PHYTOCHEMISTRY

Plant Chemistry (Phytochemistry) is concerned particularly with the chemical aspects of various metabolic processes taking place in plants. Advances in plant chemistry are progressing at a much rapid pace. An extremely large number of complex compounds are produced by plants due to the result of unlimited chemical reactions taking place in their different metabolic cycles.

PRIMARY METABOLITES

INTRODUCTION

The sum of biochemical reactions taking place in an organism (plant or animal) is known as metabolism.

Metabolism (Gr. *metabole*, change) is a very dynamic process. Molecules are constantly turning over; the composition of a cell at any given time represents the balance between synthesis and degradation.

Anabolism (Gr. *ana*, up + *bolein*, to throw) or anabolic reaction is a constructive part of metabolism such as photosynthesis, protein synthesis, lipid synthesis and so forth.

Catabolism (Gr.*kata*, down + *bolein*, to throw) or catabolic reaction is a degradative part of metabolism characterized by the breakdown of complex molecules to simpler components.

Intermediate metabolism: Central to the metabolism of the cells are the respiratory pathways: glycolysis and the citric acid cycle. These two pathways are where many of the catabolic and anabolic reactions merge. For this reason, glycolysis and citric acid cycle are commonly referred to as **intermediate metabolism.**

Plant produces various metabolic products for their growth and development. The end products of metabolism are called metabolites. The metabolites in a plant can be divided into primary and secondary. The substances which are essential for the growth and survival of the producer plant are called **primary metabolites.** These chemical substances are common to all plant species. They are mostly made up of carbon molecules that are common to all cells and required for the proper functioning (or basic machinery) of the cells of the plants.

Biosynthetically only carbohydrates, fats and amino acids are called primary metabolites. Their fundamental role is for the structure and growth and development of the plant. They are stuff of life.

Enzymes are proteinous in nature. All proteins are synthesized from amino acids. Similarly, chlorophylls are synthesized from the amino acids glycine. Hence, all proteins, enzymes and chlorophylls are naturally the secondary metabolic substances in respect to their mode of synthesis in plants. But these substances are discussed under the primary metabolite section because they are very essential for the producer plant. Enzymes are also included under this section because no chemical reaction of any metabolic process is possible in a cell in absence of an enzyme.

CARBOHYDRATES

One of the most abundant groups of organic compounds in the plant kingdom are the carbohydrates. Carbohydrates are synthesized in green plants by the process of photosynthesis from carbon dioxide and water in the presence of sunlight and chlorophyll.

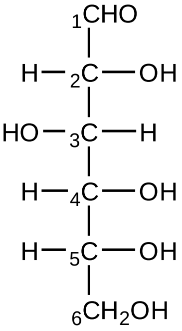
Carbohydrates are compounds which consist only of carbon, hydrogen and oxygen, where the ratio of the latter two elements is same as in water, *i.e.* 2 : 1. Carbohydrates may also be defined as a " large group of organic compounds which are either themselves polyhydroxy aldehydes or ketones or closely related compounds, or yield such compounds on acid hydrolysis".

In general, carbohydrates are white solids sparingly soluble in organic liquids but soluble in water (except certain polysaccharides). Many carbohydrates of low molecular weight are sweet to taste. Sugars, starch, cellulose are the most important examples of carbohydrates. The carbohydrates are broadly divided into major classes as monosaccharides, disaccharides, oligosaccharides and polysaccharides.

Monosaccharides

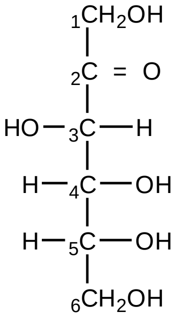
Monosaccharides (from Greek *monos* : single, *sacchar* : sugar) are the simplest carbohydrates. They cannot be hydrolyzed into simpler sugars. They consist of one sugar and are usually colorless, water-soluble, crystalline solids. Some monosaccharides have sweet taste. The general formula of monosaccharides is

$C_nH_{2n}O_n$. The common monosaccharides are glucose (dextrose), fructose, galactose, xylose, ribose etc. They are building blocks of disaccharides, oligosaccharides and polysaccharides. Monosaccharides contain the free aldehyde or ketone group and depending on the presence of aldehyde or ketone group in the molecule, they are termed as **aldoses** or **ketoses**.



Glucose

(A) Aldoses



Fructose

(B) Ketoses

Disaccharide

Disaccharide is a sugar composed of two monosaccharides. It is formed when two sugars are joined together and a molecule of water is removed. There are two basic types of disaccharides: reducing disaccharides, in which, the monosaccharide components are bonded by hydroxyl groups; and non-reducing disaccharides, in which the components bond through their aromatic centers. Examples include sucrose (glucose + fructose), lactose (glucose + galactose), and maltose (glucose + glucose).

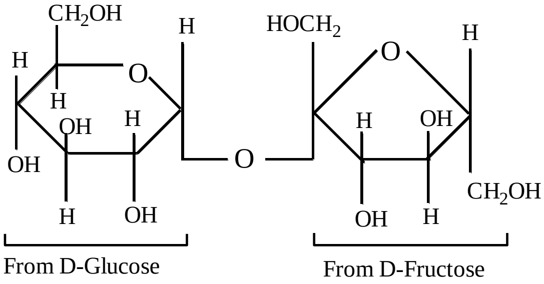


Fig: Structure of sucrose

Oligosaccharide

Oligosaccharide is a saccharide polymer containing a small number (typically 3-10) of simple sugars. Thus trisaccharides, tetrasaccharides, etc., are oligosaccharides.

Polysaccharides

These are complex carbohydrates formed by the condensation of a large number of monosaccharides. Polysaccharides are very long chains or polymers of monosaccharides. Sometimes the polymer is made up from a single monosaccharide, called homopolysaccharide, e.g. starch, glycogen, cellulose, insulin, etc. Some polysaccharides are formed by the condensation of two or more types of monosaccharides, as for example, gums and mucilage. The general formula of polysaccharides is $(C_6H_{10}O_5)_n$ which can be derived as follows :

$$(C_6H_{12}O_6)_n \longrightarrow (C_6H_{10}O_5)_n + n\,H_2O$$

Glucose starch or cellulose

In general, all the monosaccharides and oligosaccharides are collectively called as sugars. Some sugars are reducing and others are non-reducing. Sugars which have the ability to reduce Fehling's or Benedict's solution are referred to as reducing sugars while others are non-reducing sugars. The reducing sugar converts cupric hydroxide $[Cu(OH)_2]$ present in the solution to cuprous oxide (Cu_2O). The latter settles down as a red precipitate on heating. The monosaccharide, like, glucose is a reducing sugar. The reducing property of the sugar is due to the presence of aldehyde (-CHO) and ketone (= CO) group in the molecule. In the case of non-reducing sugar, the linking of the monosaccharide takes place in such a manner that the identity of the aldehyde or ketone groups of the individual monosaccharide is lost. So they show negative reaction with Fehling's or Benedict's solutions, Sucrose, a disaccharide, is a non-reducing sugar. Maltose and lactose (both disaccharides), however, possess reducing property as both the compound contain an unlinked potential aldehyde in their structure.

Starch

(a) Theory: Starch is predominantly found in plants and is abundant in the vegetative tissues and it is the form in which carbohydrate is stored in various storage organs of the plant. Starch is a heterogeneous material consisting of two chemical components ---(1) amylose (15-20%) and amylopectin (80-85%). Amylose is more soluble in water than amylopectin (below fig.). Potatoes when boiled amylose get dissolved in water turning it milky whereas amylopectin containing major percentage of starch left behind in the boiled potatoes.

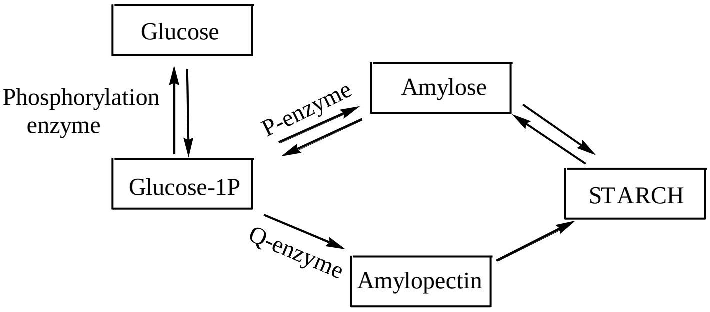


Fig. 3.3 Schematic representation of formation of starch

When treated with iodine amylose produces a typical blue colour whereas amylopectin forms a purplish colour.

Properties: Starch is insoluble in water, alcohol and ether at ordinary temperature. Starch when heated with iodine breaks down into **dextrin**. This resulting dextrin gives stiffness to clothes when starched. Starch forms a colloidal solution when extracted with hot water.

Starch is hydrolyzed by the enzyme called diastase (- amylase) to maltose. The molecular formula of starch is $(C_6H_{10}O_5)_n$.

(b) Cellulose : Cellulose is an important constituent of plant cell walls. It is the most widely distributed polysaccharide with the chemical formula $(C_6H_{10}O_5)_n$. The structure of cellulose is based on the D-glucose unit. Cellulose is known to form fibres, e.g. cotton, jute, hemp, ramie, etc. This property of cellulose reveals that it is a linear molecule.

Cellulose is a colourless solid, insoluble in water, alcohol and other organic solvents but readily soluble in Schweizer’s reagent.

Starch and cellulose are known as **hexosans** as they are derived from hexose sugars.

3. AMINO ACIDS

Introduction

Amino acids are the compounds with the properties of both acids and amines. Each amino acid contains an acidic carboxyl (-COOH) and a basic amino ($-NH_2$) group (Fig. a). R stands for the side chains which may be hydrogen atom (H) or a methyl group (-CH_3) or a more complex structure. The -carbon (i.e. the carbon to which amino group is attached of most amino acids remain attached to 4 different groups by covalent bonds. The most simplest amino acid is glycine. Amino acids (except glycine) exists in two optically active forms:

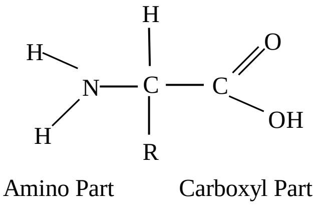
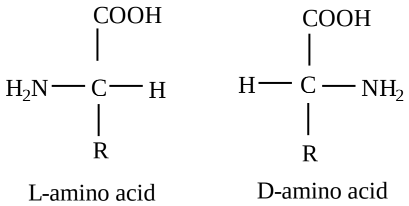


Fig. (a) Basic structure of an amino acid



L-amino acid D-amino acid

Fig. (b)Two optical isomers of amino acids

Fig.(a): Basic structure of an amino acid. R stands for single hydrogen atom in glycine(simplest amino acid); in other amino acids it represents several atoms of different kinds.

(1) D-amino acids (Dextrorotatory): They have amino (-NH_2) group to the right and

(2) L-amino acids (Levorotatory): They have amino group to the left (Fig.b).

More than 100 amino acids have been isolated and identified but only 25 are obtained upon hydrolysis of proteins. Out of 25, only 20 amino acids are entering into the composition of all proteins. The most commonly occurring amino acids in plants are tryptophan, tyrosine, histidine, aspartic acid, etc.,(**below table**). Cystine and methionine are the sulphur containing amino acids which play an important role in the sulphur metabolism of plants.

Table - Amino Acids

No.	Name of the amino acid	Chemical composition
1.	Glycine	CH_2. NH_2 .COOH
2.	Alanine	CH_3 .$CHNH_2$. COOH
3.	Valine	$(CH_3)_2$.$(CH)_2$.NH_2.COOH
4.	Serine	CH_2OH .$CHNH_2$ .COOH
5.	Leucine	$(CH_3)_2$ .CH_2.$(CH)_2$.NH_2.COOH
6.	Isoleucine	CH_3.C_2H_5 .$(CH)_2$.NH_2.COOH
7.	Threonine	CH_3.CH(OH) .CH.NH_2.COOH

8.	Aspartic acid	$CH_2 .CHNH_2. (COOH)_2$
9.	Glutamic acid	$(CH_2)_2 .CHNH_2. (COOH)_2$
10.	Tyrosine	$HO.C_6H_4.CH_2CH.NH_2.COOH$
11.	Arginine	$CNH_2.(NH)_2.(CH_2)_3CHNH_2. COOH$
12.	Lysine	$(CH_2)_4.NH_2.CH.NH_2.COOH$
13.	Cystine	$(S.CH_2.CH.NH_2.COOH)_2$
14.	Methionine	$S.CH_3.(CH_2)_2.CHNH_2.COOH$
15.	Phenylalanine	$C_6H_5.CH_2.CH.NH_2.COOH$
16.	Histidine	$C_4H_5.NCHN.(NH)_2.COOH$
17.	Tryptophan	$C_6H_4.NH.C_4H_4.NH_2.COOH$
18.	Proline	$C_4H_7.NH.COOH$
19.	Asparagine	$NH_2.CO.CH_2.CH.NH_2.COOH$
20.	Glutamine	$NH_2.CO.(CH_2)_2.CH.NH_2.COOH$

Non-protein amino acids:

There are about 200 non-protein amino acids which have been detected as natural products. Higher plants are rich in such amino acids. The exact metabolic roles of these amino acids have not been established.

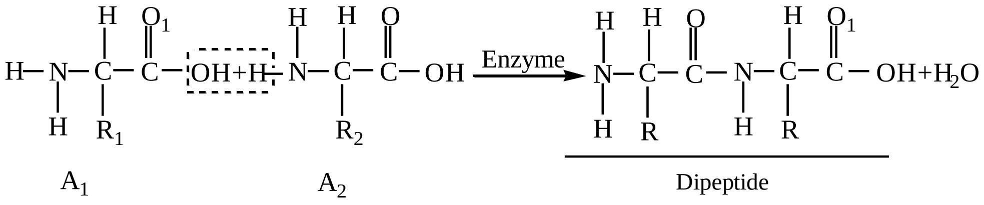
4. PROTEINS

Introduction

The name “protein”, derived from the Greek word **Proteios** meaning **first** was proposed by Berzelius (1838). Mulder in 1839 first used this term to refer the complex organic nitrogenous substances found in the cells of all living organisms. They are most abundant intracellular macromolecules and are the building blocks of protoplasm of each cell and constitute 50% of the dry weight of the protoplasm. Proteins also occur in plant cells in the form of stored foods (seeds of many species). The physical and chemical properties of these ‘reserve’ or storage proteins differ from the protoplasmic proteins. The proteins with catalytic properties (enzymes) are largely responsible for the phenotypic characters of a cell in a particular environment. Thus proteins are essential for cell structure and function.

The constituent elements of proteins are carbon (50-54%), hydrogen (about 7%), nitrogen (16-18%) and oxygen (20-25%). The plant protein also contain sulphur and phosphorus.

The main building blocks of the protein molecules are the amino acids. The backbone of protein is formed of polypeptide linkage of amino acids the number of which may very considerably (human haemoglobin contains 574 amino acids). Union between amino acids takes place by **peptide linkage**. It is a linkage between the amino group of one amino acid with the carboxyl group of other amino acid, producing a molecule of water in the reaction. The resulting molecule is termed as dipeptide (below fig.). This reaction chain is continued to produce **polypeptide, peptone, proteose** and finally **protein** is formed.



$$\mathrm{H{-}\underset{H}{N}{-}\overset{H}{\underset{R_1}{C}}{-}\overset{O_1}{C}{-}\boxed{OH+H}{-}\overset{H}{N}{-}\overset{H}{\underset{R_2}{C}}{-}\overset{O}{C}{-}OH \xrightarrow{Enzyme} \underset{H}{\overset{H}{N}}{-}\overset{H}{\underset{R}{C}}{-}\overset{O}{C}{-}\underset{H}{N}{-}\overset{H}{\underset{R}{C}}{-}\overset{O_1}{C}{-}OH+H_2O}$$

Fig. Formation of dipeptide

Classification

It is based on the physical and chemical properties of the proteins. They are classified into the following three groups:

(a) Simple protein:

Which on hydrolysis yields only amino acids. They are of following types:

(i) Albumins: These are simplest of all proteins and are soluble in water, dil. acid, dil. alkali or alcohol.

(ii) **Globulins:** These proteins are insoluble in water but soluble in salt solutions, dil. acid or alkali.

(iii) **Glutelins:** Soluble in dil. acid or alkali. Amino acids like, arginine, proline and glutamic acid are found in the composition of these proteins.

(iv) **Prolamines:** These are insoluble in water or salt solutions but soluble in dil. acid or alkali and 70% alcohol.

The Table shows some commonly found simple proteins in plants.

Table - Simple proteins

Simple roteins	Solubility	Example	Occurence in plant
1. Albumins	Distilled water	–Leucosin –Ricin	–Seeds of cereals –Castor oil seed.
2.Globulins	Dilute salt solution of neutral pH	–Legumin –Tuberin	–Pea seeds –Potato tubers
3.Glutelins	Acidic or basic solution	–Glutenin –Oryzenin	–Wheat grains –Rice grains
4.Prolamines	Alcoholic solution	–Gliadin –Zein –Hordein	–Wheat grain –Maize grain –Oat grain

(b) Conjugated protein:

This type of protein contains a non-protein part (prosthetic group) in addition to amino acids. Depending on the type of prosthetic group the conjugated proteins are of the following types :

(i) Glycoproteins : The prosthetic group is a carbohydrate. It is also known as **mucoprotein.**

(ii) Lipoproteins : The prothestic group is the lipid. Lipoprotein is found in the cell membrane.

(iii) Nucleoproteins : The prosthetic group is the nuclei acid.

(iv) Phosphoproteins : The prosthetic group is the phosphoric acid.

(v) Chromoproteins : In this type, different types of colouring compound are linked with protein. Phytochrome is a typical chromoprotein. These proteins contain metals like iron and magnesium as a prosthetic group. Human haemoglobin (containing prosthetic group
'heme') and **leghaemoglobin** found in the root nodules of leguminous plants are good examples of chromoprotein.

(c) Derived proteins

They are the degradation products of natural proteins formed by the action of acid, alkali or enzyme. Examples of such type of protein are peptones, proteoses, peptides, etc.

(d) Characteristics of Proteins

Most of the proteins are colorless (expect chromoproteins) and their molecules are usually of colloidal size. Most proteins are non-volatile and they decompose or coagulate on heating or boiling (usually above 60°C).

Coagulation is a process where **denatured** (i.e. changes in the properties of a protein) protein molecules in a true solution aggregate together to form large particles which form a precipitate. The coagulation of protein in a solution can occur due to many causes like, pH of the medium, temperature, presence of electrolytes, etc.

Denaturation of proteins is usually irreversible. A common example of this type of protein is egg albumin which on heating cause destruction of tertiary structure of protein leading to the formation of a disorganised mass of polypeptide chains. Sometimes the denaturation of certain proteins is reversible. For example, trypsin in solution undergoes denaturation at 80-90°C, but the solubility and the activity of the protein is regained when the solution is cooled at 37°C. This process of regaining normal protein properties by a denatured one is called **renaturation or refolding**.

(e) Amphoteric Nature

Like amino acids, the proteins are amphoteric in nature, i.e., they act both as an acid or as a base; it means, it can donate or accept a proton. Proteins are cations at pH values lower than the isoelectric pH and behave as anions where the pH values are higher than the isoelectric pH. The **isoelectric point** of a protein is the pH value at which the net electric charge of a protein is always zero. Thus at this point proteins are electrically neutral and do not move towards any pole. The other physical properties of proteins like, osmotic pressure, swelling capacity, etc., are minimum at isoelectric pH.

5. LIPIDS

The term ‘lipid’ was first used by German biochemist Bloor in 1943 for a group of naturally occurring compounds which are insoluble in water but soluble in fat solvents such as benzene, chloroform, ether and acetone. They are important constituents of the protoplasm and one of the principal kinds of food substances. In plants they are present in the seeds and fruits. In animals the fats serve as efficient source of energy which is stored in adipose tissues, bone marrow and nervous tissues.

Lipids are classified as follows :

1. Simple lipids:

These are esters of fatty acids with various alcohols.

(a) Fats:

Chemically defined as the esters of glycerol and fatty acids are called **triglycerides of fatty acids**. They are solid at room temperature.

(b) Oils:

These are also **glycerides** but liquid at room temperature.

(c) Waxes:

These are esters of fatty acids with alcohols other than glycerol.

2. Compound lipids:

They contain some additional groups or elements besides fatty acids and alcohols.

(a) Phospholipids:

This class of lipid contains phosphoric acid and nitrogen and are also known as phosphatides. Lectithin (fatty acids found are palmitic, stearic, oleic, linoleic and arachidonic) and cephalin (fatty acids found are stearic, oleic, linoleic and arachidonic).

(b) Glycolipids:

These are the compounds of fatty acids with carbohydrates and contain nitrogen. Compounds of this type are not definitely found in plants.

3. Derived lipids:

These compounds are derived from simple and compound lipids by hydrolysis.

(a) Fatty acids of various series.

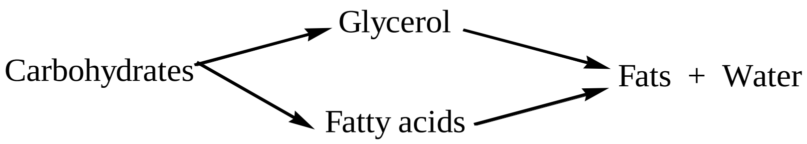
(b) Sterols: They contain no fatty acids and mostly alcohols of large molecular weight. These are soluble in fat solvents. Cholesterol ($C_{27}H_{45}OH$), and ergosterol ($C_{28}H_{43}OH$) are two good examples of sterols.

Fats:

Fats are composed of the same three elements, carbon, hydrogen and oxygen that make up carbohydrates, but they are poorer in oxygen (example : Palmitin, $C_{51}H_{98}O_6$). In plants most of the fats are present in the liquid state (“oils”).

On complete oxidation (respiration) 1g of the fat releases 9.4 k.cal of energy (heat).

The general scheme of fat synthesis in the natural condition may be represented as follows.



Both the glycerol and fatty acid molecules are derived from carbohydrates during respiration. The reaction is catalysed by the enzyme lipase. Fats on hydrolysis yield glycerol and fatty acids

$$\text{Fats} \quad + \quad H_2O \quad \xrightarrow{\text{lipase}} \quad \text{glycerol} \quad + \quad \text{fatty acids}$$

6. CHLOROPHYLLS

The chlorophylls, the green pigments are found in the leaves and many other aerial parts of the plants such as young stems and fruits and sepals of flowers. Seven different types of chlorophylls, namely chlorophyll a, b, c, d, e, bacteriochlorophyll and bacterioviridin are found to be distributed in the plant kingdom (strain, 1944). Of these pigments, chlorophylls a and b are present in all higher green plants. Chlorophyll b is however not found in the blue, green, brown and red algae (below table).

Both chlorophylls a and b are insoluble in water but readily dissolve in ethyl alcohol, chloroform, acetone and carbon bisulphide.

Chlorophyll is always accompanied by cartenoids. -carotene is the principal carotene remain associated with chlorophyll in all photosynthetic cells (except bacteria and some of the algae).

There are two major classes of carotenoids:

(1) Carotenes (orange), and **(2) Xanthophylls** (yellow).

Chlorophyll a absorb light energy directly and through transfer from other chlorophyll and carotenoids. In higher plants chlorophylls and carotenoids are present within the grana of the disc like or oral bodies called chloroplast.

Chemical nature of chlorophyll: Chlorophyll molecules are very complex which contain a tetrapyrrole skeleton formed into a ring with a magnesium atom in the centre. The tetrapyrrolic structure forms the 'head'(Porphyrin) of the chlorophyll. Attached to this porphyrin ring at one point there is an **alcohol (phytol)** 'tail' with a long chain of linked carbons (below fig.). In absence of the single magnesium atom the prophyrin 'head' of the chlorophyll is not formed. This is why the deficiency of magnesium in plants causes chlorosis.

The enzyme chlorophyllace hydrolyses chlorophylls in presence of traces of acid and liberates phytol and propionic acid. The latter causes removal of Mg from the porphyrin.

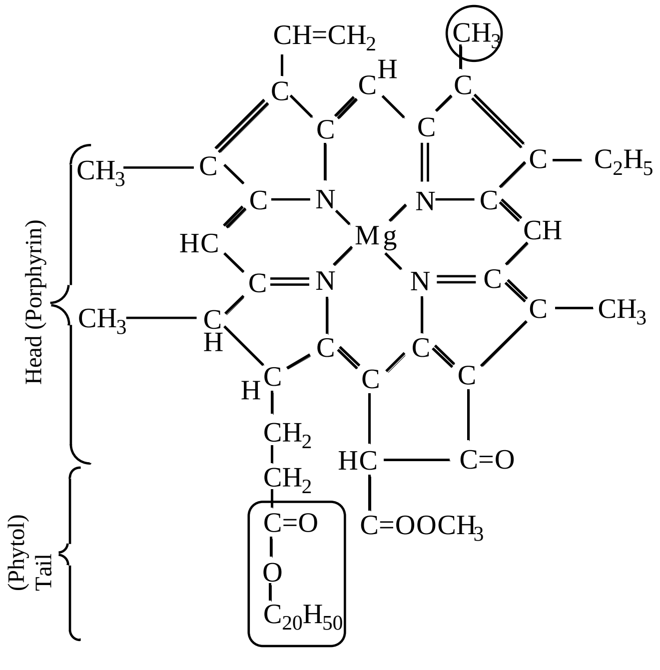


Fig : The chemical structure of chlorophyll a ($C_{55}H_{72}O_5N_4Mg$)

The distribution of different pigments in the plant kingdom are shown in the table.

Table: Distribution of Pigments in Plant Kingdom

Pigments Chemical composition Distribution in plant kingdom

I. Chlorophylls		
Chlorophyll a	$C_{55}H_{72}O_5N_4Mg$	All green plants.
Chlorophyll b	$C_{55}H_{70}O_6N_4Mg$	Higher plants and green algae
Chlorophyll c	$C_{55}H_{71}O_6N_4Mg$	Brown algae and diatoms.
Chlorophyll d	$C_{54}H_{70}O_6N_4Mg$	Only in red algae.
Bacteriochlorophyll	$C_{55}H_{74}O_6N_4Mg$	Purple sulphur bacteria.
Bacterioviridin	$C_{55}H_{72}O_6N_4Mg$	Green sulphur bacteria.
II. Carotenoids		
Carotene	$C_{40}H_{56}$	In algae and higher plants.
Xanthophyll	$C_{40}H_{56}O_2$	Higher plants, algae, mosses and ferns.

7. ENZYMES

Kuhne (1878) used the term enzyme (Gk., en = in ; zyme = yeast) for the soluble ‘ferment’ of bacteria or Yeast. Buchner (1897) gave the name ‘Zymase’ to the yeast extract which could bring about alcoholic fermentation. Sumner (1926) first isolated the pure crystalline form of urease from jack bean meal, thus confirming the proteinaceous nature of the enzyme. Since then many enzymes have been obtained in pure crystalline form and all have proved to be proteins.

In the light of modern concept, enzymes can be defined as catalytically active proteins (simple or conjugated) produced by living cells and accelerate the rate of chemical reactions without themselves undergoing any chemical change at the end of the reactions.

Many enzymes contain non-protein groups attached to the protein molecules. The non-protein part of the enzyme is called the prosthetic group or co-enzyme. When the prosthetic part is removed from the molecule the nature of the enzyme is lost.

Majority of the plant enzymes are **endoenzymes** or **intracellular**, i.e. they are active at the place of their synthesis. This type of enzyme is called **hydrolysing enzyme**. The other type of enzyme is known as **desmolysing enzyme**. These enzymes act outside the cell of their origin and thus termed as **exoenzyme** or **extracellular**.

The chemical compounds on which the enzymes act is called as **substrate. All enzymes are specific in their action**, i.e. a particular enzyme can work on a certain substrate or a group of substrates.

According to the new system of classification (recommended by the **Commission on Enzymes of the International Union of Biochemistry,1961)** enzymes have been classified into six major classes as follows:

(1) Oxido-reductases:

Catalyse oxidation-reduction reactions. Dehydrogenases, oxidases, reductases, catalases are included in this group.

(2) Transferases:

These enzymes take part in the transfer of a group of atoms from one molecule to another. Transaminases, transketolases,transaldolases,transphosphorylases are examples of this type.

(3) Hydrolases:

Catalyse hydrolytic reactions. Examples of these enzymes are invertase, amylase, pectinase, proteolytic enzymes (pepsin, typsin) and digestive enzymes like esterases proteases, phosphatases,etc.

(4) Lyases:

They take part in the reactions in which either a double bond is established due to the removal of a group or a group is added to the double bond.

(5) Isomerases:

This group of enzyme brings about isomerisation reactions. They include enzymes like isomerase, epimerase and enzymes taking part in anaerobic glycolytic pathway, etc.

(6) Ligases or synthetases:

They catalyse those reactions in which linking of two molecules is coupled with the breakdown of pyrophosphate bond of ATP or similar triphosphate.

* * *

SECONDARY METABOLITES

INTRODUCTION

The secondary metabolites may be defined as plant substances which are derived biosynthectically from primary metabolic compounds like, carbohydrates, fats and amino acids. The secondary metabolites (also known as secondary plant products) are organic molecules that are not directly involved in normal growth, development and reproduction of the plant. They are not part of the basic molecular structure of the cells. Unlike primary metabolites, absence of secondary metabolites results not in immediate death, but in long-term impairment in survival of the plant.

Secondary metabolites generally occur in relatively low quantities and their production may be widespread or restricted to particular families, genera or even species. They are normally found only in particular tissues or organs, or at particular stages of development.

Secondary metabolites are also known as **phytochemicals or natural products**, which have significant medicinal value. It is estimated that 25% of prescription drugs contain at least one chemical originally identified and extracted from the plants.

The plant produces numerous secondary substances such as alkaloids, terpenoids, phenols, resins, tanins, various phytohormones, purines and pyrimidine bases, porphyrines, different co-enzymes, etc. Out of these different substances phytohormones (auxins, gibberellins, cytokinins and abscisic acid), co-enzymes, porphyrins, etc., are very essential for the producer as they control the growth and developmental processes of the plant.

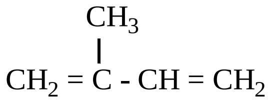
Secondary substances such as some alkaloids, resins, rubber, etc., are produced by a certain types of plants only. The functional significance of these substances to the producer plant is not properly known. The main function of the secondary metabolites is for defense against predators, parasites, fungus, virus and other harmful agents as well as for interspecies competition.

The distinction between primary and secondary metabolites is more easily visualized at the whole plant level. By this traditional rule, both chlorophyll and lignin would qualify as secondary metabolites because neither is found universally in all cells and tissues. However, the fundamental importance of both chlorophyll and lignin to growth and development surely qualifies both as primary metabolites.

TERPENOIDS

Terpenoids or isoprenoids are the largest and most diverse class of organic compounds found in plants. The name terpenoid derives from the fact that the first compounds in the group were isolated from the turpentine (Ger. *terpentin*), an essential oil (chiefly pinene) distilled from the resins of several coniferous trees.

Terpenoids are not only numerous but also extremely variable in structure, exhibiting hundreds of different carbon skeletons and a large assortment of functional groups. Terpenoids are a group of complex compounds composed of 5-carbon units called **isoprene**. The isoprene has the following structural formula:



$$CH_2 = \overset{\overset{CH_3}{|}}{C} - CH = CH_2$$

Classification of terpenoids

Terpenoids are classified according to the number of carbon atoms in the basic skeleton. Although biosynthesis is based on unit of five carbon atoms, terpenoid nomenclature is based on a unit of ten carbon atoms, since the C_{10} terpenoids were once thought to be the smallest naturally occuring representative of this class.

Designation of the C_{10} terpenoids as mono-('one')-terpenes made it necessary to name the subsequently described C_5 terpene as hemi-('half')-terpene, the C_{15} terpene as sesqui-('one-and-a-half')-terpene, and so on.

Depending on the number of isoprene units taking part in the formation of terpenoids the latter are classified into the following groups :

1. **Hemiterpenes:** One 5-carbon unit is present in the structure, e.g. coumarins,tigilic acid.
2. **Monoterpenes:** Two 5-carbon units entered into the composition, e.g. menthol, citrol, geraniol, camphor, etc.
3. **Sesquiterpenes:** Three isoprene units present in the structure, e.g. abcisic acid which functions exclusively in plant growth regulation (mainly in the abscission of leaves and fruits), artemesinine, farnesol.

4. Diterpenes: Four 5-carbon units entered into the composition, e.g. phytol and gibberellins, chlorophyll.

5. Triterpenes: Six 5-carbon units are present in the structure, e.g. steroids like saponins,cucurbitacins, calotropins,cholesterol etc.

6. Tetraterpenes: Eight 5-carbon units linked to produce these compounds. Carotenes and xanthophylls are good examples of this type of terpenoids.

7. Polyterpenes: Many isoprene units (more than eight) taking part in the construction of this group of terpenoids e.g. **rubber.** Rubber is made up of 500-5000 isoprene blocks. This polyterpene has got great industrial importance. **Hevea or Par-rubber** is obtained from the plant *Hevea brasiliensis* (Euphorbiaceae). Polyterpenes (latex) are found in some members of Apocyanaceae and Asclepiadaceae. Assam or India rubber is obtained from the latex of Ficus elastica belonging to the family Moraceae.This rubber has got little or no commercial importance because of the very low yield.

CAROTENOIDS

Carotenoids are tetraterpenes (C_{40}) almost universal in occurrence in plant kingdom. They are located in chloroplast along with chlorophyll molecules. The light energy absorbed by the carotenoids is transferred to the chlorophyll a. Thus they are working as accessory pigments in photosynthetic mechanism. Carotenoids are family of highly colored (red, orange and yellow) plant pigments. The carotenoids include **orange pigment carotenes** ($C_{40}H_{56}$) and **yellow xanthophylls** ($C_{40}H_{56}O_2$).

Carotenoids are fat-soluble plant pigments with limited solubility in water. They are soluble in most of the organic solvents. They have similar chemical and physical properties, but somewhat different biological properties. Since they are light and sensitive, their extraction procedure is to be carried out in diffused light.

The name “Carotenoid” (it is pronounced ka-rot-ten-noid) is derived from “carrot” and essentially means compounds similar to the orange-pigmented nutrients found in carrots. The red color of tomato fruit (*Lycopersicum esculantum* of Solanaceae family) is due to the presence of a Carotenoid called Lycopene ($C_{40}H_{56}$).

Mixed carotenoids occur together as a family in many fruits and vegetables. The carotenoids can be further divided into two group; carotenes and xanthophylls.

Carotenes are hydrocarbons (containing only hydrogen and carbon atoms), whereas xanthophylls also contain atoms of oxygen. Most of the carotene (not all) are pro-vitamin A but xanthophylls can not be converted into vitamin A in the body.

Major carotenoids circulating in human plasma include beta-carotene, alpha-carotene, lutein, and lycopene.

Carotenoids are also found in various animal foods, such as salmon, egg-yolk, shellfish, milk and poultry.

In human, carotenoids play two primary roles as antioxidants and provitamin-A.

Beta-carotene

Betacarotene is the most well-known and best studies member of the carotenoids. Beta-carotene has been recognized as a source of vitamin A (provitamin -A) for several decades.

Alpha-carotene

Alpha-carotene is normally found in the same foods as beta-carotene. However, foods differ in the ratios of these two carotenes. Alpha-carotene may be 10 times better than beta-carotene in protecting skin, eyes, lungs and liver against damage.

Lycopene

Lycopene is predominantly found in tomatoes. Lycopene imparts a deep red to those fruits and vegetables in which it is rich. For instance, it creates the color of ripe tomatoes and watermelon pulp. It is an effective protector against several types of cancer, especially of organs such as prostate, pancreatic and cervical cancers.

Lutein

Lutein is a xanthophyll found in many leafy green vegetables, alfafa and egg yolks. Lutein is of particular interest because of its role in preventing macular degeneration, a leading cause of blindness in the elderly.

PHENOLS

The phenols (Gk. Phene = benzene; ol = OH) are substances that bear at least one hydroxyl group attached to an aromatic ring structure. These are important group of secondary plant metabolites and are found in a wide variety of plants from algae to angiosperms.

On the basis of their structural complexity, four groups of phenolic compounds are generally recognized in plants.

(1) Simple phenols:

They contain one or more hydroxyl groups attached to the ring system which may also contain methyl group, e.g. **catechol, hydroxyquinone,** etc.

(2) Phenol carboxylic acid:

These are also simple phenols having a carboxlic group as a substituent, e.g. ***p*-hydroxybenzoic acid, gallic acid,** etc.

(3) Phenyl propane derivatives:

These are also simple phenol where three carbon atoms of phenyl propane are attached, e.g. **coumarins, lignins,** etc.

(4) Flavin derivatives:

These are characterised by having the flavin skeleton consisting of two aromatic rings A and B flanking the central oxygen containing heterocycle. e.g. flavones, anthocyanidins, etc.

All phenolic substances occur widely as glycosides or sugar esters which are found to be deposited in the vacuoles of the cell.

ROLE OF PHENOLIC COMPOUNDS IN THE PLANTS AND HUMAN SOCIETY

Usefulness of Phenolic compounds

I. For the Plants

(a) Give attractive colors for pollination by insects
(b) Provide structural build up
(c) Protect microbial invasion

II. For the Humans

(1) For the food industry:
    (a) Coloring agents
    (b) Flavoring agents
    (c) Preservatives (Antioxidants)

(2) For the pharmaceutical industry:

- (a) Antioxidants
- (b) Anti-inflammatory
- (c) Antihistamine
- (d) Antiseptic (antimicrobial)
- (e) Anticancer
- (f) Cardiovascular protection
- (g) Hepatoprotective
- (h) Antidiabetic
- (i) Antidiarrhoea
- (j) Antidotes for poisoning

A. Lignin

Lignin is widely distributed throughout the plant kingdom. It is an important constituent of the wood and other ‘woody’ plant tissues. Lignin is absent in the lower plants (lichen, mosses, fungi and mushrooms).

Lignins are found to be present in the primary and secondary walls of the cell. When associated with cellulose it occupies the spaces between the micelles and cements the cellulose fibre together. Thus it gives stiffness and rigidity to the plant tissues and protects the plant from the attack of various pathogens.

Lignins are polymers of phenyl propane units which are composed of phenolic acids like p-coumaric acids, ferulic acids and sinapic acids.

There are three classes of lignin:

(1) Soft wood or gymnospermous lignin: they contain 3-methoxy-4-hydroxyphenyl propane structure.

(2) Hard wood or dicotyledonous (Angiosperm) lignin: they contain the 3,5-dimethoxy-4-hydroxyphenyl propane structure.

(3) Grass or annual plant or monocotyledonous (Angiosperm) lignin: they contain 4-hydroxy phenyl propane structure in addition to the structures of (1) and (2).

Lignins are insoluble in water, unhydrolyzable by acids, soluble in hot alkali and bisulphite and readily condenses with phenols and thiol compounds.

B. Anthocyanidins

Anthocyanidins are the derivatives of 3,5,7-trihydroxy-flavylium chloride of trihydroxy-benzopyrylium chloride. There are various types of anthocyanidins : (a) pelargonidin, (b) cyanidin, (c) delphinidin, (d) peonidin, (e) malvidin, (f) hirsutidin, etc. These groups differ in the number, nature and position of other hydroxyl groups, methoxy groups and sugar residue.

Usually anthocyanidin forms glycoside being remain attached to the sugar molecule. Normally one sugar molecule is attached to 3-hydroxyl group of anthocyanidin. Sometimes more than one sugar molecules may remain linked in an anthocyanidin.

B. (i) Anthocyanins :

Chemically anthocyanins are **glycosides** which have been formed by a reaction between a sugar and an anthocyanidin. The most commmon sugars found in the anthocyanins are glucose, galactose, rhamnose and gentibiose. Thus sugar-free anthocyanins are called anthocyanidins.

Most of the attractive colors of the flowers, fruits, leaves, fruit juices, etc., are due to the presence of anthocynin pigment.

Anthocynins are soluble in water, hence they are found dissolved in the cell sap. Generally anthocyanins are red in acid pH and blue in alkaline solution. The different shades of the flower color depend upon the presence of anthocynins in different media of the cell sap (acidic, alkaline or neutral). Color of the foliage from green to red and purplish red during autumn is due to the formation of anthocyanin.

The exact function of anthocyanins in plants is not properly known. It is assumed that they play some role in respiration and photosynthesis. They may act as light filters and thus protecting the decomposition of chlorophyll pigments against strong sunlight. The beautiful colors of anthocyanins in the flower petals attract insects and thus helping cross pollination in plants.

B. (ii) Flavone:

Flavones are yellow pigments which occur in plant kingdom as glycosides or in the free form. Sometimes they remain associated with tannins. They are also known as anthoxanthins (See to below Figgure).

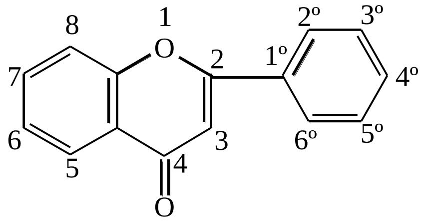


Fig. Structure of a Flavone

Flavones are structurally related to anthocyanins having hydroxyl group in their structure. Depending on the number of hydroxyl groups present in the structure, they may be mono, di, tri and tetrahydroxy flavones.

Most flavones are soluble in water, ethanol and dilute acids or alkalis. They can be precipitated by lead salt. Flavones produce a pale green or a red brown color with ferric chloride solution. Quercetin ($C_{15}H_{10}O_7$) is an example of flavone found in the bark of *Quercus tinctoria*.

C. Tannins

Tannins are a group of polyphenols. They are abundant in plant tissue. The exact physiological role of these complex substances to the producer plant is not properly known. They have got commercial importance because of their property of forming an insoluble colloidal complex (leather) with the animal hides.

Tannins are generally found in the cell sap but sometimes occur in the cell walls.

Tannins are classified into two major groups: (a) hydrolysable tannins and (b) condensed tannins. According to Haworth (1961), the hydrolysable tannins are characterized by having several gallic acid groups or acids derived from gallic acid linked by an ester linkage to central glucose residue. These esters are readily soluble in water and on hydrolysis with acids or alkalis they yield glucose and complex acids like gallic acid, hexahydroxydiphenic acid, etc. The percentage of sugar in the hydrolysable product is relatively low.

Condensed tannins are mostly flavonols and cannot be hydrolysed to simple components. These groups on acid treatment get condensed to form anthocyanidins (proanthocyanidins).

The percentage of tannin vary greatly from species to species. Tannins are generally found in the leaves of many species such as tea (15% of the dry weight), oaks, some conifers, etc. The bark of certain plants contain tannin, (e.g. oaks, chestnut, hemlock, sumac, etc.). Unripe fruits of some plant, (e.g. plum) contain relatively high amount of tannins. Among the cereals sorghum contain high percentage of these polyphenols which reduce the nutritional value.

Tannis are astringent in taste. Thus it may be regarded that they are produced by the plant to protect themselves from the plant eating insects, birds and other animals.

ALKALOIDS

The term alkaloid (meaning alkali like) was first proposed by W.Meissner (1819) to a group of nitrogen containing compounds isolated from plants. Konigs (1880) defined alkaloids as **naturally occurring organic substances which contain a pyridine ring.** Alkaloids are a large family of chemically unrelated molecules. As a group, alkaloids share three principle characters;

1. They derive from amino acids and possess at least one nitrogen atom. Often the nitrogen will accept the proton, which give it a slightly basic, or alkaline, character in solution (hence the name alkaloid).
2. They are soluble in water.
3. They exhibit high biological (pharmacological) activity.

(a) Occurance

Alkaloids have been detected in about 15% of plants, bacteria, fungi, and even in animals. There are over 12,000 alkaloids have been identified, 20% of them come from flowering plants.

(b) Classification and structure of alkaloids

Alkaloids are heterocyclic N-containing compounds and have basic properties. Most of them are highly toxic. They are classified as follows:

1.	Phenyl ethyl amine group	e.g.	Hordenine, ephedrine, etc.
2.	Pyrrolidine group	e.g.	Stachydrine.

3.	Pyridine-piperidine group	e.g.	Ricinine, conine, etc.
4.	Pyrrolidine-pyridine group	e.g.	Nicotine, hyocyamine, etc.
5.	Quinoline group	e.g.	Cinchonine.
6.	Isoquinoline group	e.g.	Papaverine, etc.
7.	Phenanthrene group	e.g.	Morphine.
8.	Indole group	e.g.	Ergotamine.

(c) Functions

The function of alkaloids to the producer plant may be as follows:

1. act as reserve materials to supply nitrogen which can be transformed when needed.
2. they may be the end-products of detoxification mechanism in plants otherwise their accumulation in the protoplasm of the cell may cause damage to the plant.
3. being poisonous they protect the producer plant from the attack of herbivorous animals and insects.

GLYCOSIDES

The term “glycoside” (*Gr. glykys*,sweet) refers to the bond formed (called *glycosidic* bond) when a sugar molecule condenses with a hydroxyl group.

Sugar may form glycosidic bonds with other sugars, such as when linked together to form polysaccharides, or with hydroxyl groups on noncarbohydrate molecules, such as amino acids (to form cyanogenic glycosides and glucosinolates) and terpenoids (to form saponins and cardiac glycoside).

The sugar most commonly found in glycosides is glucose, although rare sugars are found in specific glycosides.

Main function of glycosides

The main function of the glycoside is deterrents (discourage) to herbivores.

Types of glycosides

No.	Types of glycosides	Main components	Remarks
1.	Cyanogenic glycoside	sugar + amino acids	Natural source of HCN
2.	Glucosinolates	sugar + amino acids	Containing sulfa
3.	Saponin glycoside	sugar + terpenoids	Foaming appearance
4.	Cardiac glycoside(cardinolides)	sugar + terpenoids	Cardiostimulant

1.Cyanogenic glycosides

Cyanogenic glycosides (also known as cyanogens) are natural source of **hydrogen cyanide** (HCN). It might seem odd that plant synthesize chemicals capable of releasing deadly HCN, but more than 60 different cyanogenic compounds (cyanogenic glycosides, cyanolipids,etc.) of plant origin have been described from more than 2600 plants of a dozen plant families. Predominant among these are the **cyanogenic glycosides**.

Most cyanogenic glycosides appear to be derived from one of four L-amino acids (phenylalanine, tyrosine, valine, and isoleucine) or nicotinic acid. The biosynthesis is catalysed by the multiple enzymes in cytoplasm.

Cyanogenic glycosides are not end product of metabolism and ready for use when necessary. Since HCN cannot be stored by plants as the free hydrocyanic acid, its accumulation as a preformed defense chemical (cyanogenic glycoside) is an ingenious solution.

Laboratory analysis

Cyanogenic glycosides are easily hydrolysed by dilute acid to nitriles, which further decompose to aldehydes or ketones and HCN.

$$\text{Cyanogenic glycoside} \xrightarrow[\text{hydrolysis}]{\text{Dilute acid}} \text{Nitriles} \xrightarrow{\text{decompose}} \text{Aldehydes or ketones} + \text{HCN}$$

Functions

Both cyanogenic glycosides and glucosinolates function as prefabricated defense compounds which are activated by action of a -glucosidase in case of emergency, releasing the deterrent; toxic HCN from cyanogens or isothiocyanates from glucosinolates.

HCN is highly toxic for animals or microorganisms due to its inhibition of enzymes of the respiratory chain, cytochrome oxidase and its binding to other enzymes containing heavy metal ions.

The lethal dose of HCN in man is 0.5-3.5 mg / kg after oral application and death of man or animals have been reported after the consumption of plants with cyanogenic glycosides, whose concentration can be up to 500 mg HCN / 100 g seeds. Normally HCN contents in certain cyanogens rich foods are 50-100 mg HCN / 100 g seeds and 30-200 mg HCN / 100 g leaf.

Foods, which contain cyanogens such as **cassava** have repeatedly caused intoxications and even death in man and animals. Animals can rapidly detoxify small amounts of HCN by rhodanese. Furthermore, a number of herbivores have been studied which can tolerate HCN at least in lower concentrations. Nevertheless, cyanogens could be considered as active and potent chemical toxic defense compounds.

mechanism of Cyanogensis

Intact cyanogenic glycosides are not themselves toxic, but when the plant is damaged by the herbivores, the glycoside undergoes an enzymatic breakdown and HCN is released. HCN, a noncompetitive inhibitor of cytochrome oxidase, is acutely toxic to animals.

The enzymatic breakdown of cyanogenic glycosides is a two-step process.

1. First, the sugars are released by the enzyme -glycosidase. The resulting hydroxynitrile is moderately unstable and will slowly decompose, liberating HCN in the process.
2. Secondly, this decomposition is accelerated by a second enzyme, known as hydroxynitrile lyase.

$$\underset{\text{(amyladin)}}{\text{Cyanogenic glycoside}} \xrightarrow{\textit{B-glycosidase}} \underset{\text{(mandelonitrile)}}{\text{Hydroynitrile}} \xrightarrow{\textit{Hydroxynitrile lyase}} \text{HCN}$$

Fig. Mechanism of cyanogenesis

Ezymatic release of cyanide does not normally occur in intact plants because the enzymes and the substrate are spatially separated. In some cases, separation is maintained within the cell, but in other, the enzymes are in one cell and the cyanogenic glycoside in another. Only when the tissue is crushed, and the contents of the two cells are mixed, resulting cyanogenesis.

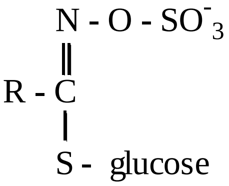
Although most animals have the ability to detoxify small quantities of cyanide, the presence of cyanogenic glycosides deters feeding by insects and other herbivores. Clearly the effectiveness of cyanogenic glycosides as a deterrent depends on many factors, such as the amount present, the rate of release of cyanide, and the ability of the animal to detoxify.

Avoidance of Cyanide poisoning in food

Cyanogenic glycoside poisoning can be avoided by careful preparation of the plants or foods. This includes grinding the root and expressing and removing the fruits, or boiling the root in several changes of water while opening of lid frequently.

2.Glucosinolates

Glucosinolates are sulfur-containing precursor to mustard oil, an economically important class of flavor constituents that gives the pungent taste to condiments such as mustards and horseradish as well as the distinctive flavor of cabbages, broccoli, and cauliflower. Glucosinolates resemble cyanogens in many respects, but contain sulfur as an additional atom.



$$\begin{array}{ll} & N - O - SO^-_3 \\ & \| \\ R - & C \\ & | \\ & S - \text{glucose} \end{array}$$

fig. Structure of glucosinolate

Source

More than 80 different glucosinolates have been found in higher plants primarily in the mustard family (Brassicaceae) and related families in the order Capparales.

Biosynthesis

Both protein or non-protein amino acids serve as precursors for biosynthesis of glucosinolates. Glucosinolates are polar molecules which are formed in the cytoplasm and stored in the vacuoles. All plants parts may accumulate glucosinolate but seeds and roots are often rich. Concentrations are in the range of 0.1-0.2% fresh weight in leaves, up to 0.8% in roots and up to 8% in seeds. Glucosinolates are dynamic metabolites and a half-life of 2days has been reported.

Phytochemistry

All glucosinolates can be classified as **thioglucoside** (*"thio"* means **sulfur;** *"glucoside"* means **glucose**).The sugar is always glucose. The diversity encountered in structure and properties is due to the 'R' group, which may range from a simple methyl group to large linear or branched chains containing aromatic or heterocyclic structures.

The biological activity of glucosinolates depends primarily on their hydrolysis to mustard oils. Hydrolysis of glucosinates is catalysed by an enzyme called myrosinase (a thioglucosidase). This process creates an unstable product that spontaneously rearranges to form the mustard oils in the thiocyanate, iso-thiocyanate (common name is mustard oil), or nitrile forms. The iso-thiocyanates are responsible for the distinctive pungent flavor and odor of mustard and horseradish.

Like the cyanogenic glycosinolates are spatially seperated from the hydrolytic enzymes so that the mustard oils (Mon-nyin-si) are normally formed only when the cells are disrupted, allowing the enzymes and substrate to come together.

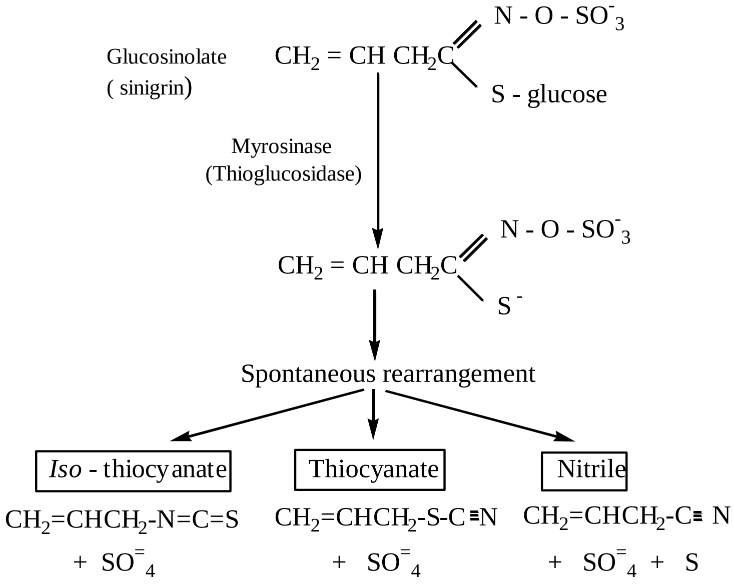


Fig : Enzymatic removal of glucose from a glucosinolate

Functions

As with other defense compounds, some herbivores are deterred or repelled by the presence of glucosinolates in a plant, while others have adapted to use the glucosinolates or mustard oil as attractants to stimulate feeding and ovipositing.

Upon cells and tissue disintegration (wounding) or increase of membrance permeability, the enzyme and its substrate come together liberating the pungent, repellent and antibiotic isothiocyanate. Depending on the environmental conditions, enzymes and other compounds present, the aglycone can rearrange to isothiocyanate as the most common product, or other products such as nitriles, thiocyanates etc.

Applications

Glucosinolates, or rather their absence, have had a significant impact on the oilseed industry.

Rape seed (principally *Brassica napus*) is a good source of vegetable oil, but its high content of glucosinolate together with erucic acid (a 22-carbon fatty acid) gives the oil undesirable taste and poor storage properties.

New strains have beeh bred with low glucosinolate and erucic acid. These strains, called canola in order to distinguish them from normal rape, are now an economically important oil source.

Isothiocyanates are antiboitic and can kill the bacteria and fungal cells by leaking of their cell wall when applied locally.

Side effects

Because isothiocyanate (mustard oil) is not volatile and can easily penetrate biomembranes, they can also interact with epidermal and mucosal skin leading to painful irritation in some individual.

If inhaled they can lead to bronchitis, and pneumonia. If ingested, they may cause gastroenteritis, diarrhea, heart and kidney disorder and even to abortion. Nitriles are toxic to the liver and kidneys.

Saponin glycosides

The name saponin is in fact derived from saponarea (*soapwort*), which at one time was employed as a soap substitute. When agitated in water saponin forms a stable soapy foam.

In much the same way as soap is the sodium salt of fatty acid, the combination of a relatively hydrophobic triterpene with a hydrophillic sugar gives saponins the properties of a surfactant or detergent.

Types of saponin

There are three forms of saponin glycosides:- 1. steroid glycosides
2. steroid alkaloid glycosides
3. triterpene glycosides

Saponins may also occur as aglycones, which are known as sapogenins.

Role of saponin in the plant

The principle role of saponins in plants appears to be as a performes defense against attack by fungi. Evidence indicates that saponins form complexes with sterols containing an unsubstituted 3- - hydroxyl group. When the saponins react with sterols in the membranes of invading fungal hyphae, the result is a loss of membrane integrity.

Another defense mechanism appears to be the development of detoxifying enzymes. Oat (*Avena*), for example, produced a triterpenoid saponin, avenacin A-1, which is localized in the root epidermal cells and effectively protects against an invasion by a fungal pathogen that infects the root of both wheat and barley.

Effect of saponin in animal

- Saponins are not significantly toxic to mammals. But it is highly toxic to fish and have been used as fish poisons. Saponins have also been implicated in reports of live-stock poisoning.
- It has bitter,acrid taste and will cause gastric irritation if ingested. For example, alfalfa saponins can cause digestive problems and bloating in cattle.
- Saponins will cause hemolysis of red blood cells, if injected into the blood stream. This action is because of their ability to disrupt RBC membrance.
- There are reports that saponin contained in alfalfa will lower serum cholesterol levels.

Use of saponin in human society

Saponin from the bark of *Quillaja saponaria* have been used as surfactants in photographic film, shampoos, liquid detergents, toothpastes, and beverages (as emulsifier)

The saponin glyscyrrhizin from licorice (*Glyscyrrhiza glabra*) has been used in medicines and as a sweetener and flavor-enhancer in foods and cigarette.

Cardiac glycosides

The cardiac glycosides are also known as cardenolides and have a wide distribution; they have been recorded in more than 200 species representing 55 genera and 12 families.

Cardiac glycosides are structurally similar to the steorid saponins and have similar detergent properties. They are distinguished from other steroid glycosides by the presence of a lactone ring and the rare sugars (found almost exclusively in this group of steroids) that form the glycoside.

Digitalis

Digitalis is the best well-known source of cardiac glycosides extracted from the seeds, leaves, and roots of purple foxglove (*Digitalis purpurea*) or Grecian foxglove (*Digitalis lanata*). The two principle cardenolides are **digitoxin** and its close analog **digoxin**.

Because they disrupt the heart muscle Na^+/K^+-ATP as pumps (hence the appellation *cardiac*) cardenolides are highly toxic to vertebrates. The extreme toxicity of cardinolides has long been exploited by African hunters, who coated their arrows and spears with digitalis extract from plants.

However, in therapeutic use, carefully regulated doses can both slow and strengthen the heartbeat. Unfortunately, the lethal and therapeutic doses are very close, so the therapy must be carefully monitored. Since the late 18th century, digitalis has been used for its therapeutic value in treating heart diseases.

* * *