the blood and tissues. Although over 200 amino acids have been isolated from biological materials, only 20 of these are commonly found as components of proteins. Amino acids are characterized by having a basic nitrogenous group, generally an amino group (-NH2), and an acidic carboxyl unit (-COOH). Most amino acids

occurring naturally in proteins are of the α type, having the amino group attached to the carbon atom adjacent to the carboxyl group, and can be represented by the general formula:
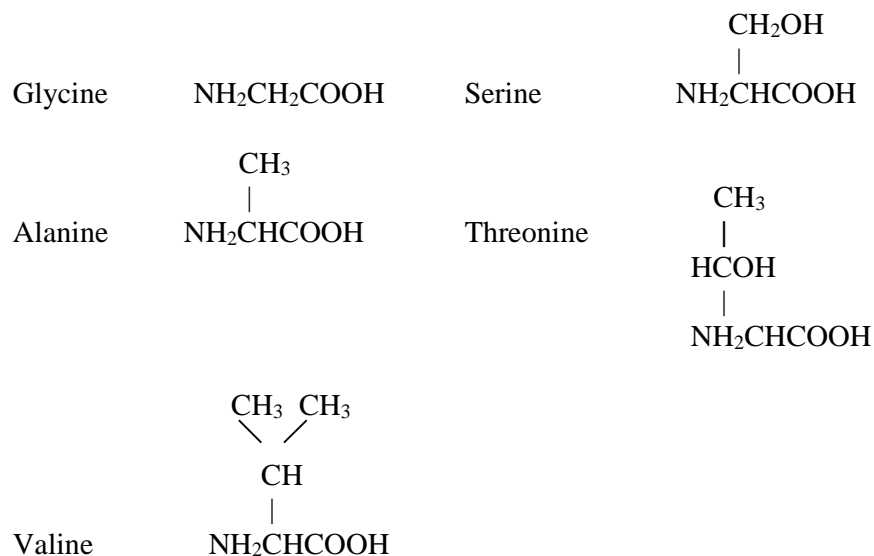
_____

$$\begin{array}{c} NH2 \\ | \\ R - C - H \\ | \\ COOH \end{array}$$
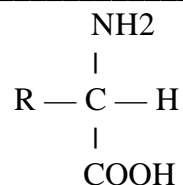
When the amino group is attached to the second or α-carbon (the one immediately attached to the carboxyl group) the amino acid is called α-amino acid.

When the amino group replaces one of the hydrogen atoms on the third or β-carbon (the third to the carboxyl group), the resulting amino acid is called β-amino acid.

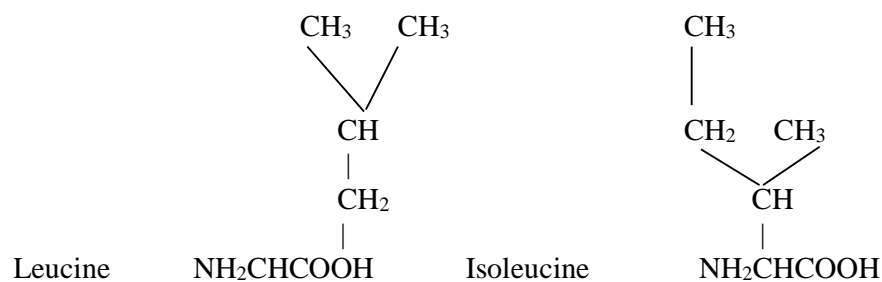Similarly, when the amino group replaces the fourth or γ-carbon, it is known as y-amino acid. About two dozen amino acids have been definitely established as occurring in proteins and most proteins contain a large proportion of these amino acids.
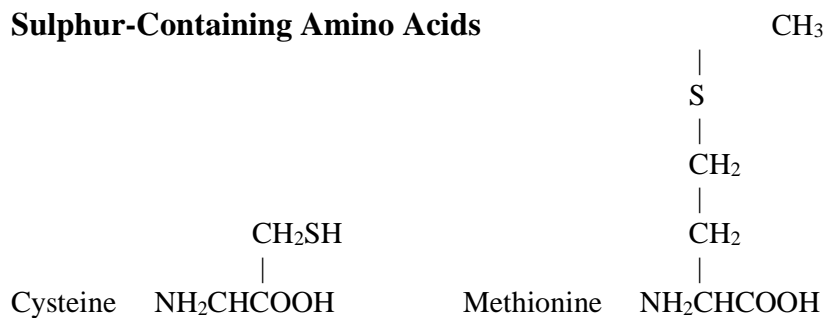
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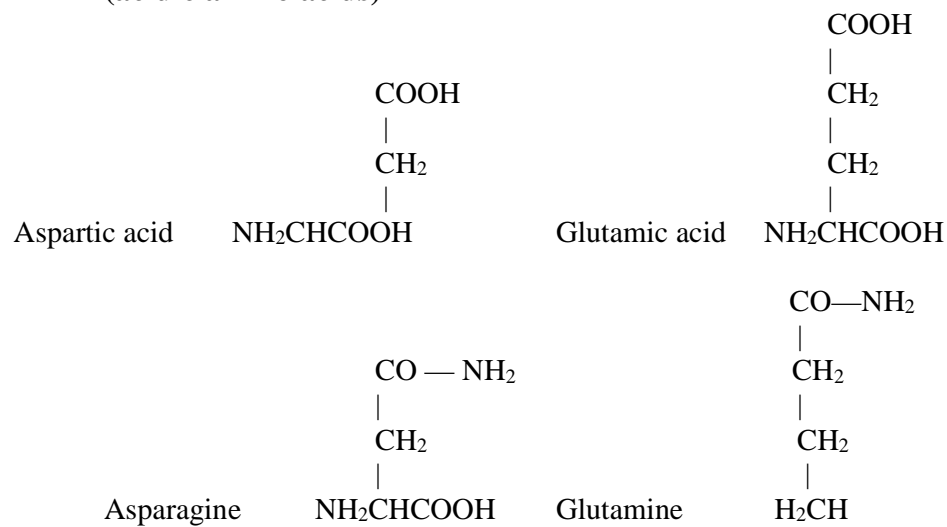1.　　**Monoamino-Monocarboxylic Acids**

Glycine　　NH_2CH_2COOH　　Serine　　$\begin{array}{c} CH_2OH \\ | \\ NH_2CHCOOH \end{array}$

Alanine　　$\begin{array}{c} CH_3 \\ | \\ NH_2CHCOOH \end{array}$　　Threonine　　$\begin{array}{c} CH_3 \\ | \\ HCOH \\ | \\ NH_2CHCOOH \end{array}$

Valine　　$\begin{array}{c} CH_3 \;\; CH_3 \\ \diagdown \; \diagup \\ CH \\ | \\ NH_2CHCOOH \end{array}$

$$
\begin{array}{cc}
CH_3 \quad CH_3 & CH_3 \\
\diagdown \diagup & | \\
CH & CH_2 \quad CH_3 \\
| & \diagdown \diagup \\
CH_2 & CH \\
| & | \\
\text{Leucine} \quad NH_2CHCOOH & \text{Isoleucine} \quad NH_2CHCOOH
\end{array}
$$

2. **Sulphur-Containing Amino Acids**

$$
\begin{array}{cc}
 & CH_3 \\
 & | \\
 & S \\
 & | \\
 & CH_2 \\
CH_2SH & CH_2 \\
| & | \\
\text{Cysteine} \quad NH_2CHCOOH & \text{Methionine} \quad NH_2CHCOOH
\end{array}
$$

3. **Monoamino-dicarboxylic acids and their amine derivatives (acidic amino acids)**

$$
\begin{array}{cc}
 & COOH \\
 & | \\
COOH & CH_2 \\
| & | \\
CH_2 & CH_2 \\
| & | \\
\text{Aspartic acid} \quad NH_2CHCOOH & \text{Glutamic acid} \quad NH_2CHCOOH
\end{array}
$$

$$
\begin{array}{cc}
 & CO{-}NH_2 \\
 & | \\
CO{-}NH_2 & CH_2 \\
| & | \\
CH_2 & CH_2 \\
| & | \\
\text{Asparagine} \quad NH_2CHCOOH & \text{Glutamine} \quad H_2CH
\end{array}
$$

4. **Basic amino acids (Diamino monocarboxylic acid)**

$$
\begin{array}{cc}
CH_2NH_2 & HC - N \\
| & \quad\quad \diagdown\diagdown \\
CH_2 & \quad\quad\quad CE \\
| & \quad\quad \diagup \\
CH_2 & C - NH \\
| & | \\
CH_2 & CH_2 \\
| & | \\
\text{Lysine} \quad NH_2CHCOOH & \text{Histidine} \quad NH_2CHCOOH
\end{array}
$$

$$NH_2$$

$$
\begin{array}{l}
| \\
C = NH \\
| \\
NH \\
| \\
(CH_2)_3 \\
|
\end{array}
$$

Arginine $NH_2CHCOOH$

5.   **Aromatic and heterocyclic amino acids**

Phenylalanine $NH_2CHCOOH$ Tyrosine $NH_2CHCOOH$

Tryptophan

Proline   NH
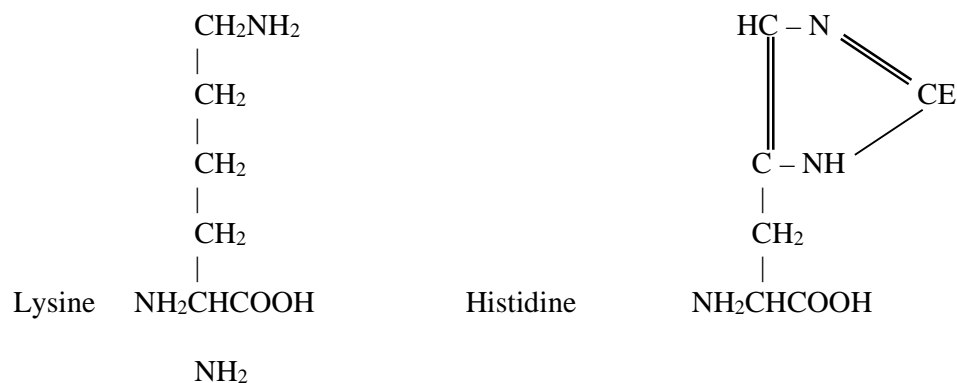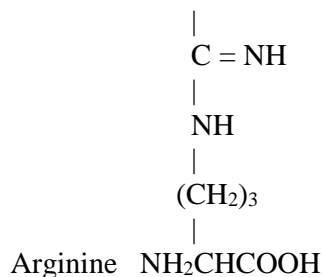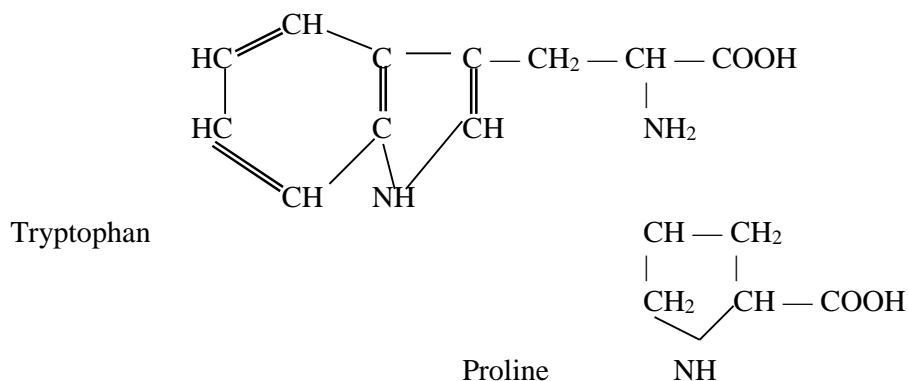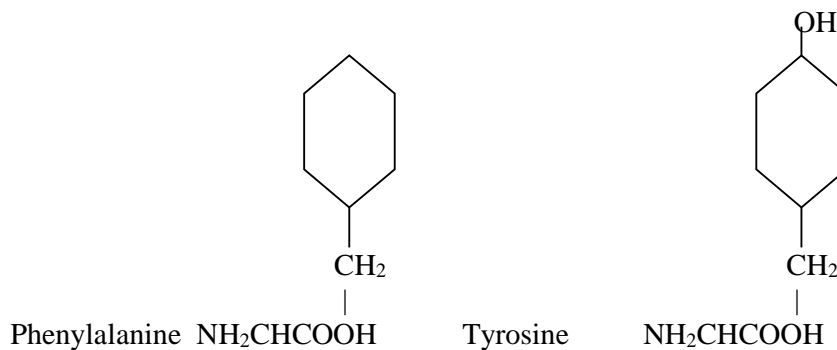
3.2   Physical Properties of Amino Acids

1.   Solubility

In general amino acids are readily soluble in water, insoluble or slightly soluble in alcohol and insoluble in ether.

- Tyrosine is only slightly soluble in cold water and more soluble in hot water.
- Cystine is sparingly soluble in both hot and cold water.
- Proline and hydroxyproline are soluble in alcohol and ether.

The amino acids are generally soluble in dilute acids and bases in which they form the amino acid salts.
2.   Melting Points

The amino acids are outstanding among organic compounds in possessing high melting points which are usually above 200oC. Many of the amino acids undergo decomposition at or near their melting point.

a.   Amino acids are usually sweet, tasteless, or bitter. Sweet amino acids include; Glycine, Alanine, Valine, Proline, Serine, Hydroxyproline, Tryptophan and Histidine.

Leucine is tasteless while Isoleucine and Arginine are bitter.

Sodium glutamate, – the sodium salt of Glutamic acid is normally used as flavouring agent to enhance the flavour of foods.

3.3   Chemical Properties of Amino Acids

Because of the presence of an amino and a carboxyl group, amino acids are amphoteric, i.e. have both basic and acidic properties. Molecules such as these, with basic and acidic groups, may exist as uncharged molecules, or as dipolar ions with opposite ionic charges, or as a mixture of these. Amino acids in aqueous solution exist as dipolar ions or 'Zwitterions' (from the German Zwitter, a hermaphrodite):

$$
\begin{array}{c}
NH_3^+ \\
| \\
R - C - H \\
| \\
COO^-
\end{array}
$$
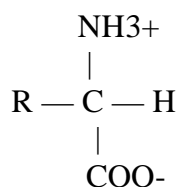
In a strongly acid solution, an amino acid exists largely as a cation, while in alkaline solution it occurs mainly as an anion. There is a pH value for a given amino acid at which it is electrically neutral; this value is known as the isoelectric point.
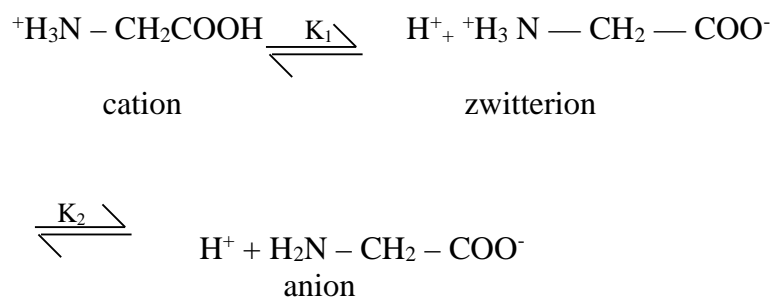
Because of their amphoteric nature, acids act as buffers, resisting changes in pH. All the α-amino acids except glycine are optically active. Glycine in its crystalline state exists as:

$$
\begin{array}{c}
NH_3^+ \\
| \\
H - C - COO^- \\
| \\
H
\end{array}
$$
Zwitterion
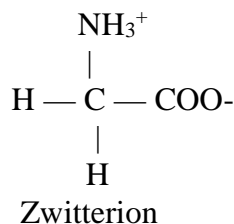
In acid solution, the zwitterion combines with H+ ions to form a cation.

$$NH_3^+$$
$$|$$
$$H — C — COOH$$
$$|$$
$$H$$
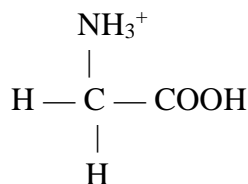
This cation dissociates its H^+ in two stages;

$$^+H_3N – CH_2COOH \underset{\longleftarrow}{\overset{K_1}{\longrightarrow}} H^+ + {}^+H_3 N — CH_2 — COO^-$$

cation   zwitterion

$$\underset{\longleftarrow}{\overset{K_2}{\longrightarrow}} H^+ + H_2N – CH_2 – COO^-$$
anion

When sodium hydroxide is added to the glycine cation solution, OH- ions combine with the H+ ions to form H20 and shift the equilibrium to the right, with the production of glycine anions: H2N – CH2 – COO-. When an acid such as hydrochloric acid is added to the glycine anion solution, H+ ions cause the equilibrium to shift to the left with the formation of glycine cations: +H3N – CH2 – COOH .

Thus, with sodium hydroxide, the amino acid forms the sodium salt, and with hydrochloric acid, it forms the amino acid chloride.

Generally, amino acids as zwitterions in solution exist as follows:

```
        1                          2                        3
+H3N-CH(R) - COOH ⇌ H++ +H3N–CH(R)–COO- ⇌ H+ + H2N –  COO-
amino acid cation        zwitterion            amino acid anion
in acid solution                               in          alkaline
solution
```
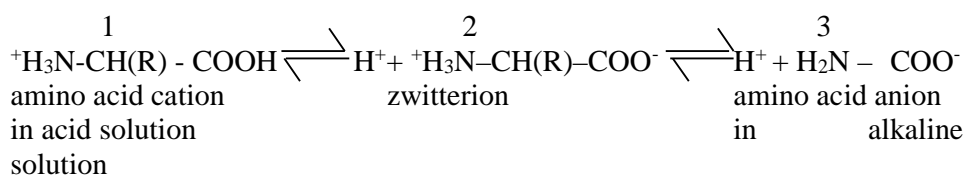
3.4   Optical Properties of Amino Acids

The α-amino carbon atoms of all the amino acids except glycine are asymmetric. When an asymmetric carbon atom is present in a molecule, the formation of stereoisomers is possible.

Compounds which have the same structural formula but differ in spatial configuration are known as STEREOISOMERS.

The number of possible isomers that can be formed depends on the number of asymmetric carbon atoms present in the compound.

An asymmetric carbon atom is one, which has its valence bonds attached to four different atoms or groups.

The number of possible isomers from a compound is 2n where n is the number of asymmetric carbon atom present in the compound. The following amino acids have two asymmetric carbon atoms; isoleucine, threonine, hydroxylysine and hydroxyproline.

Thus, all amino acids except glycine show optical activity; this is the ability of solutions of some compounds (acids, sugars) to rotate the plane of polarized light when it is passed through them.

Substances which rotate the plane of polarized light clockwise (or to the right) are said to be dextrorotatory. Similarly, substances rotating counter or anti clockwise (or to the left) are laevorotatory.

Dextrorotation is denoted by + or d-sign while laevorotation is denoted with –or l-sign.

A racemic mixture: Is one in which the amount of dextrorotation is equal to the amount of laevorotation. The resulting mixture has no optical activity since the activities of + and – cancel each other.

Optically active amino acids may be converted into the racemic forms (DL mixtures) by heating with alkali, by heating with acids under pressure and by treating the amino acids with acetic anhydride under proper conditions which convert the optically active acids into the DL–acetylated acids (racemic form) from which the acetyl groups may be hydrolyzed to yield the racemic DL mixture of amino acids.
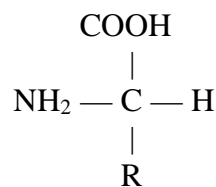
All the amino acids involved in protein structure have an L-configuration of the carbon atom. Configurations are determined by relation to the standard substance D-glyceraldehyde.

$$
\begin{array}{ccc}
CHO & COOH & COOH \\
| & | & | \\
H-C-OH & H-C-NH_2 & NH_2-C-H \\
| & | & | \\
CH_2OH & R & R
\end{array}
$$
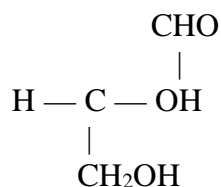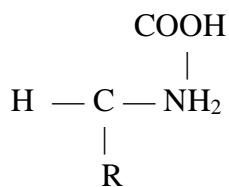
D-Glyceraldehyde   D-Amino acid   L-Amino acid

3.5   Indispensable Amino Acids

Plants and many micro-organisms are able to synthesize proteins from simple nitrogenous compounds such as nitrates. Animals cannot synthesize the amino group, and in order to build up body proteins they must have a dietary source of amino acids. Certain amino acids can be produced from others by a process known as transamination, but a number of amino acids cannot be effectively synthesized in the animal body and these are referred to as indispensable or essential amino acids. Most of the early work in determining the amino acids which could be classed as indispensable was carried out with rats fed on purified diets. The following ten indispensable amino acids are required for growth in the rat:

Arginine	Methionine
Histidine	Phenylalanine
Isoleucine	Threonine
Leucine	Tryptophan
Lysine	Valine

The chick also requires in the diet the 10 amino acids listed above, but in addition needs a dietary source of glycine. The list of indispensable amino acids required by the pig is similar to that of the rat, with the exception of arginine and histidine which can be synthesized by the pig.

In the case of the ruminant, all the indispensable amino acids can be synthesized by the rumen micro-organisms, which theoretically make this class of animals independent of a dietary source. However, maximum rates of growth or milk production cannot be achieved in the absence of a supply of dietary amino acids in a suitable form.

3.6   Classification of Amino Acids

Amino acids have been classified in various ways:

1.   They have been classified according to number of amino and carboxyl groups present in the molecule as mono-amino mono-carboxylic acids, mono-amino di-carboxylic acids, etc.
2.   Based on the presence of chain and/or ring structures e.g. Aliphatic, Aromatic and Heterocyclic amino acids.
3.   According to their reaction in solution as neutral, acidic and basic amino acids.

The natural amino acids are represented as the L-series and the unnatural or artificial acids as the D-series. However, several amino acids with the
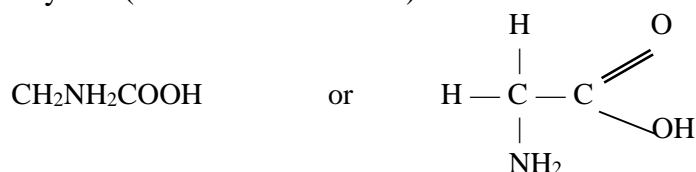
D-confirmation occur in natural peptides, most of which are antibiotics e.g. D-leycine, D-phenylalanine and D-proline.

3.6.1 Classification according to the number of NH2/COOH groups.

Aliphatic Amino Acids (chain compounds)

a)   Monoamino moncarboxylic acids – Neutral in reaction

   i.   Glycine (Amino ethanoic acid)

   CH_2NH_2COOH or

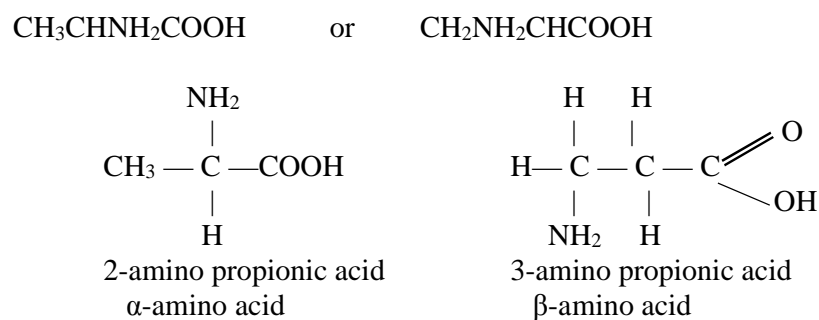$$H-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}-C\overset{O}{\underset{OH}{\diagup\diagdown}}$$

Because glycine contains only one amino group and one carboxyl group, it is described as a neutral α-amino acid and is obtained in many animal and plant proteins.

It is a white, soluble, crystalline solid with a high melting point of 2920C. It is insoluble in organic solvents.
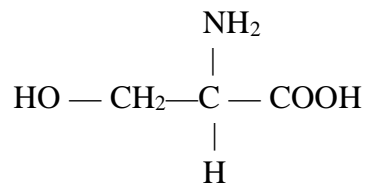
ii.   Alanine

   This could be α- or β- amino acid.

   CH_3CHNH_2COOH or $CH_2NH_2CHCOOH$

$$CH_3-\underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}}-COOH$$

$$H-\underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-C\overset{O}{\underset{OH}{\diagup\diagdown}}$$

2-amino propionic acid   3-amino propionic acid
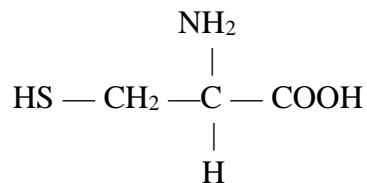   α-amino acid   β-amino acid

Both of these acids are neutral as they contain one amino and one carboxyl group. All amino acids from Alanine upward except glycine possess at least one asymmetric carbon atom. Therefore, in all amino acids except glycine the carbon atom attached to nitrogen and alpha to the carboxyl group is asymmetric. They may also be obtained in optically active dextro and levo and optically inactive racemic forms.
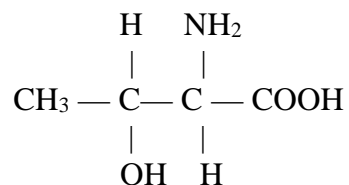
iii.

$$NH_2$$
$$|$$
$$HO — CH_2—C — COOH$$
$$|$$
$$H$$

Serine (α-amino - β-hydroxy propionic acid)

iv.

$$NH_2$$
$$|$$
$$HS — CH_2 —C — COOH$$
$$|$$
$$H$$

Cysteine (α-amino - β-thiopropionic acid

v.

$$H \quad NH_2$$
$$| \qquad |$$
$$CH_3 — C— C — COOH$$
$$| \qquad |$$
$$OH \quad H$$

Threonine (α-amino - β-hydroxy-n-butyric acid)

vi.

$$NH_2$$
$$|$$
$$CH_3 — S — CH_2 — CH_2— C — COOH$$
$$|$$
$$H$$
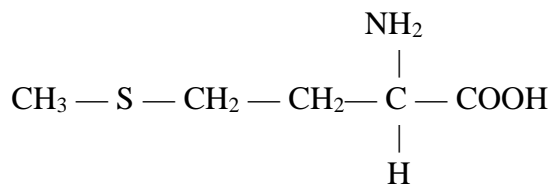
Methionine (α-amino - γ-methyl-thio-n-butyric acid)

vii.

$$CH_3 \qquad\qquad NH_2$$
$$\backslash \qquad\qquad |$$
$$CH — CH_2 — C — COOH$$
$$/ \qquad\qquad\qquad |$$
$$CH_3 \qquad\qquad H$$
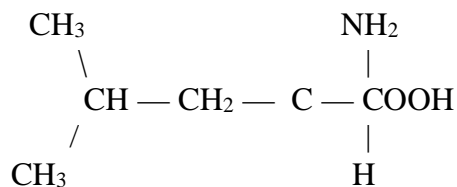
Leucine (α-aminoisocaproic acid)

viii.

$$CH_3 \qquad NH_2$$
$$\backslash \qquad |$$
$$CH — C — COOH$$
$$/ \qquad |$$
$$CH_3 \qquad H$$
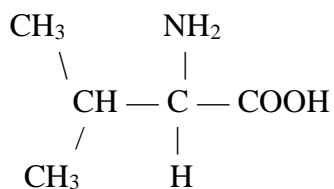
Valine (α-aminoisovaleric acid)

ix.

$$CH_3 — CH_2 — \underset{\underset{H}{|}}{\overset{\overset{CH3 \quad NH2}{|\qquad|}}{CH}} — C — COOH$$
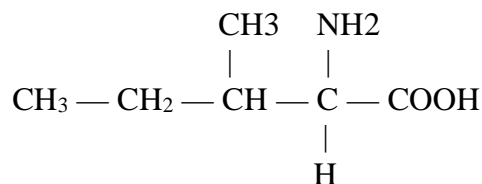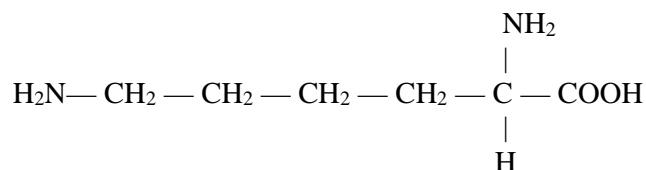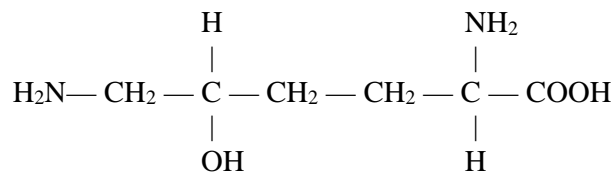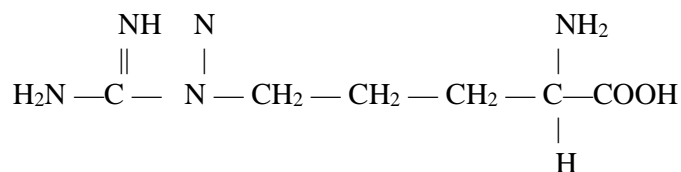
Isoleucine (α-amino - β-methyl-n-valeric acid)

b.   Mono aminodicarboxylic acids – acid in reaction (negatively charged)

$$
\begin{array}{cc}
COOH & COOH \\
| & | \\
H_2N — C — H & H_2N— C — H \\
| & | \\
CH_2 & CH_2 \\
| & | \\
COOH & CH2 \\
& | \\
& COOH
\end{array}
$$
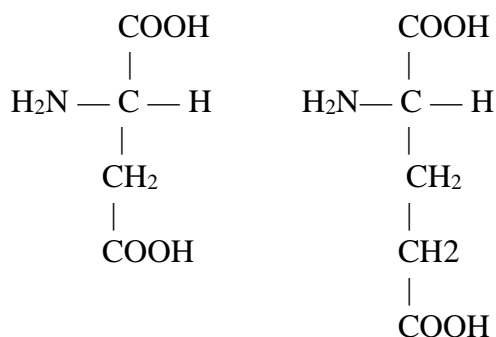
Aspartic acid   Glutamic acid
(α-amino succinic acid)   (α-Aminoglutaric acid)

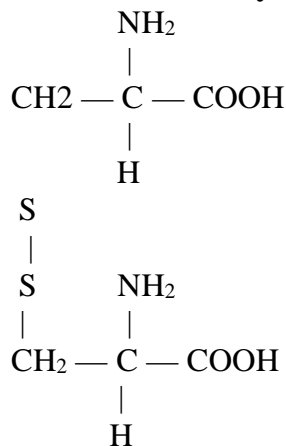**c.   Diaminomonocarboxylic acid – Basic in Reaction (Positively Charged)**

$$H_2N— CH_2 — CH_2 — CH_2 — CH_2 — \underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}} — COOH$$

lysine (α-ε-diamino – n – caproic acid)

$$H_2N— CH_2 — \underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}} — CH_2 — CH_2 — \underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}} — COOH$$

hydroxylysine (α - + - diamino - δ - hydroxy – n-caproic acid)

$$H_2N —\overset{\overset{NH}{||}}{C}— \overset{\overset{N}{|}}{N} — CH_2 — CH_2 — CH_2 — \underset{\underset{H}{|}}{\overset{\overset{NH_2}{|}}{C}}—COOH$$

arginine (α - amino - δ - guanido – n - valeric acid)

Lysine consists of positively charged amino group at the epsilon end of its structure. Thus, most of its reactions take place at the epsilon end.

Hydroxylysine (or 5-hydroxylysine) is formed from lysine and is usually found in the collagen of connective tissues.

Arginine has its NH+ at the Guanido group where its reactions take place.

d.   **Diamino-dicarboxylic acids**
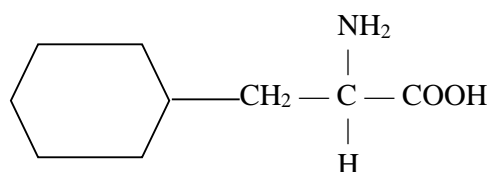
$$
\begin{array}{c}
NH_2 \\
| \\
CH2 - C - COOH \\
| \\
H
\end{array}
$$

$$
\begin{array}{c}
S \\
| \\
S \qquad NH_2 \\
| \qquad | \\
CH_2 - C - COOH \\
| \\
H
\end{array}
$$

(Di-α- amino – β-thio-propanoic acid)
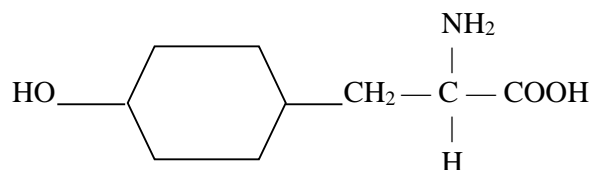
Cystine or Dicysteine

Aromatic Amino Acids

- Mono amino monocarboxylic acids
- Neutral in reaction

$$
\begin{array}{c}
NH_2 \\
| \\
-CH_2 - C - COOH \\
| \\
H
\end{array}
$$

phenylalanine (α-amino – β – phenyl propionic acid)

$$
\begin{array}{c}
NH_2 \\
| \\
HO\underline{\quad}\bigcirc\underline{\quad}CH_2 - C - COOH \\
| \\
H
\end{array}
$$

Tyrosine (α-amino - β-parahydroxy phenyl propionic acid)

3.6.2 Classification of Amino Acids based on their Polarities

The most meaningful classification of amino acids which has been related to the genetic coding for the different amino acids found in proteins is that based on their polarity.
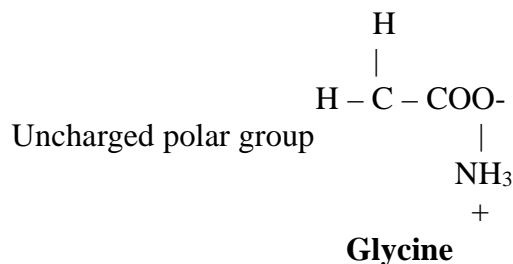
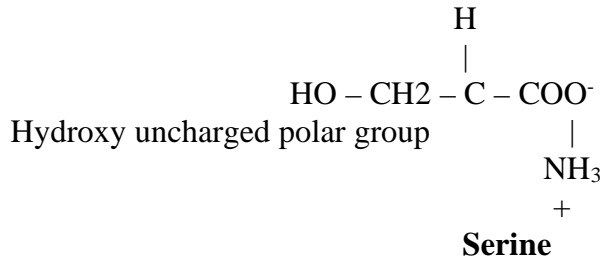There are four main classes of amino acids on this basis at pH 6.0 – 7.0, the zone of intracellular pH.

a)   Those with non-polar or hydrophobic R-groups.
b)   Neutral (uncharged) polar R-groups
c)   Positively charged R-groups
d)   Negatively charged R-groups

Within any of these classes, there is considerable variation in the size, shape and properties of the R-groups.
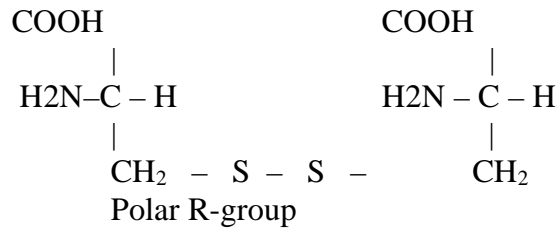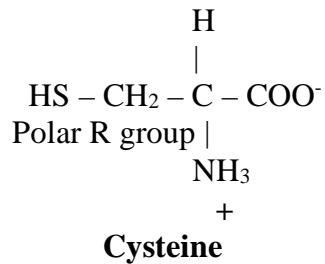
1.   The **non-polar (Hydrophobic) amino acids** have non polar R-groups. This family includes five amino acids with aliphatic hydrocarbons viz: Alanine, Leucine, Isoleucine, Valine, and Proline. It also includes two amino acids with aromatic rings e.g. Phenylalanine and tryptophan and one containing sulphur, e.g. Methionine. As a group, these amino acids are less soluble in water than the amino acids with polar R-groups.

2.   **Amino acids with polar (uncharged) R-groups**: They are relatively more soluble in water than those with non-polar R-groups. Their R-groups contain neutral (uncharged) polar functional groups which can form hydrogen-bond with water. The polarity of serine, threonine and tyrosine is contributed by their hydroxyl groups, that of asparagine and glutamine by their amide groups and that of cysteine by its sulfhydryl (-SH) group.

Glycine, the borderline member of the group is sometimes classified as a non-polar amino acid because its R-group is a single hydrogen atom which is too small to influence the high degree of polarity of the α-amino and α-carboxyl group.

$$
\begin{array}{c}
H \\
| \\
H - C - COO- \\
| \\
NH_3 \\
+
\end{array}
$$

Uncharged polar group

Glycine

$$H$$
$$|$$
$$HO - CH2 - C - COO^-$$
Hydroxy uncharged polar group $|$
$$NH_3$$
$$+$$

Serine

Note: Cysteine often occurs in protein in its oxidized form. Cystine in which the thiol groups of two molecules of cysteine have been oxidized to a disulfide group to provide a covalent cross-linkage between them.

$$H$$
$$|$$
$$HS - CH_2 - C - COO^-$$
Polar R group $|$
$$NH_3$$
$$+$$

Cysteine

COOH   COOH
$|$ $|$
H2N–C – H   H2N – C – H
$|$ $|$
CH$_2$ – S – S –   CH$_2$
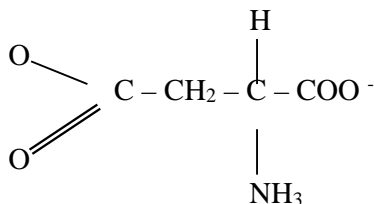Polar R-group

L-Cystine

3.   **Amino acids with positively charged (Basic) R-groups** are basic amino acids in which the R-groups have a net positive charge at PH 7.0. All members have six carbon atoms. They consist of lysine, which bears a positively charged amino group at the epsilon position of its aliphatic chain.

Others are arginine which bears its positive charge at the Guanido group and   Histidine which contains the weakly basic imidazole group.

$$H$$
$$|$$
$$+H3N - CH2 - CH2 - CH2 - CH2 - C - COO -$$
Positively charged at ε position $|$
$$^+NH3$$

Lysine
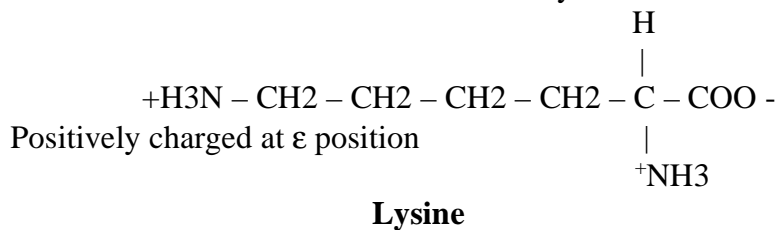
4.   There are just two members of **amino acids with negatively charged (Acidic) R-groups**; these are; Aspartic acid and

Glutamic acids, each with a second carboxyl group which is fully ionized and thus negatively charged at pH 6 to 7.

$$\begin{array}{c} O \\ \diagdown \\ C - CH_2 - \overset{\overset{\displaystyle H}{|}}{C} - COO^{-} \\ \diagup\diagup \\ O \qquad\qquad | \\ \qquad\qquad NH_3 \end{array}$$

Negatively charged R groups

5.   In addition to the 20 standard amino acids, several others of relatively rare occurrence have been isolated from hydrolyzates of some specialized types of proteins. All are derivatives of some standards amino acids and they include 4-hydroxy proline (from proline) Hydroxylysine (from lysine)

Another example is citruline found in the liver and water melon juice, ornithine found   in the liver of some vertebrates and thyroxine found in thyroid gland.

Several non protein amino acids are also known to occur in biologically free or combined form but never in proteins. Most are derivatives of the L-α amino acids found in proteins. Those from β and γ amino acids are also known e.g. β-alanine is a building block of the vitamin panthotenic acid.

Fungi and higher plants contain an extraordinary variety of non protein amino acids, the metabolic functions of most of which are still not understood e.g. Djenkolic acid found in djenkol nuts and β-cyanoalanine found in some nuts and ergothioneine found in red fungus cells (ergot).

Most of these amino acids are toxic to other forms of life apart from their sources.

4.0   CONCLUSION

Proteins are complex organic compounds that contain C, H, O, N. and S. When proteins undergo digestion through the action of enzymes, they are broken down to simpler food substances called amino acids. In nature, more than 200 amino acids exist but only 10% of these occur as component of proteins and are known as common amino acids. Certain amino acids can be produced from others by a process known as transamination**,** but a number of amino acids cannot be effectively

synthesized in the animal body and these are referred to as indispensable or essential amino acids.

6.0   TUTOR-MARKED ASSIGNMENT

1.   a.   How would you classify amino acids on the basis of their functional groups?
      b.   How would you classify amino acids on the basis of their R groups? Also use structural diagrams to explain your answer.
      c.   Describe the reaction involved in the kjeldahl procedure.
2.   a.   How would you classify amino acids on the basis of their functional groups?
      b.   How would you classify amino acids on the basis of their R groups? Also use structural diagrams to explain your answer.
3.   Based on the hydrolysis products of proteins, describe the three major classes of proteins.

7.0   REFERENCES/FURTHER READING

Dickerson, R.E. and I. Geis (1993). "*Proteins: Structures, Function and Evolution*". Benjamin (Cummings. Menlo Park, Califonia).

Lehninger, A. L. (1992). "*Principles of Biochemistry*". New York: Worth Publ.

Linder, M.C. (1991). "*Nutritional Biochemistry and Metabolism*". New York: Elsevier.

McDonald, P., R. A. Edwards, J. F. D. Greenhalgh (1997). "*Animal Nutrition*", Fourth Edition, ELBS, London.

Whitney, E. N. and S. R. Rolfes (1993). "*Understanding Nutrition*". New York: West Publ. Comp. Los Angeles.

UNIT 4   NUCLEIC ACIDS AND NUCLEOPROTEINS

CONTENTS

1.0   INTRODUCTION

Nucleoproteins play an important role as primary constituents of chromatin in the process of cell division and reproduction and in the transmission of hereditary factors.

2.0   OBJECTIVES

At the end of this unit, you should be able to:
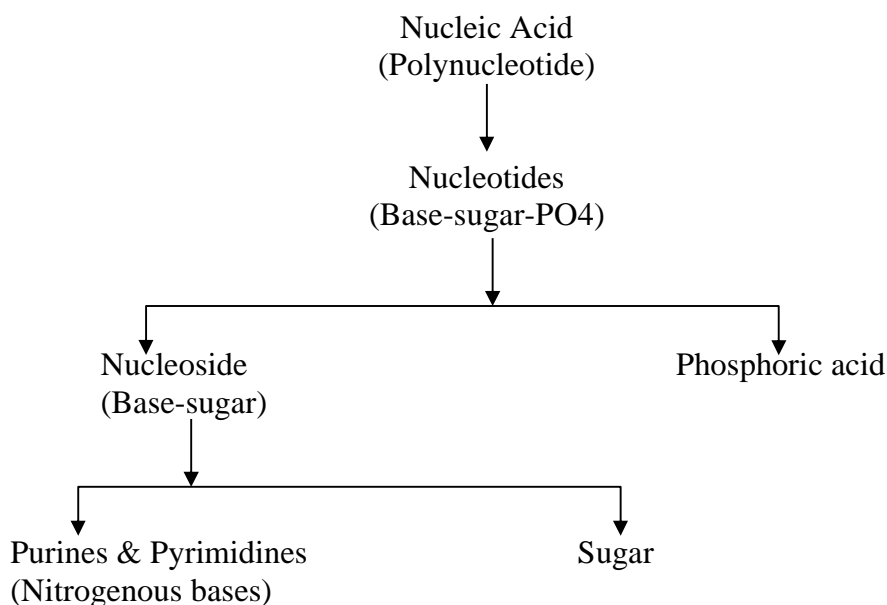
- identify the roles of different nucleoproteins in the transmission of hereditary genetic factors.

3.0   MAIN CONTENT

3.1   Nucleoproteins and Nucleic Acids

Nucleoproteins play an important role as primary constituents of chromatin, in the process of cell division and reproduction and in the transmission of hereditary factors. They are formed by combinations of

simple proteins, with nucleic acids, which are complexes of purine and pyrimidine bases, sugar and phosphoric acid. Nucleoproteins make up a large part of the nuclear material of cells and are also present in the cytoplasm. They are more than any other cell constituents and are concerned with vital cellular organisation and function.
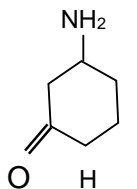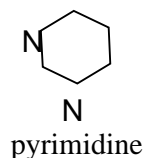
Nucleic Acid
(Polynucleotide)

↓

Nucleotides
(Base-sugar-PO4)

Nucleoside
(Base-sugar)   Phosphoric acid

Purines & Pyrimidines   Sugar
(Nitrogenous bases)

Figure 1   Components of Nucleic Acids

3.1   Nucleic acids

Nucleic acids are high molecular weight compounds which play a fundamental role in living organisms as a store of genetic information, and they are the means by which this information is utilized in the synthesis of proteins. On hydrolysis, nucleic acids yield a mixture of basic nitrogenous compounds; purines and pyrimidines, a pentose (ribose or deoxyribose) and phosphoric acids.

The main pyrimidines found in nucleic acids are cytosine, thymine and uracil. The relationships between these compounds and the parent material, pyrimidine, are given below:

pyrimidine
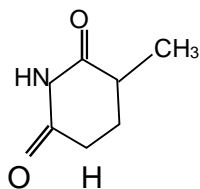
cytosine **thymine** **uracil**

Adenine and guanine are the principal purine bases present in nucleic acids
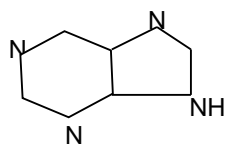
Purine
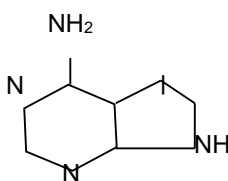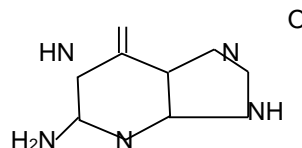
adenine **guanine**

3.2 Structure of Nucleosides

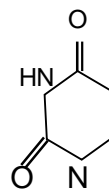The nucleosides as previously indicated are composed of a purine or pyrimidine base linked to either D-ribose of D-2 deoxyribose through a P-N-glycoside linkage. This linkage in the purine nucleosides is at position 9 of the purine and in the pyrimidine. Nucleosides at position of the pyrimidine. The furanoside ring form of the sugar is present. The representative formulae of nucleoside are as follows.

If the –OH on the 2` – position of the ribose is replaced by –H, the corresponding 2` – deoxynucleoside (in this case 2` - deoxyadenosine) is formed. Not that it is in the N-9 position on the purine ring which is involved in the N-glycosidic bond. In pyrimidine nucleoside, the N-1 nitrogen forms the linkage.

3.3 Structure of Nucleotides

A nucleotide is a nucleoside to which phosphoric acid or PO4 group has been attached. The nucleotide is attached in an ester linkage usually to the 5` - hydroxyl but sometimes to the 3` - hydroxyl of the ribose. If the position (5` or 3`) is not specified, the 5`-ester can generally be assumed for example, adenine – 5`-nu-cleotide is more usually known as adenylic acid (since the nucleotide group is acidic) or adenosine monophosphate (AMP). If additional (one or two) PO4 groups are attached to the first nucleotide (by anhydride linkages), the compounds formed are called **adenosine dinucleotide (ADP)** and **adenosine trinucleotide (ATP).**
**Note that nucleoside di and trinucleotides are exactly the same as nucleotide mono or dinucleotides. The word nucleotide already indicates the presence of one nucleotide group.**

3.4 Functions of Nucleotides

1. By means of the ATP, ADP + Pi interconversion, ATP serves as the carrier of chemical energy in the cell. The energy can be used for mechanical function (as in the ATPase of muscle) and to drive chemical reactions (as in the synthesis of glutathione, for reactions of this sort, only the terminal nucleotide anhydride is usually hydrolysed giving ADP + Pi.
2. Different parts of NTP molecules are used as carriers and activators of a variety of groups in biosynthesis reactions. (NTP is nucleoside trinucleotides).

(a) Adenosine Trinucleotide
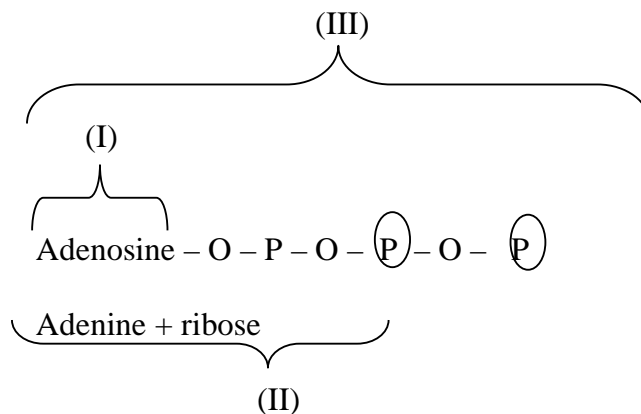
i. Adenosine, as S – adenosylmethionine, carries active methyl groups of biological methylations in the metabotion of the further – containing A2.
ii. AMP, as part of 3` - phosphoadenosine – 5` phosphosulfate provides "active sulfate" for the synthesis of the chondroitin

S04S. AMP is also the carrier of amino acids during the loading (activation) of the RNAs used in protein synthesis.
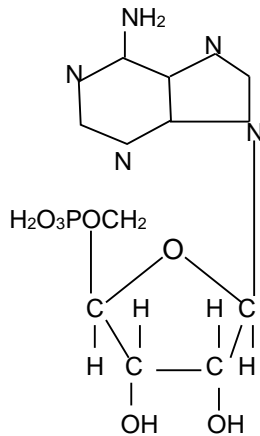
iii.   ADP is part of coenzyme A. In this and other molecules containing NDP's, even though ATP is the immediate source of adenosine, usually only one nucleotide comes along with it. The other nucleotide was already part of the molecule to adenosine mono-nucleotide is being added.

For example:

$4 - phosphopantetherne + ATP \rightarrow dephospho - COH + PPi$

This also illustrates the release of inorganic pyronucleotide (PPi) and other feature of many reactions in which a NMP is incorporated into some other molecules.

The pyronucleotidetase PPi + H20 pyrophosphatase 2Pi

About 7.3k cal is released per mole of PPi hydrolysed. This helps to make the re-synthesis of ATP by the reversal of these reactions quite difficult.

2.   Uridine trinucleotide is used to synthesize UDP-glucose, UDP-galactose, UDP-glucuronic acid and other UDP-sugars. These compounds are used in the biosynthesis of polysaccharides and for other reactions like glycogen synthesis, galactose metabolism and bilirubin (haemoglobin) metabolism.

3.   A number of coenzymes involved in electron transfer reactions contain nucleotides. These include NAD+, NADP+ and FAD. Coenzyme A is also a nucleotide enzyme.

4.   Nucleotides act as intracellular hormones or 'second messengers'. This is best typified by cyclic AMP.

Adenine   D-ribose   Adenosine
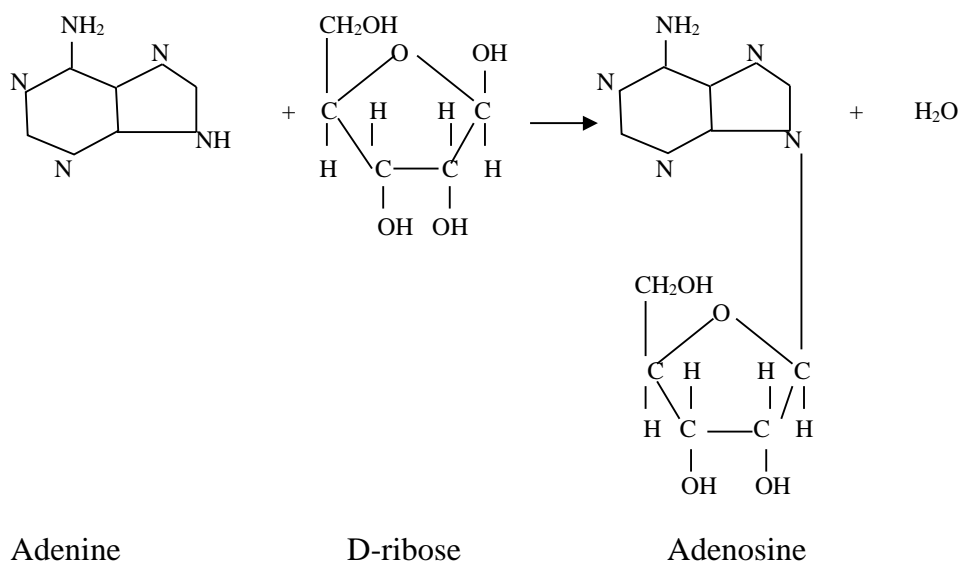
If nucleosides such as adenosine are esterified with phosphoric acid they form nucleotides, e.g. adenosine monophosphate (AMP):

Nucleic acids are polynucleotides of very high molecular weight, generally measured in several millions. A nucleotide containing ribose is termed ribonucleic acid (RNA) while one containing deoxyribose is referred to as deoxyribonucleic acid (DNA).

3.5   Deoxyribonucleic acid (DNA)

The nucleotides are arranged in a certain pattern; DNA normally consists of a double-strand spiral or helix (see figure below). Each strand consists of alternate units of the deoxyribose and phosphate groups. Attached to each sugar group is one of the four bases, cytosine, thymine, adenine or guanine. The bases on the two strands of the spiral are joined in pairs by hydrogen bonds, the thymine on one strand always being paired with the adenine on the other and the cytosine with the guanine. The sequence of bases along these strands carries the genetic information of the living cell. DNA is found in the nuclei of cells as part of the chromosome structure.

There are several distinct types of ribonucleic acids, which are defined in terms of molecular size, base composition and functional properties. They differ from DNA in the nature of their sugar moiety and also in the types of nitrogenous bases present. RNA contains the pyrimidine, uracil, in place of thymine. There is evidence to indicate that unlike

DNA, most RNA molecules exits in the forms of RNA, termed messenger RNA, ribosomal RNA and transfer RNA.

Apart from their importance in the structure of nucleic acids, nucleotides exist as free monomers and many play an important role in cellular metabolism.   Reference has been made previously to the phosphorylation of adenosine to form adenosine monophosphate (AMP).   Successive additions of phosphate residues give adenosine diphosphate (ADP) and then the triphosphate (ATP).

Diagrammatic representation of part of the ladder-like DNA molecule, showing the two strands of alternate phosphate (P) and deoxyribose (D) molecules. The horizontal rods represent the pairs of bases held by hydrogen bonds (represented by dotted lines). A = Adenine, T = Thymine, C= Cytosine, G = Guanine.PP D ATDP AT DP G DPDPCDP D ATDPPCG DPPPD
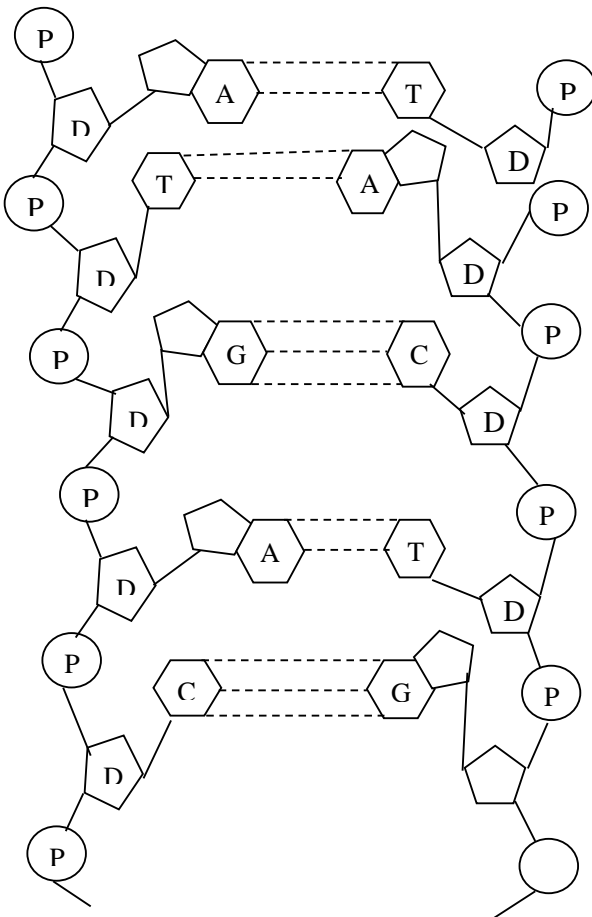
3.6   Ribonucleic Acid (RNA)

There are at least 3 characteristic forms of ribonucleic acid RNA.

3.6.1 Messenger RNA (mRNA)

mRNA is a single stranded molecule. It is made in the nucleus of the cells as a complement to one strand of DNA, so that, according to the pairing run, thymine, cytosine, guanine and adenine in a DNA strand direct the incorporation, respectively, of adenine, guanine, cytosine and uracil in the complementary RNA stand. The reaction is catalysed by RNA polymerize. Only one strand of DNA serves as a template for synthesis of mRNA and a message may be derived only from certain discrete sections of the DNA strand. The unit of information of one protein peptide chain is termed the Cistron. A DNA strand may therefore contain information for the synthesis of several protein peptide chains i.e. several Astons working together as an operon to provide information necessary for the synthesis of a sequence of enzyme proteins involved in a metabolic pathway. As just noted, as active DNA strand contains information for synthesis of several different proteins. Messenger RNA serves as the means of transcribing the structure (Amino acid sequence) of proteins being synthesized within the endoplasmic reticulum of the cell. In order to regulate the special metabolic activity of the cells only certain of the protein peptides the cell is capable of synthesizing should be produced at a given time. This, only a small amount of the total information in DNA may be used by the cell at any one time.

3.6.2 Ribosomal RNA (rRNA)

A second form of RNA is that associated with the ribosome of the endoplasmic reticulum in the cytoplasm. Like mRNA, ribosomal RNA is formed so as to be complementary to some region of DNA. It is thus apparent that not all of the genetic information in DNA is associated with coding for synthesis of cellular protein through messenger RNA. It is required to bind messenger RNA and the specific enzymes utilized for peptide bond synthesis. The ribosomes are composed of two parts which can be separated by varying concentrations of divalent cations (mgH is often used). The subunits of the ribosomes are classified in terms of their sedimentation rates (s); the commonly studied ribosomes of E. coli for example are compressed of 30 s and 50 s components; mammalian ribosomes are comprised of 40s and 60s components. Each part contains RNA along with several proteins. The 30s component (in E. coli) possesses an initiator site which binds the first codon on messenger RNA and the corresponding transfer RNA. The 50s components bind the growing polypeptide chain by means of a specific transfer RNA molecule.

3.6.3 Transfer RNA (t RNA)

This type of RNA accomplishes the transfer of amino acids to the proper site on the RNA template of mRNA. For each amino acid to be incorporated into the 1o structure of a protein molecule there is therefore a specific tRNA molecule to which the amino acid is attached. Although transfer RNAs are a mixture of different molecular species of similar size, they can be differentiated by the ability of each of them to accept only one A2 and to transport that A2 for use in protein synthesis.

The amino acid carrying end of all of the tRNA molecules contains the same trinucleotide, having the base sequence C – C – A, which is two cytidylic acid and an adenylic acid nucleotide residue, attached to a terminal adenosine residue. On the hydroxyl group of carbon 3 of the ribose of the terminal adenosine residue, the amino acid carried on the t RNA molecule is attached by a minoacyl linkage as shown.
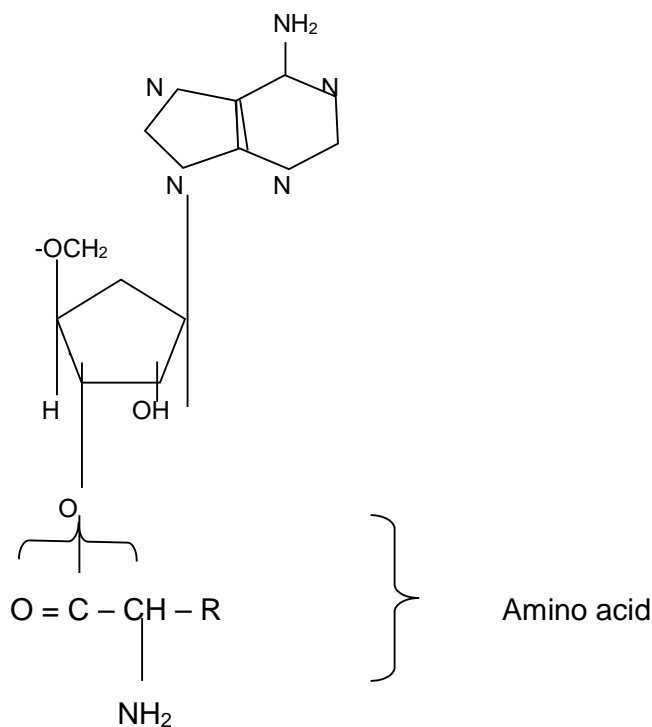
A guanine nucleotide frequently occurs at the S1 nucleotide terminus of the tRNA. (although thymine was generally stated to occur only in DNA). A thymine – containing nucleotide occur at the 23rd position in the tRNA molecule. Finally, the sequences A – G – DU, G – T – C, and G – C – M2G also appear in each tRNA molecule.

3.7   Other Nitrogenous Compounds

A considerable variety of nitrogen-containing compounds, other than proteins and nucleic acids, occur in plants and animals. In plants, free amino acids are usually present; those in greatest amount include glutamic acids, aspartic acid, alanine, serine, glycine and proline. Other compounds are nitrogenous lipids, amines, amides, purines, pyrimidines, nitrates and alkaloids. In addition, most members of the vitamin B complex contain nitrogen in their structure.

It is clearly impossible to deal with these compounds in any detail and only some of the important ones not previously mentioned will be discussed.

3.7.1 Amines

Amines are basic compounds present in small amounts in most plant and animal tissues. Many occur as decomposition products in decaying organic matter and have toxic properties.

Table 1   Some important amines and their Parent Amino Acids

Amino acid	Amine
Arginine	Putrescine
Histidine	Histamine
Lysine	Cadaverine
Phenylalanine	Phenylethylamine
Tyrosine	Tytamine
Tryptophan	Tryptamine

A number of microorganisms are capable of producing amines by decarboxylation of amino acids (Table 4.1). These may be produced in the rumen under certain conditions and may give rise to physiological symptoms; histamine, for example, is an amine formed from the amino acid, histidine, and in cases of anaphylactic shock is found in the blood in relatively large amounts. Silages in which clostridia have dominated the fermentation usually contain appreciable amounts of amines.

Betaine is a tertiary amine which is formed by the oxidation of choline. Betaine occurs in sugar beet, and the young leaves may contain about 25g/kg; it is this amine which is responsible for the `fishy' aroma frequently associated with the commercial extraction of sugar from beet. In the animal body, betaine may be transformed into trimethylamine and

it is this which gives the fishy taint to milk produced by cows that have been given excessive amounts of sugar beet by-products.

3.7.2 Amides

Asparagine and **glutamine** are important amide derivatives of the amino acids, aspartic acid and glutamic acid. These two amides are also classed as amino acids (Table 4.1) and occur as components of proteins. They also occur as free amides and play an important role in transamination reactions.

Urea is an amide which is the main end-product of nitrogen metabolism in mammals, although it also occurs in many plants and has been detected in wheat; soya bean, potato and cabbage.

Urea
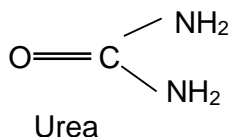
In man and other primates, **uric acid** is the end product of purine metabolism and is found in the urine. In sub primate mammals, the uric acid is oxidized to **allantoin** before being excreted.

In birds, uric acid is the principal end-product of nitrogen metabolism and thus corresponds, in its function, to urea in mammals.

Uric Acid   *Allantoin*
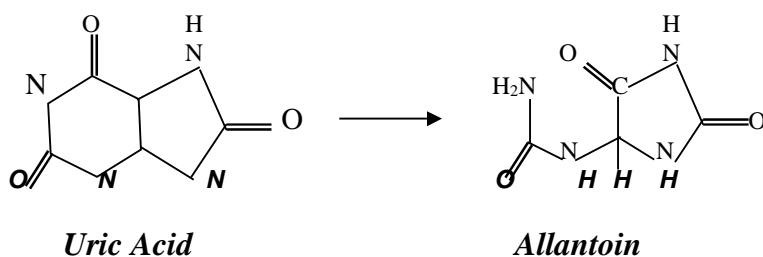
3.7.3 Nitrates

Nitrates may be present in plant materials and, while nitrate itself may not be toxic to animals, it is reduced readily under favourable conditions, as in the rumen, to nitrite, which is toxic. 'Oat hay poisoning' is attributed to the relatively large amounts of nitrate have been reported in herbage given heavy dressings of nitrogenous fertilizers.

3.7.4 Alkaloids

These compounds occur only in certain plants, and are of particular interest since many of them have poisonous properties. Their presence is restricted to a few orders in the dicotyledons. A number of the more important alkaloids, with their sources, are listed in Table 4.2.

Table 2   **Some important alkaloids occurring in Plants**

Name	Source
Coniine	Hemlock
Nicotine	Tobacco
Ricinine	Castor plants seeds
Atropine	Deadly nightshade
Cocaine	Leaves of coca plant
Jacobine	Ragwort
Quinine	Cinchona bar
Strychine	Seeds of Nux vomica
Morphine	Dried latex of opium poppy
Solanine	Unripe potatoes and potato sprouts

4.0   CONCLUSION

- Nucleoproteins play an important role as primary constituents of chromatin, in the process of cell division and reproduction and in the transmission of hereditary factors

- They are formed by combinations of simple proteins, with nucleic acids, which are complexes of purine and pyrimidine bases, sugar and phosphoric acid.

- Nucleoproteins make up a large part of the nuclear material of cells and are also present in the cytoplasm. They are more than any other cell constituents and are concerned with vital cellular organisation and function.

- Nucleotides are the building blocks for nucleic acids; they are involved in a wide variety of metabolic processes such as: serve as the carriers of high energy phosphate and as the precursors of several coenymes.

- Nucleic acids play a fundamental role in living organisms as a store of genetic information, and they are the means by which this information is utilised in the synthesis of proteins

- On hydrolysis, nucleic acids yield a mixture of basic nitrogenous compounds; purines and pyrimidines, a pentose (ribose or deoxyribose) and phosphoric acids.

- The main pyrimidines found in nucleic acids are cytosine, thymine and uracil, while adenine and guanine are the principal purine bases present in nucleic acids
- A nucleotide containing ribose is termed ribonucleic acid (RNA), while one containing deoxyribose is referred to as deoxyribonucleic acid (DNA).
- DNA normally consists of a double-strand spiral or helix. Each strand consists of alternate units of the deoxyribose and phosphate groups. The sequence of bases along these strands carries the genetic information of the living cell.
- DNA is found in the nuclei of cells as part of the chromosome structure.
- There are at least 3 characteristic forms of ribonucleic acid, RNA; messenger RNA, ribosomal RNA and transfer RNA.

6.0   TUTOR-MARKED ASSIGNMENTS

1. What are nucleic acids?
2. Discuss the constituents of nucleic acids?
3. Discuss the principal purine and pyrimidine bases present in nucleic acids. (With accompanying chemical structures)

7.0   REFERENCES/FURTHER READING

Dickerson, R.E. and I. Geis (1993). "*Proteins: Structures, Function and Evolution*". Benjamin (Cummings. Menlo Park, California).

Lehninger, A.L. (1992). "*Principles of Biochemistr"y.* New York: Elsevier.

McDonald, P.R.A. Edwards, J.F.D. Greenhalgh (1997). "*Animal Nutrition",* Fourth edition, ELBS, London.

Whitney, E.N. and S.R. Rolfes (1993). "*Understanding Nutrition"*. New York: West Publ. Comp. Los Angeles.

MODULE 2

Unit 1   The Chemistry of Lipids
Unit 2   Minerals in Animal Nutrition
Unit 3   The Vitamins and Their Functions
Unit 4   The Nature, Classification and Function of Enzymes and Hormones

UNIT 1   THE CHEMISTRY OF LIPIDS

CONTENTS

1.0   INTRODUCTION

Lipids are biological substances that are soluble in organic solvents. Apart from being structural components of biological membrane, they also play a major role in the nutrition of the animal. Just as carbohydrates can supply energy, lipids can also carry out this function.
In this chapter, we will focus on functions of lipids, their classification and the structures of some common lipids.

2.0   OBJECTIVES

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

- state what lipids are
- explain the functions of lipids
- describe the structures of some lipids..

3.0   MAIN CONTENT

3.1   Definition of Lipids

Lipids are biological molecules that are soluble in organic solvents. Lipids therefore include fats, oils, waxes, and related compounds. Occasionally, the term **lipoid** may be used in place of lipid. These two terms are synonymous and therefore can be used interchangeably.

3.1.1 Importance of Lipids

Lipids have the following biological functions:

Certain lipids, fats, serve as efficient reserves for storage energy. Such lipids are found in the adipose tissues.

Fats serve as carriers for the fat soluble vitamins. The fat-soluble vitamins are, Vitamins A, D, E and K (A, D, E, K).

Lipids constitute the major structural element of membranes. When lipid is in combination with a protein the resulting substance is termed **lipoprotein,** i.e. lipid-protein.

Fat serves as insulating material in the subcutaneous tissues around certain organs.

Cholesterol, an example of a lipid, is a major substance from which Vitamin D and sex hormones are synthesized.

3.2   Classification of Lipids

Bloor classified lipids as follows:

Simple Lipids

These are esters of fatty acids with various alcohols. Example of simple lipids include fats (esters of fatty acids with glycerol), waxes.

Compound Lipids

These are ester of fatty acids but containing in addition, alcohol and a fatty acid. Examples of compound lipids include phospholipids, e.g. (glycerophospholipids), sphingophospholipids, cerebrosides (glycolipids) – compounds containing the fatty acids with carbohydrates, containing nitrogen but no phosphoric acid. Other compound lipids include sulpholipids, aminolipids, and lipoproteins.

Derived Lipids

These are substances derived from the hydrolysis of simple lipids and compound lipids. The derived lipids include fatty acids, glycerol, steroids, alcohols in addition to glycerol and sterols, fatty aldehydes and ketone bodies. Because glycerides (acylglycerols), cholesterol and cholesteryl esters are unchanged they are also termed neutral lipids.

3.3   Fatty Acids

Fatty acids are a group of aliphatic carboxylic (-COOH) acids, which contain from 2 to 24 or more carbon atoms. Fatty acids are obtained from the hydrolysis of fats. However, fatty acids can also occur in natural fats and such fatty acids normally contain an even number of carbon atoms (i.e. from 2-carbon units) and are also straight-chain derivatives (aliphatic).

Fatty acids can either be saturated or unsaturated. We shall elaborate on this shortly. Fatty acids can also be straight-chain or branched. However, the most abundant types of fatty acid are saturated and unsaturated straight-chain fatty acids. Before we get to discuss how fatty acids are named (nomenclature), let us first look at saturated and unsaturated fatty acids.

3.4   Saturated Fatty Acids

These are fatty acids that do not contain any unsaturated bonds (i.e. having single bonds). The general formula for the saturated fatty acid is **CnH2n + 1COOH** – the first member of this group is acetic acid. Others will be discussed later.

3.5   Unsaturated Fatty Acids

These are fatty acids that contain one or more double bonds (unsaturated bonds). Unsaturated fatty acids with only one double bond are called **monounsaturated fatty acids** or **monoethenoid acids**. Those with more

than one double bond are referred to as **polyunsaturated fatty acids (PHFA)** or **polyethenoid acids**.

3.6   Naming of Fatty Acids (Nomenclature)

Genevan System

This is the most frequently used systematic nomenclature. This system is based on naming the fatty acid after the hydrocarbon with the same number of carbon atoms. In this case – **oic** is substituted for the final –**e** in the name of the hydrocarbon. This is illustrated with the examples below.

Butan/e becomes butan/oic acid

Methane becomes methanoic acid

But for unsaturated fatty acid – **enoic** is added in place of –**oic**.

Carbon atoms are numbered from the carbonyl carbon (i.e. carbon number 1). The next carbon atom after the carboxyl carbon (i.e. carbon 2) is also known as the α - carbon (alpha carbon). Carbon atom number 3 is the β – carbon (Beta carbon) and end methyl carbon is known as **ω**-carbon (omega carbon).

The second convention uses the number of carbon atoms between the methyl carbon and the nearest double bond and uses the **n –** (n minus) notation. This convention is particularly useful for identifying formulas of fatty acids derived from common precursor fatty acids as ▲9, 12 (18, 2 or C18: 2n – 6).

It is conventional to indicate the position of the double bond by the following ▲9, i.e. it indicates a double bond between carbon atoms 9 and 10 of the fatty acid.

Methyl carbon

Carbonyl Carbon

$^{4w}CH3 – {}^{3\beta}CH2 – {}^{2\alpha}CH – {}^{1}COOH$
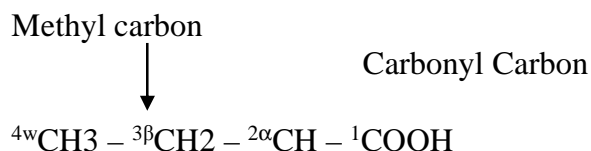
3.6.1 Monosaturated Fatty Acids (CnH2n + 1COOH)

_____

Name	Formular	Occurrence
Acetic acid	CH$_3$COOH	Major end products of carbohydrate fermentation by rumen microbes.
Propionic acid	C2H5COOH	Major end products of carbohydrate fermentation by rumen microbes.
Butyric acid (Butyric)	C3H7COOH	In certain fats in small amounts as butter. Fermentation in rumen.
Caproic (Hexanoic)	C5H11COOH	In certain fats in small amounts as butter. Fermentation in rumen.
Caprylic (Octanoic)	C7H15COOH	Butter.
Capric (Decanoic)	C9H19COOH	Butter.
Lauric (Dodecanvic)	C11H23COOH	Spermacetic, cinnamon, palm kernel , coconut oils.
Myristic(Tetradeconoic)	C13H27COOH	Nutmeg, palm kernel, coconut oils.
Palmitic (Hexadecanoic)	C15H31COOH	Common in all animal and plant fats.
Stearic (Octadecanoic)	C17H35COOH	Common in all animal and plant fats.
Arachidic (Eicosanoic acid)	C19H39COOH	Peanut (arachis) oil.

_____

Other higher members also occur in waxes.

A few branch-chain saturated fatty acids have also been isolated from both plant and animal sources. The long chain saturated fatty acids have lower rates of absorption than the shorter chain or the unsaturated fatty acids in both non-ruminants and the ruminants.

3.6.2 Monounsaturated Fatty Acids

General formula $C_nH_{2n} - 1COOH$

_____

Trivial Name	Systematic Name	Shorthand
Palmitoleic acid	C_{15} - $\blacktriangle^9$ - hexadeconoic acid	$\blacktriangle^9$ C16 : 1
Oleic acid	C_{15} –- $\blacktriangle^9$ - octadecenoic acid	$\blacktriangle^9$ C18 : 1
Gondoic acid	C_{15} -$\blacktriangle$11 - eicosenoic acid	$\blacktriangle^{11}$ C20 : 1
Erucic acid	C_{15} -$\blacktriangle$13 - decosanoic acid	$\blacktriangle^{13}$ C22 : 1
Nervonic acid	C15 -$\blacktriangle$15 - tetrasenoic acid	$\blacktriangle_{15}$ C24 : 1

Palmitoleic and oleic acids are more nutritional significance than other mentioned above.

3.6.3 Polyunsaturated Fatty Acids

2 double bonds

General formulae

$C_nH_{2n} - 3COOH$ e.g. Linoleic acid (C18:2; 9, 12)

3 double bonds

General formulae

$C_nH_{2n} - 5COOH$ e.g. Linolenic acid (C18:3; 9,12, 15)

4 double bonds

General formulae

$C_nH_{2n} - 7COOH$ e.g. Arachidonic acid (C20: 4; 5, 8, 11, 14).

Linoleic acid	C_{15} –- $\blacktriangle^{9, 12}$ - Octadecadienoic acid	$\blacktriangle^{9, 12}$ (C18:2)
[8] Unoleic acid	C_{15} –- $\blacktriangle^{6, 9, 12}$ - Octadecatrienoic acid	$\blacktriangle^{6, 9, 12}$ (C18:3)

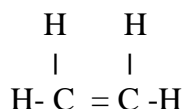| α - Linolenic acid	C_{15} –- $\blacktriangle^{9, 12, 15}$ - octadecatrienoic acid	$\blacktriangle^{9, 12, 15}$ (C18:3)
Arachidonic acid	C_{15}–- $\blacktriangle^{5,8, 11, 14}$ eicosatetrempoc acid	$\blacktriangle^{5, 8, 11, 14}$ (C20:4)

Linoleic, Linolenic and Arachidonic acids are called **essential fatty acids** because animals are unable to synthesis (de novo) by themselves – for this reason they must be included in the diets.
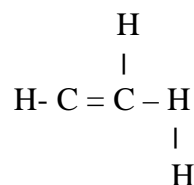
3.7   CIS and Trans Configurations

The polyunsaturated fatty acids also exhibit isomerism just as the carbohydrates do. But in the case of polyunsaturated fatty acids (PUFA) the isomerism depends on the orientation of atoms or groups around the axis of the double bonds. These two forms of isomerism are described as C15 and trans configurations.

As a general rule, when the H atoms are found on the same sides of a double bond this is referred to as C15 , while if the H atoms are found on different sides of the double bond, this is referred to as trans (See figure below):

```
  H     H                            H
  |     |                            |
H- C  = C -H              H- C = C – H
                                     |
                                     H

  Cis
                            Trans
```

The double bonds in most naturally occurring unsaturated fatty acids have the cis - configuration, although fatty acids with trans double bonds are found in bacterial lipids. PUFAS with a combination of both cis and trans double bonds are produced from Cis unsaturated fatty acids by chemical hydrogenation of vegetable oils, during the manufacturing of margarines and during biohydrogenation of dietary PUFAS in rumen of ruminant animals.

3.8   Branched Chain Fatty Acids

This term is normally reserved for fatty acids which contain one or more methyl (aid rarely ethyl) substituents along the carbon chain. Many microorganisms contain branch-chain fatty acids which are mainly iso and anteiso type.

$$CH_3 – CH – (CH_2)_n – COOH \qquad CH_3 – CH_2 – CH – (CH_2)_n – COOH$$
$$\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\quad CH_3 \qquad\qquad\qquad\qquad\qquad\qquad CH_3$$
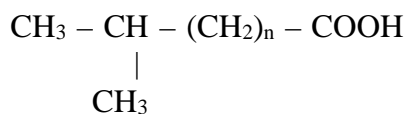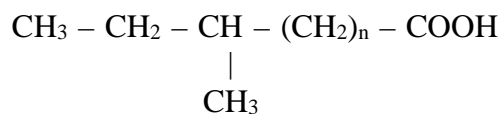
iso-branched fatty acids   anteiso-branched fatty acids

The fatty acid is iso-type if the methyl (branch) is on the same carbon atom as the last methyl group of the fatty acid. It is anteiso – type if the methyl group (branch) is found on any carbon atom other than the one on which the last methyl group is attached (See Fig. Y).

These fatty acids are typical of most gram positive and some gram-negative organisms. Trace qualities of iso and anteiso fatty acids (0.1 – 0.3%) are found in ruminant animal fat deposits. They arise as a result of the digestion and absorption of lipids from the rumen microorganisms as they pass through the small intestine. When certain unusual diets are provided, the proportion of branch-chain fatty acids in sheep and goat fat can be greatly increased.

4.0   CONCLUSION

Lipids are a diverse group of naturally occurring organic compounds that are related by their solubility in non polar organic solvents (chloroform, acetone & benzene) and general insolubility in water. Other functions includes provision of   ,protection and insulation.

5.0   SUMMARY

In this Unit, you have learnt that:

- Lipids are biological molecules that are soluble in organic solvents.

- Lipids play important role as sources of stored energy and structural components of biological membranes.

- Lipids are classified into three major groups namely; simple, compound and derived lipids.

- Fatty acids are obtained when fats are hydrolysed and they can be obtained from foods or synthesized de novo.

- Fatty acids are either saturated or unsaturated or short or, long or straight or branched-chained.

- The saturated fatty acids contain single bonds and examples are acetic, propionic, butyric, stearic, arachidic acids, etc, while the long chain polyunsaturated fatty acids (PUFAS) contain one or more double bonds. Examples of PUFAS are palmitoleic, oleic, linoleic, linolenic and arachidonic acids.

- The last three PUFAS (linoleic linolenic and arachidonic acids) are classified as essential fatty acids because the body cannot synthesize enough hence they must be included in the diets.

6.0 TUTOR-MARKED ASSIGNMENT

1. What are lipids?
2. Discuss the importance of lipids in the animal.

3.   a.   What are saturated and unsaturated fatty acids?
          b.   Name 3 unsaturated fatty acids and 3 saturated fatty acids.
          c.   Give the chemical structures of the fatty acids mentioned above.

7.0 REFERENCES/FURTHER READING

Chessworth, J.M.; Stuchbury, T. and Scaife, J.F (1998). *"Agricultural Biochemistry"*, (1st Edition). Published by Chapman and Hall Publishing. 1st Edition.

Maynard, L.A., Loosli, J.K., Hintz, H.F and Warner, R.G (1983). *"Animal Nutrition"*. (7th Edition). Tata: McGraw-Hill Publishing Company Limited.

Zubay, G (1993). "*Biochemistry*", (3rd Edition). Published by Wm. C. Brown Publishers.

UNIT 2   MINERALS IN ANIMAL NUTRITION

CONTENTS

1.0   INTRODUCTION

Minerals are indispensable part of a complete diet of farm animals. In this unit, dietary essential minerals functions, factors affecting the requirements and sources will be discussed.

2.0   OBJECTIVES

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

- define essential and non-essential minerals
- list essential functions of minerals
- enumerate factors that affect minerals in the body of animals
- identify the major sources of minerals
- define macro and micro minerals
- Give some examples, functions and deficiency symptoms of macro and micro minerals.

3.0   MAIN CONTENT

3.1   What are Essential Minerals?

Essential minerals are those **minerals recognised to carry out vital roles and which must be present in the feed**. About forty minerals have been discovered to occur naturally in the tissues of animals and plants. Out of these forty, the dietary essential minerals are those that have been shown by research to have essential metabolic roles in the body. The proof that each of these elements is essential rests upon experiments with one or more species. If the experimental animals develop deficiency symptoms, the omitted mineral in the diet is considered to be essential to the animal's diet. There are twenty seven basic dietary essential minerals that have been recognised, it includes: calcium, phosphorous, magnesium, sodium, potassium, chlorine, sulphur, manganese, iron, copper, iodine, zinc, fluorine, vanadium, cobalt, molybdenum, selenium, chromium, nickel, silicon and tin.

3.1.1 Fundamental Roles of Minerals

1.   A very prominent function is in the formation of skeletal framework. The skeletons of the vertebrates are made up of minerals especially calcium and phosphorus as constituents of bones and teeth; they give rigidity and strength to the skeletal structures.

2.   Minerals are constituents of the soft tissues, examples is in phospholipids that are present in protoplasm. They are components of body fluids, e.g. iron bond to protein in the blood.

3.   The acidity and alkalinity of digestive juices are maintained by minerals and the acidity arises from hydrochloric acid which is formed from sodium chloride.

4.   Many of their vital functions are due to an ionic inter-relationship which finds expression in the terms **"antagonistic action"** and **"balanced solution"**. For example a certain balance between calcium, sodium, and potassium in the fluid which bathes the heart muscle is essential for the normal relaxation and contraction which constitutes its beatings.

5.   Minerals are important in the activation of many enzymes and hormones.

6.   Mineral salts are sometimes fed to dairy and feedlot cattle beyond the established requirements because in their role as buffers, the

salts have been reported to improve feed intake, milk production, milk composition and animal health. Mineral salts used as buffers control excess hydrogen ion concentration in the rumen, intestines, tissues and body fluids or increase the rate of passage of fluids from the rumen or both.

3.1.2   Factors Affecting Mineral Requirements

Many factors determine the utilisation of minerals.

a.   Inter-relationship among minerals or relationship between minerals and organic fractions may result in enhanced or decreased mineral utilization. Because of the many inter-relationships among minerals, almost any minerals, may influence directly or indirectly the utilisation of any other mineral.

b.   The actual amount of mineral in the diet may also influence utilisation. For example, if the diet contains more calcium than that required, the efficiency of absorption is usually decreased.

c.   The minerals status of the animal may also influence absorption. A magnesium deficient animal is more efficient in the absorption of magnesium better than animal with sufficient magnesium stores.

d.   The form of the mineral is also an important determinant of utilisation. Iron oxide is not available, but ferrous sulphate can be readily utilised.

e.   Many genetic-nutrition relationships have also been demonstrated. Examples of the extreme genetic effects are shown by one strain of mice that requires a high dietary level of copper and by another strain of mice that requires a very high level of manganese. A strain of cattle that has a genetic defect in zinc metabolism has been identified. On the other hand, a strain of mice that is resistant to zinc depletion has been reported.

f.   Many more subtle differences exist. The copper requirements of merino sheep is reported to be 1 to 2 ppm higher than that for the British breeds.

g.   Changes in management practices may also influence the minerals requirement. For example, the calcium requirement of growing pigs has been studied at many experiments stations but there is still disagreement as to the optimum dietary level.

3.1.3 Sources of Minerals

The mineral content of plants depends largely on the mineral content and pH of the soil in which the plants are grown. Many soils are deficient in specific minerals, and crops raised on these soils have same mineral deficiencies. Plant calcium and phosphorus content are especially important since animals need fairly large amounts of calcium and phosphorus. Other plants usually contain minute amounts of calcium or levels lower than animals need. Seeds are low in calcium but contain high levels of phosphorus. Leaves contain higher level of both calcium and phosphorus than stems. The main minerals in bone are calcium, phosphate and carbonate. Small quantities of magnesium, sodium, lead, citrate, fluoride hydroxide and sulphate are present in the bone.

3.1.4   Mineral Supplements

As mentioned earlier in this unit, in certain parts of the world, the soils may be insufficient in one or more minerals that animals need and therefore, the plants grown in those soils are mineral deficient. However, for animals to survive in these areas, their rations must include minerals fortification. When selecting a mineral supplement one should consider its:-

1.   Mineral composition.

2.   Availability in the immediate environment.

3.   Cost per unit of mineral compare to other supplements.

3.1.5 Macro-and Micro-Minerals

Macro minerals, also called **major elements** are essential minerals that are required in large amount by the animals. These include calcium, phosphorus, magnesium, sodium, potassium, sulfur and chlorine.

Micro-minerals, also called **trace elements** are those that animals need in small amounts but that are indispensable to animals' productivity and health. Such minerals include manganese, iron, copper, iodine, fluorine, vanadium, cobalt, molybdenum, chromium, tin, nickel and silicon; some of these trace elements could be potentially toxic if used in large quantities.

3.1.6 Specific Functions and Deficiencies of Minerals

3.6.1.1 Calcium

Calcium is the most abundant mineral in the body of the animals with over 99% of it present in the bones and teeth. It is an important constituent of most living cells and tissue fluids; it functions in blood coagulation, bone formation, homeostatic relations and as enzyme co-factors.

Calcium Deficiency

a)   **Rickets:** In young growing animals, bone growth is affected as sub-normal calcification of bone occurs. Thus the joints become swollen, stiffness and lameness of the limb. Such deformations are seen in the chicken breasts, arched back in claves and bowed legs in humans.

b)   **Osteomalacia:** This occurs in mature vertebrates. The bones become weak, porous and soft. They break readily hence fractures are common in farm animals and human suffering from osteomalacia. In pregnant sows, the fractured vertebrate may pinch the spinal cord leading to paralysis.

c)   **Osteoporosis:** There is a decrease in the absolute amount of calcium in the skeleton. The rate of bone formation may be normal but increased bone resorption occurs in an attempt to maintain blood calcium.

3.6.1.2 Phosphorus

Apart from the large amounts of phosphorus in the bones and teeth, a range of 20-25% of phosphorus in the body is found in the extracellular soft tissues. The major functions of phosphorus are:

1. Needed for bone and teeth formation.
2. Carbohydrate metabolism as sugar phosphate, adenosine phosphates and creatinine phosphate.
3. In lipid metabolism, it is essential for the formation of lecithin.
4. Formation of phospholipids that are essential components of nerve tissues.
5. Formation of nucleoproteins of the chromatin material of genetic importance.
6. Regulate acid-base balance.

Phosphorus Deficiency

Phosphorus deficiency manifests in rickets in young growing animals and osteomalacia in adults. In rickets due to phosphorus deficiency, reduction occurs in blood phosphorus levels. Depraved appetite called "Pica" also occurs in cattle. The animals eat woods, rags, bones, rocks. They have rough hair coat and become emaciated. Reproductive disorders, reduced growth and reduced milk production can also occur in cattle.

3.6.1.3 Magnesium

The skeleton contains 60% of the Mg found in the body. Magnesium functions in relation to enzymes in several ways:

1. Component of an enzyme. Metalloproteins contain inorganic elements. Arginase that breaks arginine into ornithine and urea contains magnesium as a component of its molecules.

2. Activator of enzyme; for example, kinase and mutases that catalyze phosphorylation by ATP and molecular rearrangement respectively require magnesium.

3. Enzyme inactivator; in muscles, myosin ATP is activated by calcium but inactivated by magnesium contrast with actomyosin ATP.

Magnesium Deficiency

Magnesium deficiency can be due to low dietary magnesium intake. However, trace elements studies show absorption as low as 10-20% in some cases, from feeds and forages.

Results of magnesium deficiency are:

1. Vasodilatation with reduced blood pressure,
2. Hyperirritability ,and
3. Tetany followed by death.

"Grass staggers", "Grass Tetany" and Magnesium Tetany are conditions of magnesium deficiency in adult ruminants.

3.6.1.4 Sodium

Sodium is supplied to animals mainly in the form of sodium chloride. Most feed and forages are low in sodium. However, plants that grow in alkaline soil have fair amounts of sodium. Two major functions of sodium are:

1.   Regulation of osmotic pressure
2.   Maintenance of acid-base balance.

Sodium Deficiency

1.   There is reduced growth.
2.   Reduced utilization of protein and energy.
3.   Lowered egg production in poultry.
4.   In laboratory animals, reproductive disturbances are observed.

3.6.1.5 Potassium

Potassium is found abundantly in plants and animals. It functions in the regulation of intracellular osmotic pressure; it regulates intracellular acid-base balance, stimulates muscular irritability like sodium, and takes part in the metabolism of proteins and carbohydrates. Potassium (K+) and sodium (Na+) in adrenal arterial – blood are important regulators of aldosterone secretion, potassium is also important in the pyruvic kinase reaction.

Potassium Deficiency

When hypopotassemia occurs, the general effects are muscular weakness, lethargy, anorexia, myocardial degenerative changes, pulmonary oedema, and peripheral paralysis.

3.6.1.6 Chlorine

Chlorine is supplied to animals mainly as sodium chloride like sodium; chlorine is present biologically in ionic form. The functions of chlorine include:

1.   Regulation of osmotic pressure.
2.   Acid-base equilibrium.
3.   Chief anion of gastric juice that plays major roles in digestion and absorption of foods and feeds.

Deficiency of Chlorine

Animals deficient in chlorine exhibit decreased appetite, reduced growth rate, lowered milk production, feather picking and cannibalism in poultry. There is also heamoconcentration and retention of nitrogenous waste products.

3.6.1.7 Sulphur

Found mainly in organic form as components of proteins (cysteine, cystine and methionine), and in the hormone insulin, glutathione, thiamine, biotin and lipoic acid. In ruminants, traces of inorganic sulphur tend to improve the utilization of urea as a nitrogen source. Large inorganic sulphur intake is injurious to these animals as the rumen microflora produces hydrogen sulphide-H2S which is absorbed and then causes disturbances.

3.6.1.8 Manganese

Manganese is found in fairly constant amounts in plants and animals. Manganese functions as the activator of many enzymes systems. The major ones are:

a)   Pyruvate carbonylase which contains the minerals and Mn functions in the trans carboxylation phase of enzymatic reactions.

b)   In the synthesis of micropoly saccharine of cartilage, manganese acts as a catalyst in the glucosamine-serine linkages.

c)   Others are bone phosphatase, muscle adenosine – tri-phosphate, peptidases and choline esterases.

d)   Manganese is also needed for normal reproduction in mammals.

Deficiency of Manganese

In deficiency states, the sexual maturity of the female is delayed, irregular ovulation experienced and weak young ones are produced. In males, testicular degeneration leads to sterility. In cattle there is poor growth, leg disorders, poor fertility and frequent abortion. In pigs, the deficiency symptoms are poor bone growth, shortening of leg bones, enlarged hocks, muscular weakness, increase back fat and irregular oestrus. In poultry, slipped tendon, malformation of bones of leg, reduced egg-shell thickness and reduced hatchability.

3.6.1.9 Iron

Iron is present in small amount, 70% of which is found in the haemoglobin, the remainder is found mainly in the liver, spleen, bone-marrow, plasma myoglobin and various oxidation reduction enzymes. Iron functions as respiration pigments (haemoglobin, myoglobin) and in enzyme systems.

Deficiency of Iron

More than half of iron in the body is found in haemoglobin and the formation of pigment is affected by iron deficiency. Anaemia is the result. Iron deficiency is not common in ruminants. Iron deficiency in sheep and cattle causes depraved appetite (pica) similar to phosphorus deficiency. It is characterised by diarrhoea, loss of appetite and anaemia.

3.6.1.10   Copper

Copper like iron is needed for haemoglobin formation. Like iron, copper is stored in the liver but smaller amounts are stored in the brain, bone marrow, spleen, heart and kidneys. Like iron, copper may also be components of enzymes systems especially oxidation reduction systems. However, copper also functions in the neurological systems.

Deficiency of Copper

Anaemia results from low intake of either copper or iron. Other results are depressed growth, bone disorders, depigmentation of hair and wool, demyelination of spinal cord and lesion in the brain. There is muscular incoordination, gastrointestinal disturbances and diarrhoea.

Young lambs tend to be more susceptible to neonatal ataxia or sway back. Falling disease in grazing cattle is an atrophy of the myocardium with replacement fibrosis. The animal staggers, falls and sudden death tends to ensue due to acute heart failure.

Peat scours in cattle is due to low copper and high molybdenum. In cattle, copper deficiency delays or depresses oestrus thereby decreasing fertility. In poultry, hatchability is reduced and embryonic abnormalities may occur.

Copper functions as a growth promoter as it has antibacterial properties against a broad spectrum of microorganisms.

3.6.1.11   Zinc

Very small amount of zinc is needed by animals and many plants contain zinc adequately. The major role of zinc is as component of the enzyme carbonic anhydrase. It is also present in metalloenzymes like pancreatic carboxy-peptidase, alkaline phosophatase, various dehydrogenases as well as tryptophan desmolase. Zinc is also a cofactor in enzymes like arginase enolase, peptidases, carnosinase and oxaloacetic decarboxylase.

Deficiency of Zinc

The deficiency of Zinc results in reduced appetite, retarded growth, gross lesions in the epithelial tissues hence poor reproductive organ development. In pigs, there are skin lesions on the legs and belly, in poultry, poor feathering occurs. In ruminants, there is disorder of the hair coats and low milk production.

4.0 CONCLUSION

Minerals are inorganic nutrients obtained within mineral salts. They are considered as essential if they must be present in the diet to carry out vital roles.

5.0 SUMMARY

In this Unit, you have learnt that:

- Mineral elements are solid crystalline, chemical elements that cannot be decomposed and synthesized by ordinary chemical reactions.

- They are present in both plants and animals to execute specific functions.

- The amount to be required by animals is largely determined by certain inherent factors.

- Minerals although nutritionally required in smaller amounts are essential for maintenance and production purposes by the livestock.

- However the major and trace minerals are needed by the body in large and small amount respectively.

- Generally, deficiencies of most minerals are shown by a reduced appetite and production, slow growth and occasionally death.

6.0 TUTOR-MARKED ASSIGNMENT

1. Differentiate between essential minerals and non essential minerals.
2. State the factors that determine the mineral requirements by the livestock.

7.0   REFERENCES/FURTHER READING

Allen, D.T., E.R. Harlanm and R.G. Will (1986). *"A Guide to the Feeding and Nutrition of Ruminants in the Tropics"*. U.S.A.: Winrock International Institute for Agricultural Development Petit Jean Mountain Morrilton, AR 72110.

Anke, M.A Hennig, M. Grun, M. Partschelfield, B. Groppel, and H. Ludke (1976). "*Arsenic, a New Essential Trace Element*", Archiv. Tierern-ahrung. 26:742743

Babayemi, O.J., A.O. Akinsoyimi, O.A. Isah, A.A. Adeloye, M.A. Bamikole and M.K. Adewumi (1999). "*Effect of Magnesium Supplement on Performance Characteristics of Lactatin*"g West Africa Dwarf Goats. Trop. Animal Prod. Invest. 2:61-68.

Matnard, L.A. J.K. Lossh, F.H. Harold and G.W. Richard (1983). *"Animal Nutrition." (*Seventh Edition). Tata: McGraw-Hill Publishing Company Limited.

Menecty, G.R and H.D. Battarec (1976). *"Sodium and Potassium in Present Knowledge in Nutrition*", (4th ed). New York: Nutrition Foundation.

Pamp, D.E, R.O Goodrich, and J.C Meiske (1976). "*A review of the Practice of Feeding Minerals Free Choice",* World Rev. Animal Prod; 12:13-31.

Posuer, A.S (1973). "*Bone Mineral on the Molecular Level",* Fed; proc., 32.

Underwood, E.J. (1977). *"Trace Elements in Human and Animal Nutrition",* (4th ed). New York: Academic Press.

UNIT 3   THE CHEMISTRY OF VITAMINS COENZYMES AND THEIR FUNCTIONS

CONTENTS

1.0   Introduction
2.0   Objectives
3.0   Main Content
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1.0   INTRODUCTION

The roles played by vitamins-of dietary sources or synthesized, in man and livestock cannot be over-emphasized. This is further emphasized by the discoveries of deficiency, symptoms, syndromes and toxicity conditions. This study is to open us to the importance of vitamins in agriculture and to provide an adequate knowledge view of the biochemistry of vitamins

2.0   OBJECTIVES

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

- explain the chemistry of vitamins
- explain the role of vitamins in livestock and human well-being of these vitamins
- state the sources of these vitamins.

3.0   MAIN CONTENT

3.1   Vitamins

Vitamins are organic nutrients that are required in small quantities for a variety of biochemical functions and which, generally, cannot be synthesized by the body and therefore must be supplied by the diet.

Absence or relative deficiency of vitamins in the diet leads to characteristic deficiency states and diseases. Vitamin deficiencies can be avoided by consumption of food/feed of a wide variety in adequate amounts. Many vitamins are destroyed by oxidation a process sped up by the action of heat, light and certain metals such as iron.

Some compounds function as vitamins only after undergoing a chemical change; such compounds are described as **provitamins** or **vitamin precursors**.

Vitamins are classified into two groups based on their solubility:

1.   Water Soluble Vitamins
2.   Fat Soluble Vitamins

Due to the water solubility of water soluble vitamins, excesses of water soluble vitamins are excreted in urine, so the rarely accumulate and manifest in toxicity conditions. Owing to this characteristic too, storage of water soluble vitamins is limited, thus must be provided regularly.

The body on the other hand, is able to store surplus soluble vitamins, thus toxicity conditions known as **hypervitaminosis** can result from excessive intake of fat soluble vitamins.

3.2   Water Soluble Vitamins

Water soluble vitamins consist of Vitamin B and Vitamin C.

3.2.1   Vitamin B

Vitamin B exists as a complex and these vitamins are essential for animal nutrition.
Vitamins of the B-complex function as **co-factors;** accessory non-protein compounds necessary for the activity of an enzyme in enzymatic reactions. Deficiency of a single

Table 1   B-Complex Vitamins and their chemical names

_____

Vitamin	Chemical Name
Vitamin B_1	Thiamin
Vitamin B_2	Rioflavin
Vitamin B_3	Niacin
	(nicotinic acid, nicotinamide)
Vitamin B_5	Pantothenic acid
Vitamin B_6	Pyridine
	(Pyridoxal, Pyridoxamine)
Vitamin B_{12}	Cobalamin
	(Cyanocobalamin)
	Choline
	Biotin
	Folic Acid

_____

Vitamin of the B-complex is rare; nevertheless, definite syndromes are characteristics of deficiencies of specific vitamins.

Table 2   Syndromes of Deficiencies of B Complex Vitamins

_____

Vitamins	Deficiency Syndromes
Thiamin	Beriberi
Riboflavin	Cheilosis, Glossitis, Seborrhea,
	Photophobia
Niacin	Pellagra
Pyridoxine	Peripheral neuritis
Cobalamin	Megaloblastic anaemia, Methylmalonic
	Aciduria
Folic Acid	Megaloblastic anaemia

_____

Table 3   Some Enzymes and Enzyme Prosthetic Groups involving the B-Vitamins

Vitamins	Coenzyme of Prosthetic Group	Enzymic Actions and other Functions
Thiamin	Thiamin diphosphate (TDP)	Oxidative decarboxylation
Riboflavin	Flavin mononucleotide (FMN)	Hydrogen carrier
	Flavin adenine dinucleotide (FAD)	Hydrogen carrier
Nicotinamide	Nicotinamide adenine dinucleotide (NAD)	Hydrogen carrier
	Nicotinamide adenine dinucleotide phosphate (NADP)	Hydrogen carrier
		Hydrogen carrier
Pyridoxal	Pyridoxal phosphate	Transaminases and decarboxylases
Pantothenic acid	Coenzyme A (CoA)	Acyl transfer
Folic Acid	Tetrahydrofolic acid	One carbon transfer
Biotin	Biotin	Carbon dioxide transfer
Cobalamin	Adenyl cobalamide	Group transfer

3.2.1.1 Vitamin B$_1$

Thiamin is a complex nitrogenous base containing a pyrimidine ring joined to a thiazole ring.
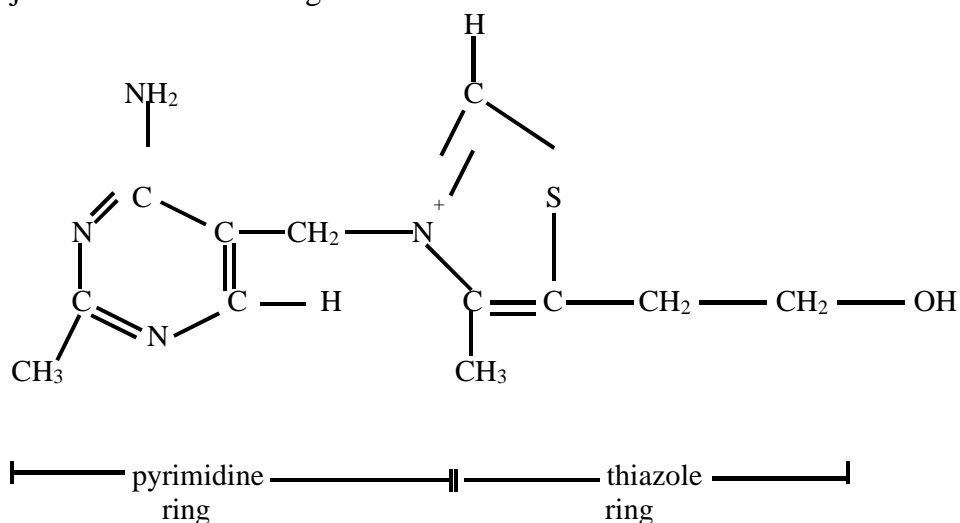
Figure 1: Vitamin B1- Thiamin

Because of the presence of a hydroxyl group at the end of the side chain, it can form esters. Main forms of thiamin in animal tissues are thiamin

diphosphate (TDP), Thiamin monophosphate (TMP) and Thiamin Triphosphate (TTP) also occur.

Sources

Thiamin is widely distributed in foods; brewers' yeast, unrefined cereal grains, beans, peas, green leafy crops, egg yolk, kidney and pork muscle.

Deficiency Symptoms

Symptoms of thiamin deficiency include loss of appetite, emaciation, muscular weakness and a progressive dysfunction of the nervous system.

3.2.1.2 Vitamin B$_2$

Riboflavin consists of a dimethyl-isoalloxazine nucleus combined with **ribitol**. It is a yellow crystalline compound, relatively heat stable but decomposes in the presence of visible light.

Riboflavin is an important constituent of flavoproteins e.g. flavin mononucleotide (FMN), flavin adenine dinucleotide (FAD). Flavoproteins are concerned with reactions of hydrogen transport and are important in carbohydrate and amino acid metabolism.
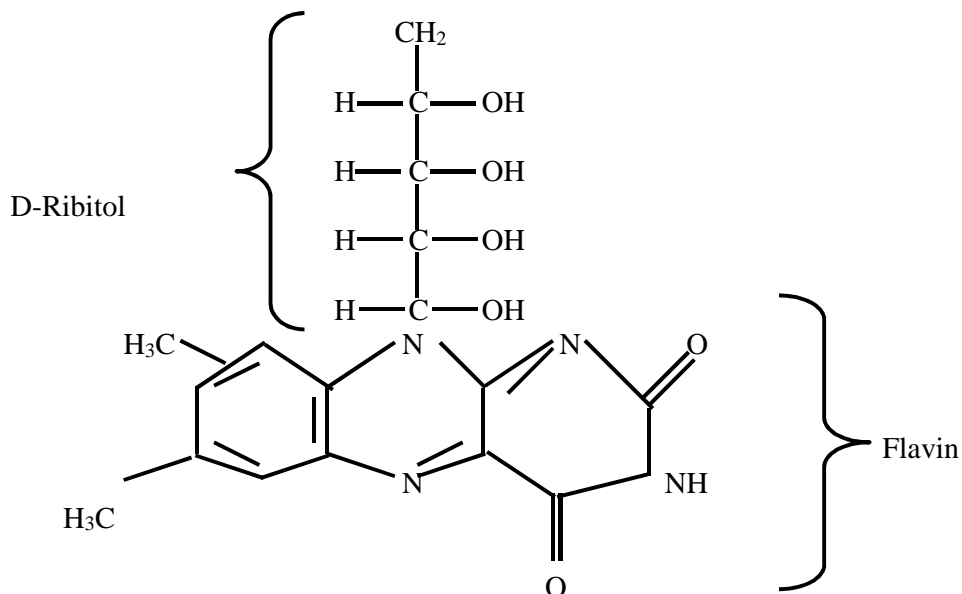

**Figure 2   Riboflavin**

Sources

Riboflavin is found in yeast, liver, kidney, milk (especially whey) and leafy crops.

Deficiency Symptoms

Symptoms of riboflavin deficiency include poor appetite with consequent retardation in growth, vomiting, skin eruptions and eye abnormalities. Also results in poor reproduction in sows and curled toe paralysis-caused by a peripheral nerve degeneration, resulting in chicks walking on their hocks with toes curled inwards, decreased hatchability and clubbed down condition-down feathers of chicks continue to grow inside the follicle resulting in a coiled feather.

3.2.1.3 Vitamin B$_3$

Niacin is the generic name of **nicotinic acid** and **nicotinamide**, of which may act as a source of the vitamin in the diet. Tryptophan acts as a precursor of vitamin B$_3$.

Nicotinamide   Nicotinic acid
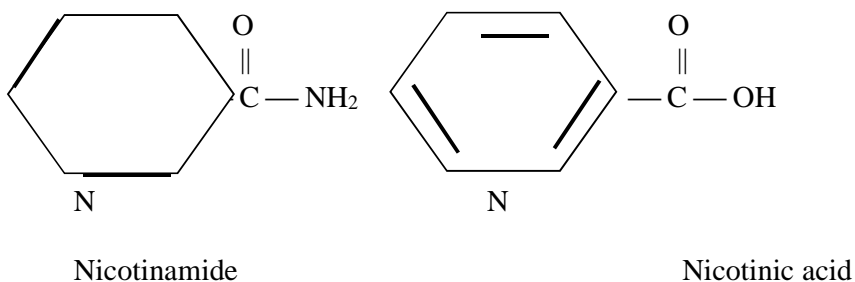
Figure 3   Chemical Structures of Nicotinamide and Nicotinic Acid.

Nicotinamide functions in the animal body as active groups of two important enzymes, nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) which is involved in the mechanism of hydrogen transfer in living cells.

Sources

Nicotinic acid can be synthesized from tryptophan in the body tissues which can be further converted to nicotinamide-containing coenzyme. Rich sources of niacin are liver, yeast, groundnut and sunflower meals. Milk and eggs though devoid of niacin are rich in the precursor tryptophan.

Deficiency Symptoms

Deficiency symptoms include poor growth, enteritis, dermatitis, bone disorders and inflammation of the mouth and upper part of the oesophagus.

3.2.1.4 Vitamin B₅

Pantothenic acid is an amide of pantoic acid and β-alanine.
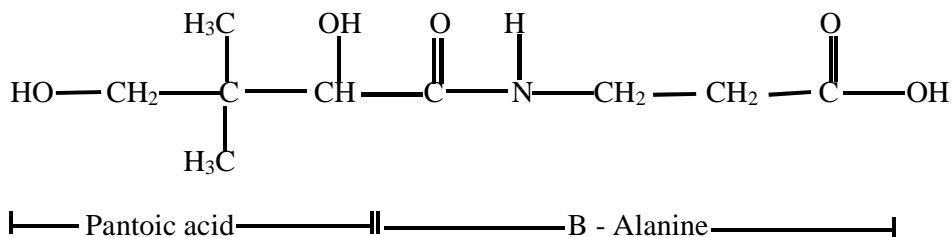
Figure 4   Pantothenic acid

Pantothenic acid is a constituent of co-enzyme A which is an important coenzyme in **acyl transfer**. Co-enzyme A is known as 3-phospho-adenosine-5-diphospho-pantotheine.

Sources

Found in liver, egg yolk, groundnuts, peas, yeast, animal tissues and molasses.

Deficiency Symptoms

Deficiency of Pantothenic acid results in slow growth, diarrhea, and loss of hair-**alopecia,** scaly skins and a characteristic "goose stepping" gait in pigs and retarded growth, dermatitis in chicks.

3.2.1.5 Vitamin B6

Vitamin B6 consists of three related pyridine derivatives; **pyridoxine, pyridoxal** and pyridoxamine**.**

Pyridoxal is the most actively functioning form of Vitamin B6 in the form of its phosphate. Pyridoxal phosphate plays a central role as a coenzyme of several enzymes of amino acid metabolism as well as glycogenolysis.
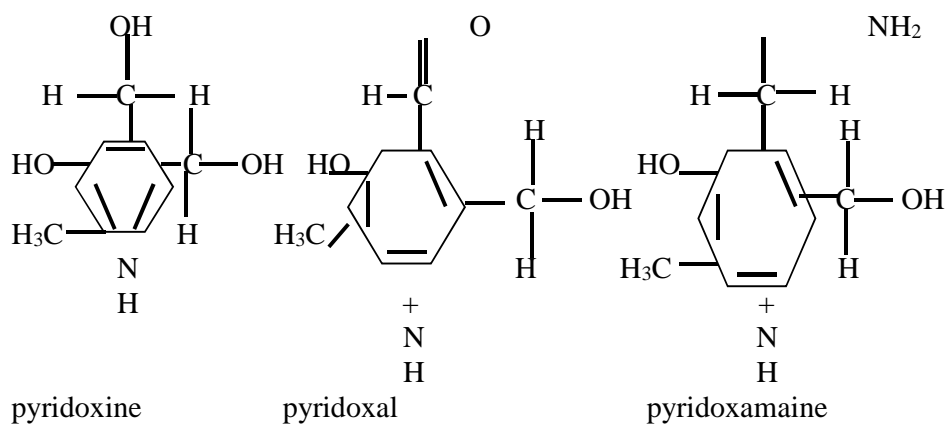
Figure 5　　**Chemical Structures of Pyridoxine, Pyridoxal and Pyridoxamine**

Sources

Vitamin B6 is widely distributed in yeast, liver, mackerel, milk, avocados, eggs, meat, pulses and cereal grains.

Deficiency Symptoms

In practice, Vitamin B6 deficiency is unlikely to occur in farm animals because of its wide distribution. In poultry, deficiency symptoms include jerky movements in chicks and poor hatchability and egg production in adult birds. In pigs, reduced appetite and anaemia may develop.

3.2.1.6 Folic acid

Folacin is the generic name covering folic acid and related substances having the biochemical activity of folic acid. Folic acid or **folate** consists of the base pteridine attached to one molecule each of ρ-aminobenzoic acid (PABA) and glutamic acid. Folic acid in the form of tetrahydrofolate (H4 folate) functions as a coenzyme.
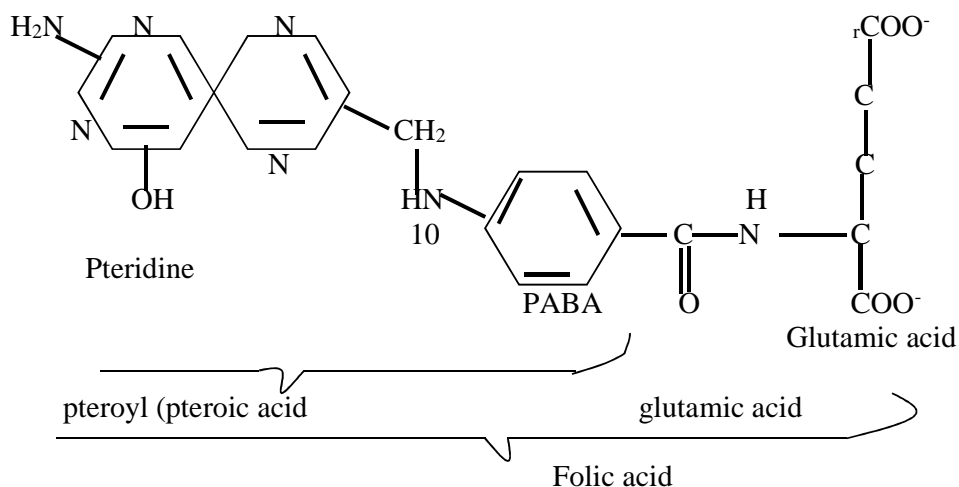
Figure 6   Chemical Structure of Folic Acid

Sources

Folic acid is widely distributed in nature; green leafy materials, cereals, extracted oil seed meals and animal protein sources.

Deficiency Symptoms

Deficiency of folic acid is characterised by nutritional anaemia and poor growth.

3.2.1.7 Biotin

Chemically, biotin is 2-keto-3, 4 imidazolido-2- tetrahydrothiophene-n-valeric acid.
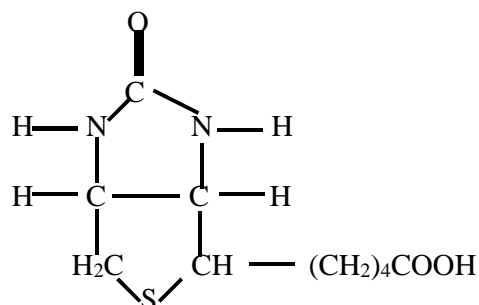
Figure 7   Chemical Structure of Biotin

Biotin is a coenzyme of carboxylase enzymes which catalyze the transfer of carbon dioxide from one substrate to another.

Sources

Biotin is widely distributed in foods; liver, yeast, milk and vegetables.

Deficiency Symptoms

Deficiency of biotin is characterised by foot lesions, alopecia (loss of hair) and dry scaly skin in pigs and reduced growth, dermatitis, cracked feet, poor feathering and fatty liver and kidney syndrome (FLKS) in poultry.

Biotin deficiency can be induced by giving animal **avidin**-a protein present in the raw white of eggs, which combine with biotin, preventing its absorption from the liver.

3.2.1.8 Choline

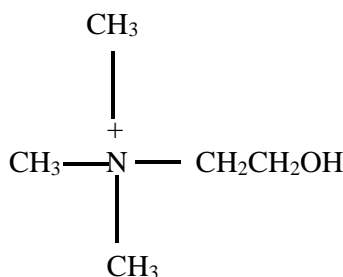Unlike other B vitamins, choline does not function as a metabolic catalyst but forms an essential component of body tissues.

Choline is a component of lecithins which play a vital role in cellular structure and activity. It also plays an important role in lipid metabolism in the liver. Choline can be synthesized in the liver from methionine.

$$CH_3 - \overset{\overset{\displaystyle CH_3}{\displaystyle |}}{\underset{\underset{\displaystyle CH_3}{\displaystyle |}}{\overset{+}{N}}} - CH_2CH_2OH$$

Figure 8   Chemical Structure of Choline

Sources

Green leafy materials, yeast, egg yolk and cereals are rich in choline.

Deficiency Symptoms

Deficiencies include slow growth and fatty infiltration of the liver in chicks and pigs.

3.2.1.9 Vitamin B12

Cobalamin has a complex ring structure to which is added a cobalt ion at the centre. The commercial preparation of cobalamin is **cyanocobalamin**. Cobalamin is a significant coenzyme in the process of gluconeogenesis.
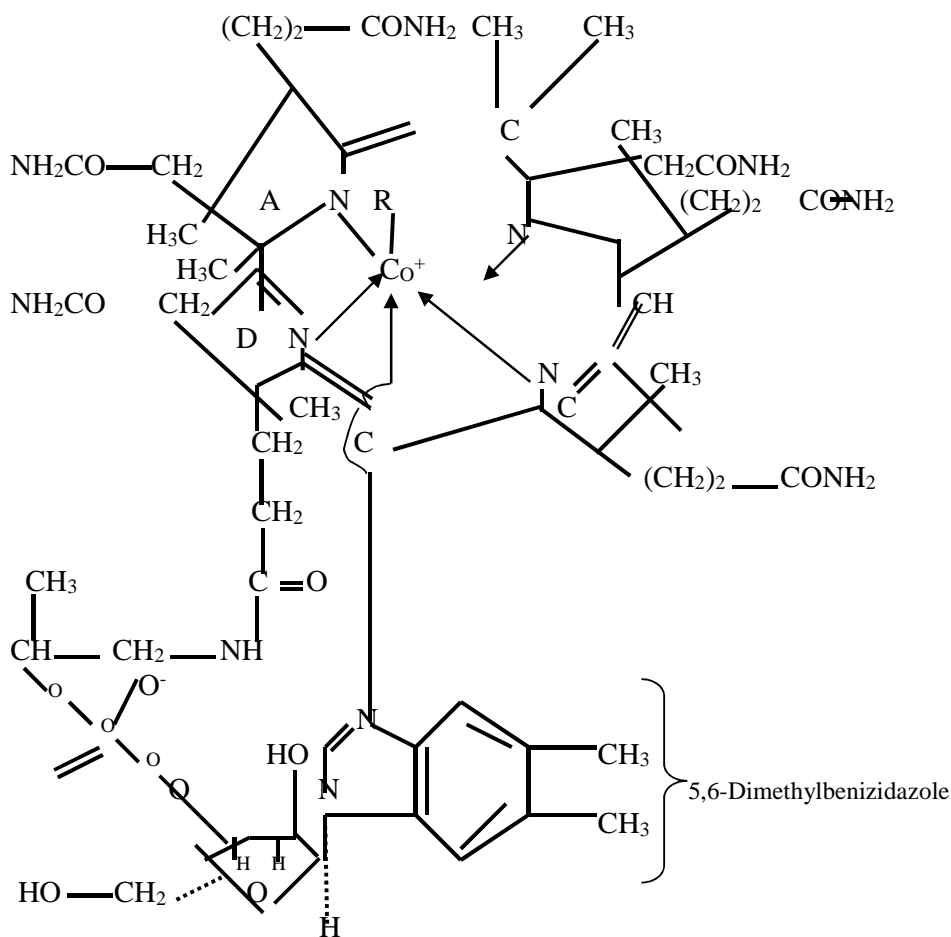
Figure 9   Chemical Structure of Cobalamin

Sources

Cobalamin is synthesized exclusively by microorganisms thus is only found in foods of animal origin e.g. liver.

Deficiency Symptoms

Deficiency symptoms include severe growth retardation and high mortality in young growing animals.

3.2.2 Vitamin C

The vitamin C chemically known as **l-ascorbic acid** is reminiscent of glucose, from which it is derived in the majority of mammals. Ascorbic acid is colourless, crystalline and its destruction is accelerated by exposure to light.
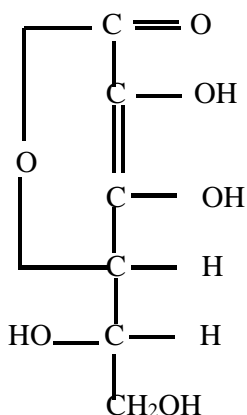
Figure 10: Chemical Structure of Vitamin C-Ascorbic Acid

Ascorbic acid and its oxidant product-**dehydroascorbic acid** play a role in collagen synthesis, bile formation and iron absorption. It may also act as a general water-soluble antioxidant.

Sources

Sources of vitamin C are citrus fruits and green leafy vegetables. Synthetic ascorbic acid is also available.

Deficiency Symptoms

A classical deficiency condition of vitamin C is **scurvy**. This is characterized by oedema, emaciation and diarrhea. Failure in collagen formation results in structural defects in bone, teeth, cartilage, connective tissues and muscles.

3.3.0 Fat Soluble Vitamins

Also known as **lipid soluble vitamins.** These vitamins require normal fat absorption in order to be absorbed efficiently.

Table 4   Functions and Syndromes of Deficiencies of Fat Soluble Vitamins

Vitamins	Functions	Deficiency Syndrome
Vitamin A (Retinol)	Vision	Night Blindness, Xerophthalmia
Vitamin D	Calcium and Phosphate Metabolism	Rickets, Osteomalacia
Vitamin E	Antioxidant	Neurological disorders, anaemia
Vitamin K	Blood clotting	Bleeding, Haemorrhage

3.3.1 Vitamin A

Vitamin A- C20H29OH is chemically known as **retinol**. Vitamin A is a generic name for referring to all compounds from animal sources that exhibit the biological activity of vitamin A. They are **retinol, retinoic acid** and **retinal** or **retinaldehyde**.

In vegetables, vitamin A exists as a provitamin in the form of the yellow pigment, **β-carotene** which consists of two molecules of retinal (retinaldehyde) joined at the aldehyde end of their carbon chain. Retinaldehyde can be reduced to retinol and oxidized to retinoic acid.

Conversion of carotene to vitamin A occurs in the intestinal mucosa and vitamin A is stored in the liver.
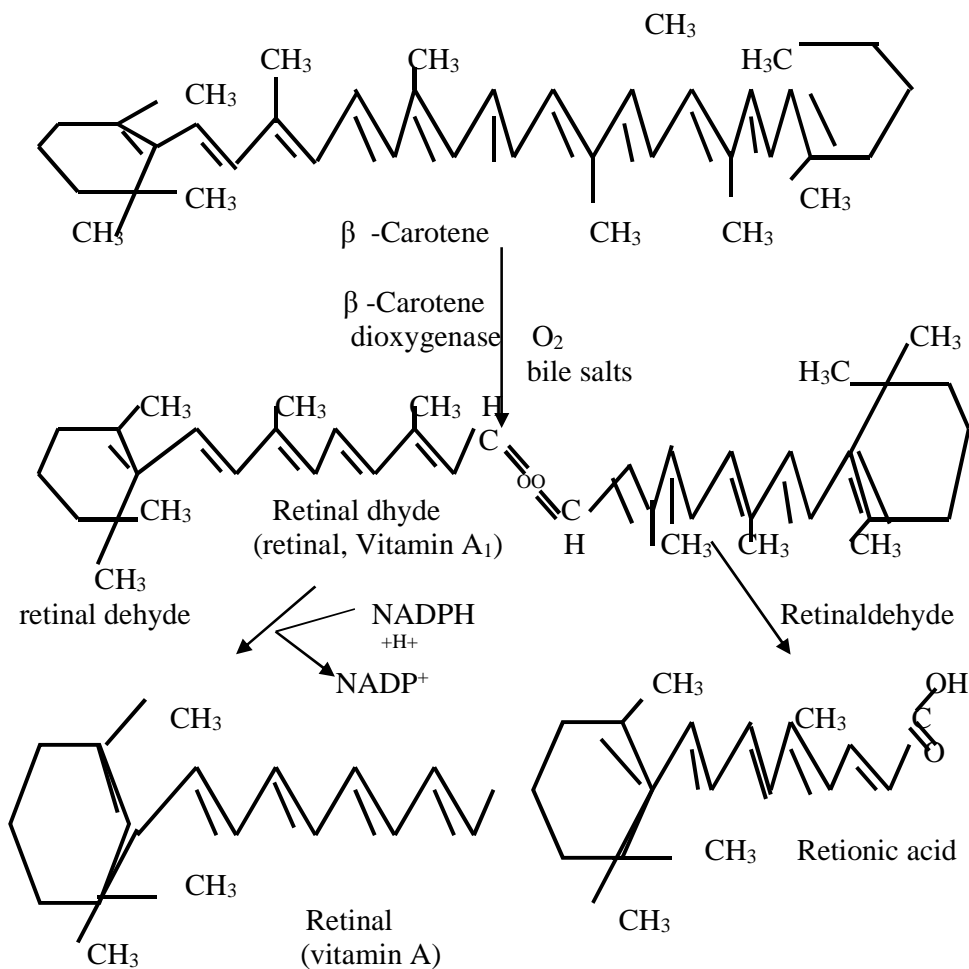
Figure 11   **Formation of various forms of Vitamin A from the Vitamin A precursor- β-carotene**

Vitamin A functions thus:

1.   In the formation of rhodopsin (visual purple), this is the photo-receptor for vision at low light intensity.

2.   In the formation and protection of epithelial tissues and mucous membranes.

3.   Due to the steroid hormone-like function of vitamin A, it is required for normal reproduction.

4.   β-carotene is an antioxidant which may account for its possible anticancer activity.

Sources

The provitamins of vitamin A, β-carotene, are usually accompanied by chlorophyll in plants, thus green foods are excellent sources of β-carotene. Other plant materials such as carrots, tomatoes and yellow maize are also rich in carotene.

Deficiency Symptoms

A deficiency of vitamin A is **defective night vision** (**night blindness**) which occurs when liver stores are depleted. Further depletion leads to **keratinization** of epithelial tissues of the eyes, lungs, gastrointestinal and genitourinary tracts. Deterioration in the tissues of the eyes; **xeropthalmia**, leads to blindness. A deficiency of β-carotene results in certain fertility disorders such as retarded ovulation and early embryonic mortality.

3.3.2 Vitamin D

Vitamin D is a steroid prohormone. Vitamin D exists in different forms: **Vitamin D2-ergocalciferol**; formed in plants and **Vitamin D3-cholecalciferol**; formed in exposed skin in animals.

The D vitamins are generated from the provitamins **ergosterol** in plants and **7-dehydrocholesterol** in animals. Ultraviolet irradiation from sunlight cleaves the B-ring of both compounds.
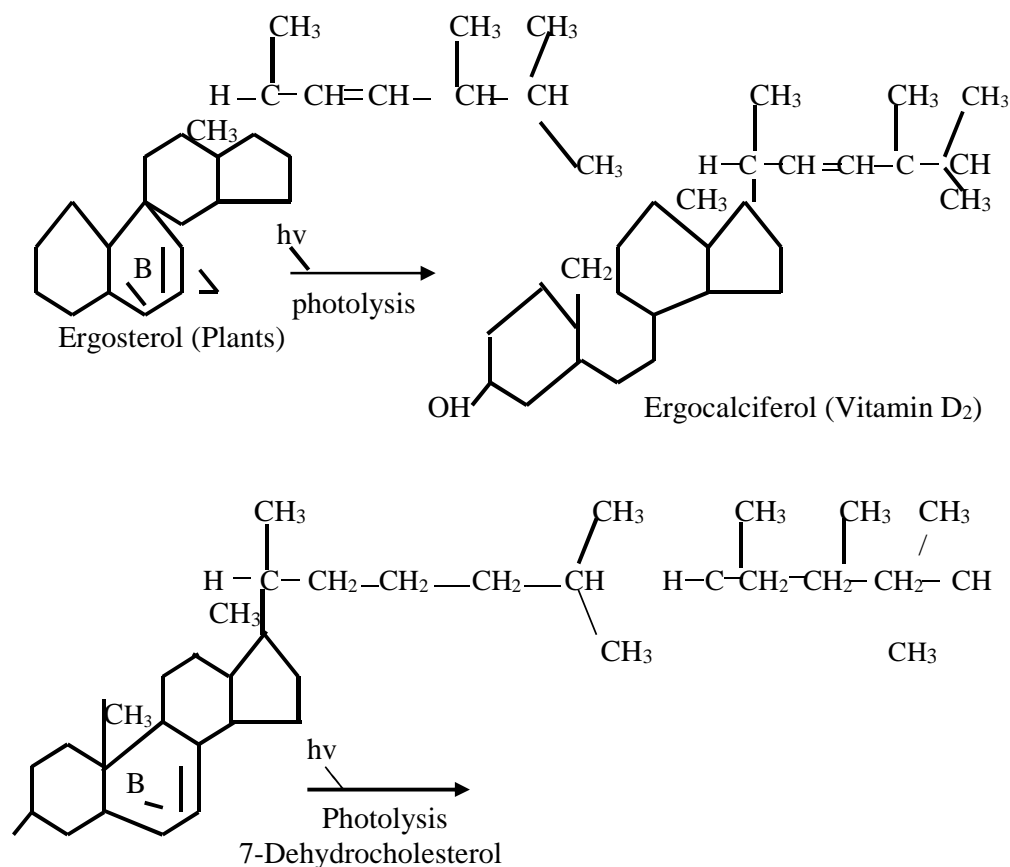
Figure 12   **Conversion of Ergosterol and 7-Dehydrocholesterol to Ergocalciferol and Cholecalciferol respectively by Photolysis**

Dietary vitamin D2 or D3 is absorbed through the small intestine and transported in the blood to the liver where it is converted to 25-hydroxycholecalciferol. The latter is then transported to the kidney where it is converted to 1, 25-dihydroxycholecalciferol, which is the most biologically active form of the vitamin. This is now transported in the blood to the various target tissues; the intestines and the bones.

Vitamin D functions in:

1.   Calcium and phosphate metabolism

When the level of calcium in the blood is low; **hypoglycemia**, the parathyroid gland is stimulated to excrete more parathyroid hormone, which induces the kidney to produce more 1, 25-dihydrocholecalciferol which in turn enhances the intestinal absorption of calcium. 1, 25-dihydrocholecalciferol increases the absorption of phosphorus from the intestine and also enhances calcium and phosphorus reabsorption from the kidney and bones.

Sources

The D vitamins are limited in distribution. They rarely occur in plants except in sun dried roughages and the dead leaves of growing plants. In animals, vitamin D3 occurs in small amounts in certain tissues, and abundantly only in some fishes. Halibut and cod liver oils are rich in vitamin D3.
Feeds of pigs and poultry contain little or no vitamin D, thus the vitamin is administered in the form of synthetic preparations.

Deficiency Symptoms

A deficiency of vitamin D in young animals result in **rickets**; a disease of growing ones in which the deposition of calcium and phosphorus is distributed. As a result, the bones are weak and easily broken, the legs may be bowed. Rickets is confined to young growing animals.

In older animals, vitamin D deficiency causes **osteomalacia**; in which there is re-absorption of calcium and phosphorus from already laid out ones. In farm animals, this condition occurs mostly in pregnant and lactating animals as there is increased physiological need for calcium and phosphorus at these times.

Rickets and osteomalacia are not necessarily diseases of vitamin D deficiency, but can also be caused by calcium or phosphorus deficiency or calcium and phosphorus imbalance.
A deficiency of vitamin D in poultry causes soft and rubbery bones and beak, retarded growth, bowed legs, rickets, reduced egg production and egg shell quality.

In pigs, the symptoms are usually enlarged joints, broken ones, stiffness of joints and occasionally paralysis. Growth rate is generally adversely affected.

3.3.3 Vitamin E

Vitamin E, **tocopherol** is a group name which includes a number of closely related active compounds. Eight naturally occurring forms of vitamin E are known and can be divided into two groups according to whether the side chain of the molecule is saturated. The four saturated forms of vitamin E are designated α, β, γ and δ-tocopherol and the unsaturated forms are α, β, γ and δ-tocotrienols.
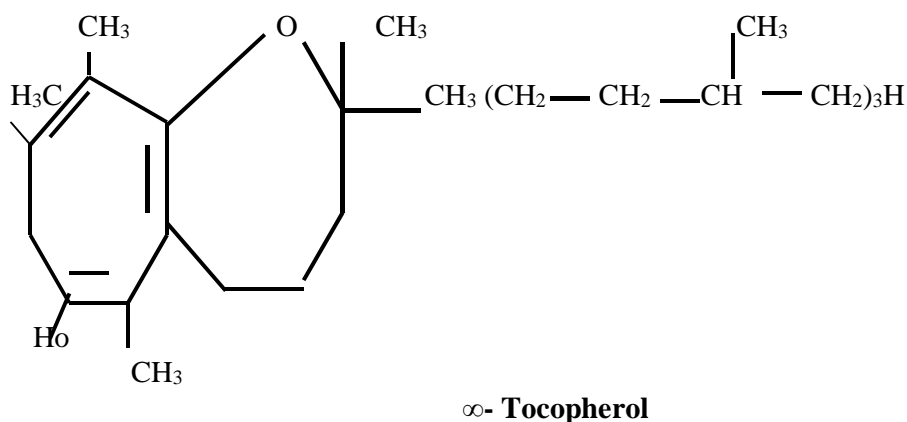
∞- **Tocopherol**

Figure 13   Chemical Structure of Vitamin E; α-Tocopherol

Vitamin E is a naturally occurring antioxidant which functions as the first line of defense against peroxidation of polyunsaturated fatty acids contained in cellular and sub-cellular membrane phospholipids. Vitamin E also acts in synergy with selenium to reduce each other's requirement and reinforce each other in their actions against lipid peroxides.

Sources

Vitamin E is very widely distributed in foods; green fodder, cereal grind. Animal products are relatively poor sources of the vitamin. Synthetic α-tocopherol and the acetate are available as commercial preparations.

Deficiency Symptoms

Deficiency of vitamin E has been implicated in reproductive failures, muscular degeneration; **myopathy**.

In lambs, symptoms of vitamin E deficiency results in **"white muscle disease"** and **"stiff lamb disease".**

In pigs, muscular weakness and severe liver damage are deficiency signs. **"Fatal Synscope"**; a condition where heart muscles fail resulting in sudden death, occurs in calves and pigs. Vitamin E deficiency in chicks may lead to **muscular dystrophy, encephalomalacia (crazy chick disease);** a condition in which the chick is unable to walk or stand and is accompanied by haemorrhages and necrosis of the brain or **exudative diathesis;** vascular disease of poultry characterised by a general oedema of the subcutaneous fatty tissues, associated with abnormal permeability of the capillary walls.

3.3.4 Vitamin K

Vitamin K is also known as **"coagulation factor "**or **"K factor"** due to its role in prevention of hemorrhagic symptoms produced in chicks. The two most important naturally occurring forms of vitamin K are vitamin K_1-**phylloquinone**; found in green plants and vitamin K_2-**menaquinone**; a product of bacterial growth. Both compounds are derivatives of the parent compound, vitamin K_3; **menadione**-2-methyl-1, 4-naphtoquinone.

menadione (Vitamin K_3)

Menaquinone-n (Vitamin K_2; n = 6,7 or 9)
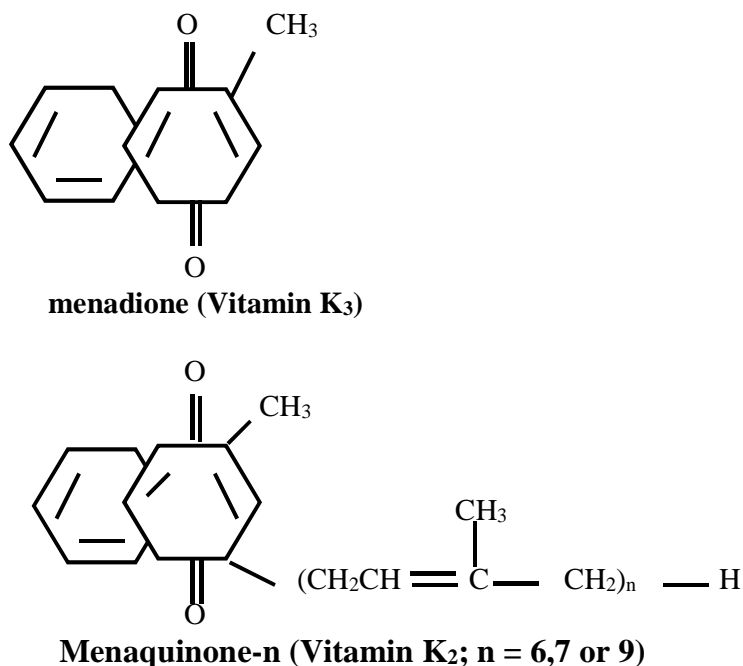
Figure 14   Naturally occurring forms of Vitamin K

All forms of vitamin K are converted in the liver into manaquinone suggesting that vitamin K2 is the metabolically active form of the vitamin.

Vitamin K is necessary for the synthesis of prothrombin in the liver, which is the inactive precursor of thrombin, an enzyme in the blood clotting process.

Sources

Vitamin K_1 is present in most green leafy materials, Lucerne, kale and cabbage. Animal sources include egg yolk, liver and fish meal. Vitamin K_2 is synthesized by bacteria in the digestive tract.

Deficiency Symptoms

Symptoms in chicks are anaemia and delayed clotting time. Birds are easily injured and may bleed to death. In birds, microbial synthesized vitamin K is not available by direct absorption from the digestive tract because the site of its formation is distal to permit absorption of adequate amounts except by ingestion of feacal material; **coprophagy**.

4.0   CONCLUSION

Vitamins are organic nutrients that are required in small quantities for a variety of biochemical functions and which, generally, cannot be synthesized by the body and therefore must be supplied in the diet. An absence or relative deficiency of vitamins in the diet leads to characteristic deficiency states and diseases which are detrimental to the management of any agricultural enterprise.

Vitamin deficiencies can be avoided by provision of feed of a wide variety in adequate amounts.

Many vitamins are destroyed by oxidation-a process sped up by the action of heat, light and certain metals such as iron. These are conditions to which feed materials are subjected during processing and preservation.

5.0   SUMMARY

In this Unit, we have learnt that:

- Vitamins can be classified based on their solubility; water soluble vitamins (vitamin B complex and C) and fat/lipid soluble vitamins (vitamins A, D, E and K).

- Vitamin B-complex consists of vitamins that function mainly as coenzymes.

- Save for vitamin D, other vitamins can be sourced from the appropriate plant and animal sources.

- Vitamins are easily destroyed by processing factors, e.g. heating, cooking, exposure to light sources etc.

- Severe deficiencies and toxicity of these vitamins could prove to be lethal.

60   TUTOR-MARKED ASSIGNMENT

1.   What are vitamins?
2.   Discuss the coenzyme functions of the B-vitamins.
3.   Define in brief, the following:

a)   Alopecia
b)   Enteritis
c)   Dermatitis
d)   Anaemia
e)   Oedema
f)   Coprophagy

7.0   REFERENCES/FURTHER READING

McDonald, P., Edwards, R.A and Greenhalgh, J.F.D (1926). *"Animal Nutrition"*, 4th Edition, pp 58-89.Longman Scientific and Technical and John Wiley and Sons, Inc, New York. ISBN 0-582-40903-9.

Robert K. Murray, Peter A Mayes, Daryl K. Granner and Victor W. Rodwell (1990). 22nd Edition, pp 547-562. Appleton and Lange, SanMateo, CA/Norfolk, CT.

UNIT 4 THE NATURE, CLASSIFICATION AND FUNCTION OF ENZYMES AND HORMONES

CONTENTS

1.0 INTRODUCTION

The roles of enzymes and hormones in life cannot be overemphasized. There exists no anabolic or catabolic reaction in life that is not mediated by an enzyme or prompted by a hormone. Listing of enzymes and hormones inexhaustible and roles played by many is have not even been discovered. For the purpose of this course, enzymes and hormones that are extremely necessary for life are studied.

2.0 OBJECTIVES

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

- distinguish between enzymes and hormones
- identify the nature of enzymes and hormones
- explain the mode of action of enzymes and hormones
- explain the classification and functions of enzymes and hormones.

3.0   MAIN CONTENT

3.1   What are Enzymes?

Enzymes are naturally occurring macromolecular substances composed wholly or largely of protein, that catalyses one or more biochemical reactions at relatively low temperatures.
Enzymes are often easily inactivated by heating or by protein denaturing agents. The substances on which they act are known as **substrates**, for which the enzyme possesses a specific binding or **active site.**

3.1.1 Nature of Enzymes

Many enzymes require a specific, heat-stable low molecular weight organic molecule, a **coenzyme** to enhance their activity. Reactions that require co-enzymes include oxido-reductions, lyase and isomerization reactions and reactions that form covalent bonds (IUB classes 1, 2, 5 and 6).

Example; in the oxidation of pyruvate, the hydrogen released must be removed. This is done by a substance nicotinamide-adenine dinucleotide (NAD) or nicotinamide-adenine dinucleotide phosphate (NADP).In the above illustration, NAD and NADP play the role of co-enzymes.

Another example of the nature of enzymes is the cytochromes. Cytochromes are stet proteins which are important in certain oxidation reactions during which they accept electrons from a reduced substance which is consequently oxidized. Without the iron containing haem group, the enzyme will be inactive as electron exchange takes place at the iron atom. Active groups as these are known as **prosthetic groups** when they are part of the enzyme molecule. The remainder of the molecule is then known as the apoenzyme and the whole molecule as the holoenzyme. Thus it could be said that the **holoenzyme** is a catalytically active complex comprising of the protein part; **apoenzyme combined** with the appropriate **coenzymes** or **cofactors**.

3.2   Specific Nature of Enzymes

Enzyme specificity is said to be "**absolute"** if the reaction of a single substrate only is catalysed. Example; **urease** shows a high degree of specificity, catalysing only the breakdown of urea to ammonia and carbon dioxide.

$$
\begin{array}{l}
NH2 \\
\quad \backslash \\
\quad C = O + H_2O \rightleftharpoons 2NH_3 + CO_2 \\
\quad / \\
NH_2
\end{array}
$$
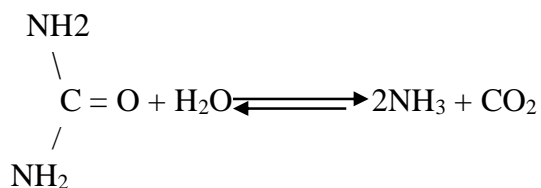
Enzyme specificity is said to be "**relative**" if the enzyme reacts with a number of substrates. Examples are the **esterases**; a group of enzymes which may catalyse several reactions of the general type:

$$R.\, CO.\, OR_1 \; + H_2O \rightleftharpoons R.\, CO.\, OH \; + R_1OH$$

    Ester   **Acid**   **Alcohol**
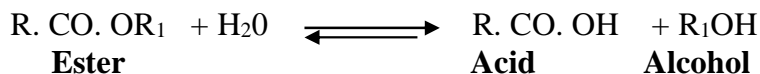
Specificity may arise from the need for spatial conjunction of the active groups of the substrate with the active centre of the enzyme.

In the **lock and key model** the molecular geometry of both enzyme and substrate must allow these reacting groups to come together to give a precise fit.

In the **induced fit model** the conformation of the enzyme may not be absolute, but may change in response to the presence of the substrate to allow the formation of the enzyme-substrate complex.

In other instances, where more than one substrate is involved, union of substrate 2 and enzyme may not take place until and unless, substrate1 and the enzyme have united.
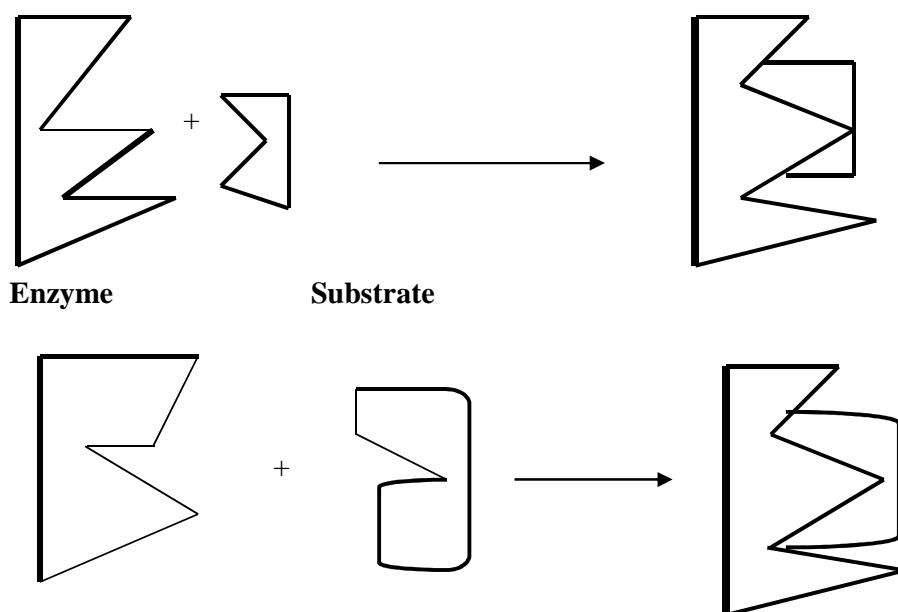
    Enzyme   **Substrate**

Figure 1   **Pictorial representation of the lock and key model and induced fit model**

3.3   Factors Affecting Enzyme Activity

Factors that affect the activity of enzymes include; substrate concentration, enzyme concentration, inhibitors, temperature and pH.

1.   Substrate Concentration

In a system where the enzyme is in excess and the concentration remains constant, then an increase in substrate concentration increases reaction velocity. If the substrate concentration continues to increase, there is no further increase in reaction rate. Continued increase in substrate concentration may lead to a reduction in rate of the reaction.

2.   Enzyme Concentration

In a system where the substrate is present in excess, an increase in further increase in the enzyme concentration may result in some limitations. It is worthy of note that the enzymes are rarely saturated with substrates under physiological conditions.

3.   Inhibitors

The catalytic action of enzymes may be inhibited by substances which prevent the formation of a normal enzyme-substrate complex. The extent of inhibition then depends entirely upon the relative concentrations of the true substrate and the inhibitor.

Such inhibition, which depends on competition with the substrate for the active sites of the enzyme, is termed **competitive inhibition**. In other cases, the inhibitor combines with the enzyme-substrate complex to give an inactive enzyme-substrate-inhibitor complex, which cannot undergo further reaction to give the usual product. This is termed **uncompetitive inhibition**. **Non competitive inhibition** involves combination of the inhibitor with the enzyme or the enzyme substrate complex, to give inactive complexes. In this case, the inhibitor binds to sites, on the enzyme other than enzyme sites, resulting in deformation of the enzyme molecule so that the formation of the enzyme-substrate complex is slower than normal. Some enzymes undergo irreversible inactivation; reaction of the inhibitor with a functional group of the enzyme, resulting in a loss of its catalytic activity.

4.   Temperature

All enzymes have a temperature range within which they are most efficient. As temperatures rise, **denaturation**; a molecular arrangement

which causes a loss of the active sites of the enzyme surfaces and results in a loss of efficiency, of enzyme protein begins.

5.   pH

Many enzymes are most efficient in the region of pH6-7, which is the pH of the cell. Outside this range, enzyme activity drops off very rapidly. Reduction in efficiency caused by changes in the pH is due to changes in the degree of ionization of the substrate and enzyme. Highly acidic or alkaline conditions bring about a denaturation and subsequent loss of enzymatic activity.

3.4   Nomenclature and Classification of Enzymes

Enzymes initially were named by adding the suffix **–ase** to the name of the substrate on which they acted. Enzymes that hydrolyzed starch; amylon were termed amylases, those that hydrolyzed fats; lipos, were termed lipases, those that hydrolyzed proteins were termed proteinases. Somewhat later, enzymes that catalyzed similar reactions were given names that indicated the type of chemical; reaction catalyzed. These were termed dehydrogenases, oxidases, decarboxylases, acylases etc.

The naming and classification of enzymes on the basis of chemical reaction type and reaction mechanism is the underlying principle of the **International Union of Biochemistry (IUB) Nomenclature System.**

Major features of the IUB system are:

1.   Reactions and enzymes that catalyse them form 6 classes, which are:

a.   **Oxidoreductases;** catalyse oxidation and reduction reactions.

$$A^- + B \rightleftharpoons A + B^-$$
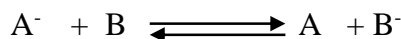
b.   **Transferases ;** catalyse the transfer of a functional group from one molecule to another.

$$A - B + C \rightleftharpoons A + B - C$$
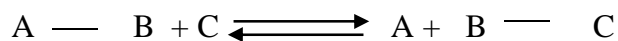
c.   **Hydrolases;** catalyse bond cleavage by the introduction of water molecules.

$$A - B + H_2O \rightleftharpoons A - H + B - OH$$
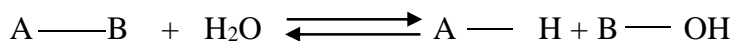
d. **Lyases;** catalyzes the removal of a group to form a double bond or the addition of a group to a double bond.

$$
\begin{array}{ccc}
X & Y & \\
| & | & \\
A\text{---}B & \rightleftharpoons & A=\!\!\!=B + X\text{---}Y
\end{array}
$$
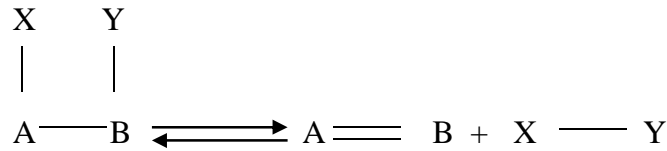
e. **Isomerases;** catalyse intermolecular rearrangement.

$$
\begin{array}{cccc}
X & Y & Y & X \\
| & | & | & | \\
A\text{---}B & \rightleftharpoons & A\text{---}B
\end{array}
$$
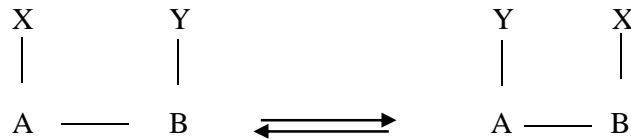
f. **Ligases or synthases;** catalyse reactions that join two molecules.

$$
A + B \rightleftharpoons A\text{---}B
$$
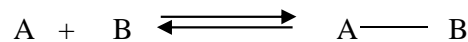
2.   The enzyme name has two parts. The first name indicates the substrate or substrates. The second, ending in –ase indicates the type of reaction catalysed.

3.   Additional information, if needed to clarify the reaction, may follow in parentheses.

      e.g. the enzyme catalysing;

      l-malate + NAD+ = Pyruvate + CO2 + NADH + H+
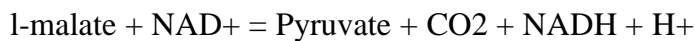
      is designated 1.1.1.37, l-malate: NAD+ oxidoreductase (decarboxylating)

4.   Each enzyme has a code number (EC) that characterises the reaction type as to class (first digit), sub class (second digit), and sub subclass (third digit). The fourth digit is for the specific enzyme.

Thus, EC 2.7.1.1 denotes class 2; a transferase, subclass 7; transfer of a phosphate, sub subclass 1; an alcohol which functions as the phosphate acceptor. The final digit denotes hexokinase or ATP: d-hexose 6-phosphotransferase, an enzyme catalysing phosphate transfer from ATP to the hydroxyl group on carbon 6 of glucose.

Other examples of this system are:

Table 1 Examples of Enzyme Nomenclature by the IUB Nomenclature System

Reaction	Recommended name	Systematic name	Code Number
L-Lactate + NAD^+ = Pyruvate + NADH + H^+	Lactate Dehydrogenase	L-Lactate NAD^+ oxidioreductase	1.1.1.27
Hydrolysis of terminal non reducing 1,4-linked α-D-glucose residues with release of α-glucose e.g. maltose to glucose .	α-glucosidase	α- D- glucosidase glucohydrolase	3.2.1.20
L-glutamate = 4- aminobutyrate + CO_2	Glutamate decarboxylase	L-glutamate 1- carboxylase	4.1.1.15

3.5   What are hormones?

The classic definition of hormones states that:

A hormone is a substance that is synthesised in one tissue and transported by the circulatory system to act on another organ.

Overtime, it is now appreciated that hormones act on adjacent cells that synthesize hormones and secrete them directly into the blood, lymph or other intercellular fluids.

A hormone may have one target tissue or it may affect a number of tissues. A **target tissue** is said to include any tissue in which the hormone can be demonstrated to bind to its **receptors**.

Several factors determine the overall response of a target tissue to a hormone.

1.   The local concentration of a hormone around the target tissue which depends on:

a.   The rate of synthesis and secretion of the hormone.
b.   The proximity of target and source.
c.   The association-dissociation constants of the hormone with specific carrier proteins in the plasma; if such exist.
d.   The rate of conversion of an inactive or optimally active form of the hormone into the active form.
e.   The rate of clearance of the hormone from the blood by degeneration or excretion, primarily accomplished by the liver and kidneys.
2.   The actual response of the target tissue to the hormone depends on:

a.   The relative and state of occupancy, or both, of the specific hormone receptors on the plasma membrane or within the cytoplasm or nucleus.
b.   The post receptor sensitization-desensitization of the cell.

3.6   Hormone Action

The principle of endocrine actions, using the thyroid gland as an example.

Figure 1:

hormone

Inhibition
(negative feed-back)

Pituitary gland (anterior lobe)

Thyroid stimulating

(Thyrotrophin)

Thyroid gland

Thyroxine

Increased basal metabolic rate
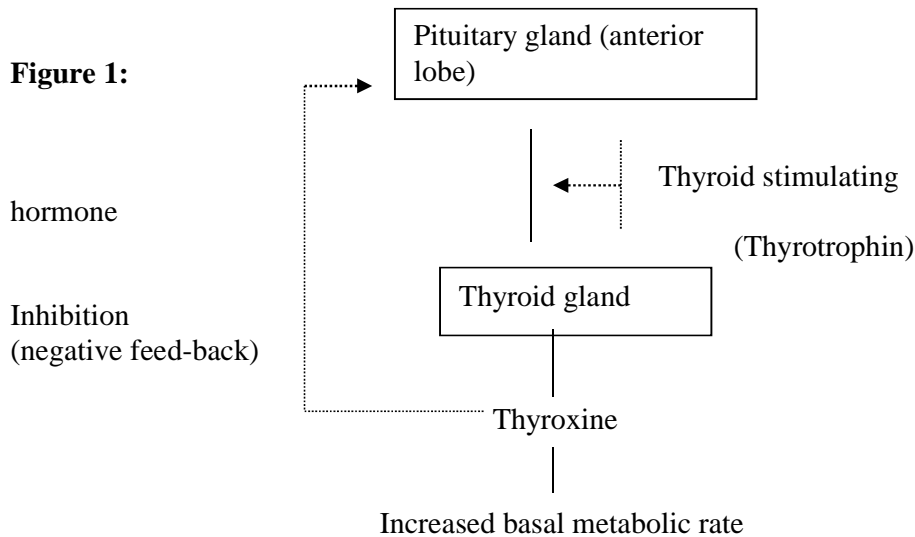
The thyroid gland secretes thyroxine, which is a complex organic compound containing iodine. Thyroxine is responsible for controlling the basal metabolic rate and is therefore important in growth regulation. The release of thyroxine into the blood stream is triggered by a hormone secreted by the anterior lobe of the pituitary gland. This hormone is called thyroid stimulating hormone or thyrotrophic hormone. The production of this hormone is regulated by thyroxine itself. A slight excess in the level of thyroxine in the blood stream acts on the pituitary to secrete less thyrotrophic hormone and this in turn reduces the activity of the thyroid gland leading to the reduction in the production of thyroxine.   This reduction of thyroxine in the blood stream removes the inhibiting influence on the pituitary so that more thyrotrophic hormone will be produced again. This example illustrates the principles of hormone action and this is referred to as negative feed-back mechanism.

3.7   Hormonal Control Mechanisms

Various types of endocrine control systems have been recognised. Some of these are:

1.   The simplest appears to be a system in which the hormone acts on specific cells,   thereby promoting a change in the controlled

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variable in the extracellular fluid, which in turn regulates the output of hormone by gland (fig 2). This negative feed-back system can be changed by endocrine and neural action exerted either upon the gland itself or upon the hormonally responsive effector cells. Systems of this type appear to operate in the case of insulin, parathyroid hormone (PTH) and aldosterone. An important feature of this type of system is the absence of direct hypothalamic or pituitary control.

Fig. 2: X ⟶ ⋯N⋯▶ Negative feedback (h), hormone

EG, endocrine gland
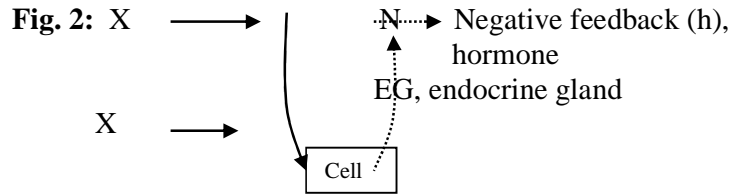
X and X1, represent other factors operating independently of feedback loop and influencing respectively, the activity of EG and cell.

2. A hormonogen (a hormone precursor) is secreted into the blood streamby one organ, which is acted upon in the blood by an enzyme from another organ and is converted to a tropic hormone, which stimulates the production of a hormone by another organ. The hormone then acts on a target organ stimulating a response which leads to a decrease in enzyme production.

Fig. 2:

EO – A, endocrine organ A

EO – B, endocrine organ B
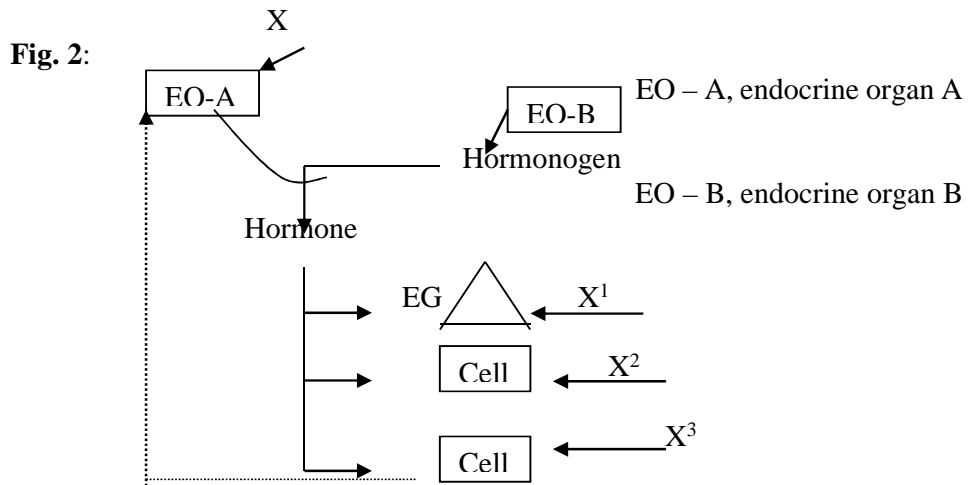
An example is angiostensonogen (hormonogen) converted into angiostensin, then into aldosterone (hormone).

3. In this case, the hormonal precursor hormonogen can be derived from the diet or synthesized within the organism. It goes through successive transformations in several additional organs before becoming a biologically active substance. An example is the

conversion of cholecalciferol to 25 – hydroxyl – and 1, 25 – dihyroxycholecalciferol.

Fig. 4:

```
        ┌─────────┐
        │ EO - A  │
        └─────────┘
             │        Dietary Substrate
             ↓   ←──────────────
   Hormonogen 1  ⇄  Hormonogen 1¹
             │
             ↓
        ┌─────────┐                                    ┌─────────┐
        │ EO - B  │                                    │  Cell   │
        └─────────┘                                    └─────────┘
             │                                              ↑
             ↓                                              │
   Hormonogen II    ──────→        Hormone II
   (Hormone I)                 ┌─────────┐
             │                 │ EO - C  │
             ↓                 └─────────┘
        ┌─────────┐
        │  Cell   │        EO – C, endocrine organs C
        └─────────┘
```
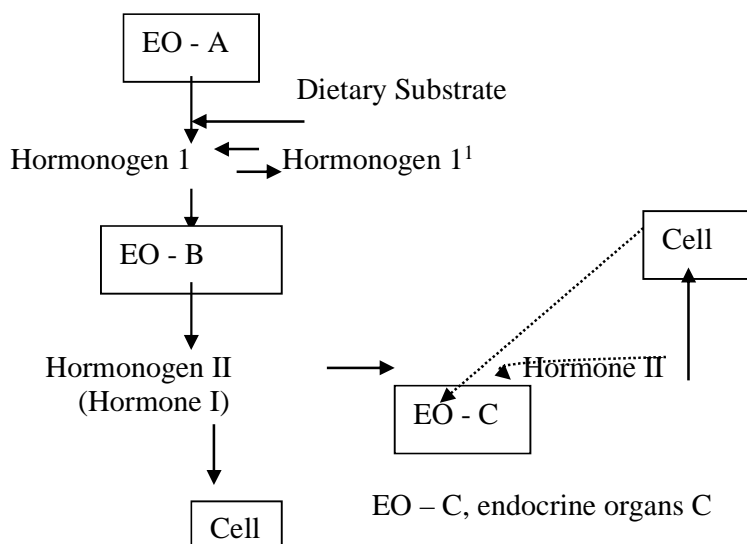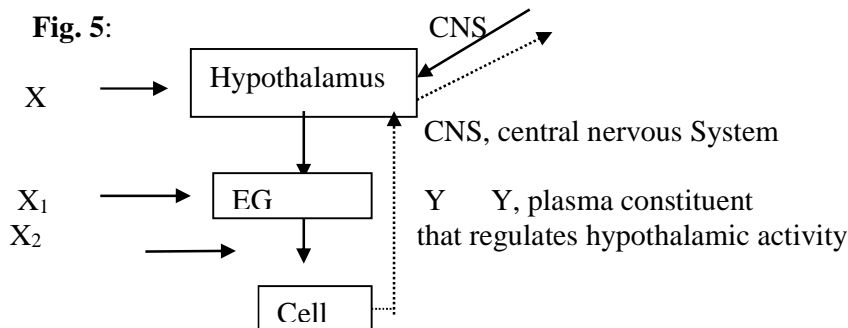
1.   In this type of system, the activity of the endocrine gland is under the control of the hypothalamus, the control of secretion of growth hormone by the anterior pituitary, and of vasopressin by the posterior pituitary are examples. A differentiating feature of this type of system is that feedback control is exerted not on the endocrine gland directly, but upon hypothalamic function, which in turn regulates gland function. The feedback effector appears to be one or more plasma constituents

Fig. 5:

```
                              CNS
        X  ──→  ┌──────────────┐
                │ Hypothalamus │
                └──────────────┘
                       │         ↑     CNS, central nervous System
                       ↓         ┊
       X₁  ──→  ┌──────────┐     ┊
       X₂  ──→  │    EG    │     Y   Y, plasma constituent
                └──────────┘         that regulates hypothalamic activity
                       │         ┊
                       ↓         ┊
                ┌──────────┐     ┊
                │   Cell   │·····┘
                └──────────┘
```

3.8   Classification of Hormones

Hormones can be classified according to:

1.   Chemical composition
2.   Solubility properties
3.   Location of receptors

4.   Site of production
5.   Nature of the signal used to mediate hormone action within the cell.

For the purpose of this course, hormones will be studied based on their site of production. Hormones can be classified thus:

1.   Hormones of the Pituitary and Hypothalamus
2.   Thyroid hormones
3.   Hormones of Calcium metabolism
4.   Hormones of the Adrenal Cortex
5.   Hormones of the Adrenal Medulla
6.   Hormones of the Gonads
7.   Hormones of the Pancreas and Gastrointestinal Tract

Table 2: Hormones of the Pituitary and Hypothalamus

Hormone	Acronym	Functions
Hypothalamic Hormones		
Corticotropin-releasing factor	CRF or CRH	Stimulates ACTH and β-endorphin secretion
Gonadotropin- releasing factor	GnRF or GnRH	Stimulates LH and FSH secretion
Prolactin-releasing factor	PRF	Stimulates prolactin secretion
Prolactin-release inhibiting factor	PIF	Inhibits prolactin secretion
Growth hormone-releasing factor	GRH or GRF	Stimulates GH secretion
Somatostatin (Growth hormone release inhibiting factor)	SIF	Inhibits GH and TSH secretion
Thyrptropin-releasing factor	TRF or TRH	Stimulates TSH and prolactin secretion
Pituitary Hormones		
Oxytocin		Uterine contraction, milk ejection
Vassopressin (Antidiuretic hormone)	ADH	Blood pressure, water balance
Melanocyte-stimulating hormones	MSH	Pigmentation
Lipotropin	LPH	Fatty acid release from adipocytes
Corticotropin (Adrenocorticotropic hormone)	ACTH	Stimulates adrenal steroid synthesis
Thyrotropin (Thyroid-stimulating hormone)	TSH	Stimulates thyroid hormone synthesis
Growth Hormone or somatotropin	GH	General anabolic effects; stimulates release of insulin like growth factor-I
Prolactin		Stimulate milk synthesis
Luteinizing hormone	LH	Ovary: luteinization, progesterone synthesis. Testes:

		interstitial cell development, androgen synthesis
Follicle stimulating hormone	FSH	Ovary: follicle development, ovulation, estrogen synthesis. Testes: spermatogenesis.

Hormones of the Pituitary and Hypothalamus

The anterior pituitary, under control of hypothalamic hormones, secretes a number of hormones (trophic hormones) that regulate the growth and function of other endocrine glands or influence metabolic reactions in other target hormones. The posterior pituitary produces hormones that regulate water balance and milk letdown from lactating mammary glands.

Thyroid Hormones

Thyroid hormones regulate gene expression, tissue differentiation and general development. The thyroid gland produces two hormones: **3, 5, 3'-triiodothyronine (T3)** and **3, 5, 3', 5'-tetraiodothyronine (T4, thyroxine).**

Hormones of the Adrenal Cortex

The adrenal cortex synthesises dozens of different steroid molecules, but only a few of these have biologic activity. Hormones of the adrenal cortex can be sorted into 3 classes: glucocorticoids (cortisol and corticosterone), mineralocorticoids (aldosterone) and androgens (androgen precursors; dehydroepiandrosterone and androstenedione).

Hormones of the Adrenal Medulla

The adrenal medulla is a specialized ganglion without axonal extensions. Its chromaffin cells synthesize, store and release products that act on distant sites, thus functions as an endocrine organ. Hormones of the adrenal medulla **the catecholamine** are **dopamine**, **norepinephrine** and **epinephrine**. These hormones are the major elements in the response to severe stress.

Hormones of the Gonads

The gonads are bifunctional organs that produce germ cells and the sex hormones. The **ovaries** produce ova and the steroid hormones; **estrogen** and **progesterone** while the **testes** produce spermatozoa and **testosterone**.

Hormones of the Pancreas and Gastrointestinal Tract

The pancreas functions as an exocrine organ; secreting into the duodenal lumen the enzymes and ions used for the digestive process, and an endocrine organ. The endocrine portion consists of the Islets of Langerhans. The pancreatic islets secrete at least four hormones: **insulin**, **glucagons, somatostatin** and pancreatic **polypeptide**.

Table 3: Hormones of the Thyroid, Adrenal Cortex, Adrenal Medulla, Gonads and Pancreas and Gastrointestinal Tract.

Hormones	Acronym	Functions
Thyroid Hormones		
3, 5, 3'-triiodothyronine	T_3	General stimulation of many cellular reactions.
3, 5, 3', 5'-tetraiodothyronine	T_4, thyroxine	General stimulation of many cellular reactions.
Calcitonin		Ca^{2+} and P_i metabolism.
Calcitonin gene-related peptide	CGRP	Vasodialator.
Parathyroid hormone	PTH	Ca^{2+} and P_i metabolism.
Hormones of the Adrenal Cortex		
Glucocorticoids	Cortisol, corticosterone	Essential components of adaptation to severe stress.
Mineralocorticoids	Aldosterone	Maintain normal Na^+ and K^+ balance.
Hormones of the Adrenal Medulla		
Dopamine		Major element in the response to severe stress.
Norepinephrine	Noradrenalin	Artiole contraction, lipid release.
Epinephrine	Adrenalin	Smooth muscle contraction, heart function, glycogenolysis, lipid release.
Hormones of the Gonads		
Estrogen (ovary)	Estradiol, estrone	Maturation and function of secondary sex organs, mammary gland development.
Progestins (ovary)	Progestrone	Ovum implantation, maintenance of pregnancy, mammary gland development.
Androgens (testes)	Testosterone	Maturation and function of secondary sex organs.
Inhibins A and B		Inhibits FSH secretion.

| Placental   lactogen (Placenta) | | Similar to prolactin. |

Hormones of the Pancreas and Gastrointestinal tract
Hormones of the Pancreas

Insulin		
Glucagon		
Pancreatic polypeptide	PP	
Somatostatin		

Hormones of the Gastrointestinal Tract

Gastrin		Stimulates acid secretion from stomach and pancreatic secretion.
Secretin		Regulates pancreas secretion of water and bicarbonate.
Cholecystokinin		Secretion of digestive enzymes.
Motilin		Controls gastrointestinal muscles.
Vasoactive intestinal peptide	VIP	Gastrointestinal relaxation; inhibits acid and pepsin secretion.
Gastric inhibitory peptide	GIP	Inhibits gastrin secretion.
Somatostatin		Inhibits gastrin secretion, inhibits glucagons secretion.

4.0   CONCLUSION

Enzymes and hormones, though produced in small quantities, are crucial to the maintenance of life. Their functions are conducted in a uniquely ordered fashion. Unlike vitamins, deficiencies of enzymes and hormones cannot be corrected by dietary manipulations.

Hormones act to change the activities of cells or the number of responsive cells. The activity of the entire endocrine system is highly integrated such that a disturbance from one gland leads to change in the functions of many other glands and changes in the activities of hormones. The basic mechanism of hormonal action is referred to negative feedback and this is well demonstrated in the release of thyroxine into the blood stream by the thyroid stimulating hormonal, whereby the regulation of this release is effected by thyroxine itself. This example illustrates the basic principle of hormone action. Several mechanisms of hormonal control have been described, from the simplest such as occurred in a negative feedback system, where there is an absence of direct hypothalamic or pituitary control to that, in which the activity of the endocrine gland is under the control of the hypothalamus.

5.0   SUMMARY

In this Unit, you have learnt that:

- Enzymes are naturally occurring macromolecular substances composed wholly or largely of protein, that catalyze one or more biochemical reactions at relatively low temperatures.

- Enzymes are often easily inactivated by heating or by protein denaturing agents.

- Factors that affect the activity of enzymes include: substrate concentration, enzyme concentration, inhibitors, temperature and pH.

- The naming and classification of enzymes on the basis of chemical reaction type and reaction mechanism is known as the **International Union of Biochemistry (IUB) Nomenclature System.**

- The classic definition of hormones identifies a hormone as a substance that is synthesized in one tissue and transported by the circulatory system to act on another organ.

- Hormones can act on adjacent cells in a given tissue; **paracrine function**, as well as on the cells in which they are synthesized; **autocrine functions.**

- The **endocrine system** consists of glands or group of cells that synthesize hormones and secrete them directly into the blood, lymph or other intercellular fluids.

- Hormones can be classified according to chemical composition, solubility properties, location of receptors, site of production and nature of the signal used to mediate hormone action within the cell.

6.0   TUTOR-MARKED ASSIGNMENT

1.   Distinguish between enzymes and hormones.
2.   Write short notes on the following:

a)   Substrates
b)   Active site
c)   Target tissue
d)   Paracrine function

e)   Autocrine function

f)   Holoenzyme

3.   Highlight and discuss the features of the IU nomenclature system

7.0   REFERENCES/FURTHER READING

McDonald, P., Edwards, R.A and Greenhalgh, J.F.D (1926). *"Animal Nutrition",* (4th Edition), pp 58-89.Longman Scientific and Technical and John Wiley and Sons, Inc, New York. ISBN 0-582-40903-9.

Robert K. Murray, Peter A Mayes, Daryl K. Granner and Victor W. Rodwell (1990). (22nd Edition), pp 547-562. Appleton and Lange, SanMateo, CA/Norfolk, CT.

Geoffrey L. Zubay, William W. Parson and Dennis E. Vance (1995). *"Principles of Biochemistry"*, (1st Edition), pp 135-224, 562-597. Wm. C. Brown Publishers, Dubuque, Iowa, Melbourne, Australia, Oxford, England.

J.S. Ross and K.J.W., Wilson (1981).   *"Foundations of Anatomy and Physiology",* (5th Ed). London: Churchill Livingstone.

M.B.V. Roberts (1972). *"Biology: A Functional Approach"* (2nd Ed). London: Cox and Wyman Ltd.

Robert H. Williams (1974). *"Test Book of Endocrinology*". (5th Edition). Philadelphia: W.B. Saunders Company.