

**COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH**  
**UNIVERSITY GRANTS COMMISSION**

CHEMICAL SCIENCES

CODE:01

**3.12. Chemistry of natural products**

**3.12.1. Introduction**

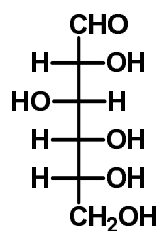
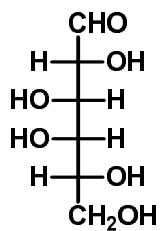
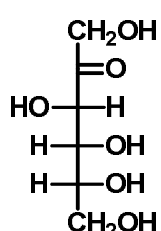
- Carbohydrates: Carbohydrates are naturally occurring in the animal and vegetable kingdom. Sugar, starch and cellulose are the member of this family.
- Carbohydrates are polyhydroxy aldehydes or ketones or the substances which produce those compounds upon hydrolysis.

**3.12.2. Classification:** Carbohydrates are classified as (a) Monosaccharides, (b) Oligosaccharides

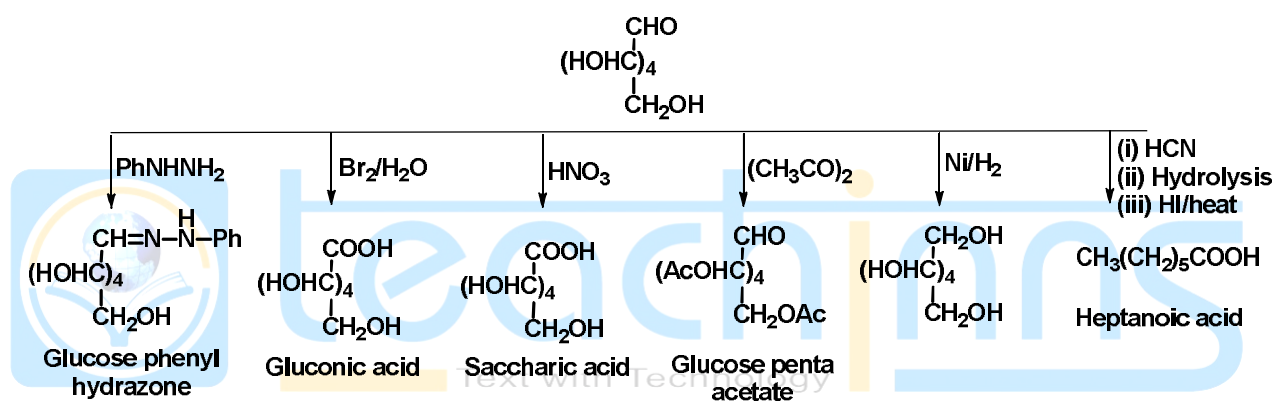
- ❖ Another classification of carbohydrates: According to reducing ability carbohydrates are also classified as reducing and non-reducing sugar.
- ❖ The carbohydrates which can reduce Fehling's solution is called reducing sugar and the others are called non-reducing sugar.

(a) Monosaccharides:

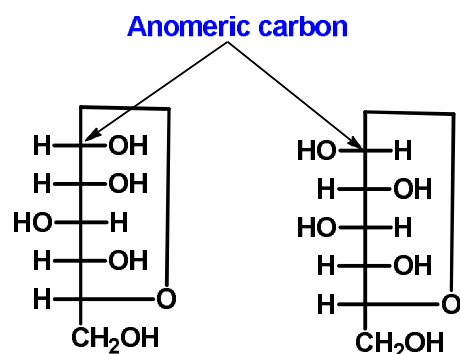
- These are called simple sugar
- These cannot be hydrolyzed further to simple sugar.
- Aldoses are polyhydroxy aldehyde (glucose, galactose etc.)
- Ketose is polyhydroxy ketone (fructose)
- Glucose is alternatively called grape sugar or blood sugar.
- Fructose is also called fruit sugar.

**D-glucose****D-galactose****D-fructose**

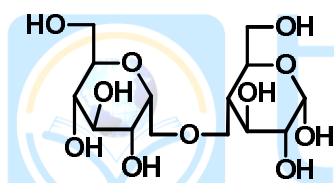
- **Monosaccharides:** These are the straight chain aldehydes or ketones with hydroxyl group on all or nearly all the carbon atoms. The most common example of monosaccharides are glucose, fructose, levulose and ribose.
- **Glucose:** Glucose undergoes some chemical reactions which indicates that it is a six carbon straight chain penta hydroxy aldehyde.
- On heating with concentrated NaOH solution, glucose first turns into yellow, then brown and finally gets resinified. However, upon treatment with dilute NaOH solution, glucose undergoes a racemization reaction and produces a mixture of D-glucose, D-mannose and D-fructose. This reaction is known as Lobry de Bruyn-van Ekenstein rearrangement



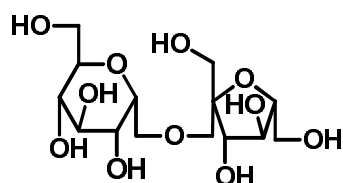
- **Anomers and anomeric carbon:** If the configuration of two cyclic forms of a carbohydrate is different only at the hemiacetal carbon, then these are said to be anomers and the corresponding carbon atom is called anomeric carbon.



- **Mutarotation:** If the specific rotation of an optically active compound is spontaneously changed, then that is called mutarotation. The hemiacetal form of  $\alpha$ -D-glucose and hemiketal form of D-fructose are stable in solid state but in aqueous solution, the cyclic form gets opened to give a solution of constant specific rotation.
- (b) **Oligosaccharides:** These are the carbohydrates which yield a definite number (2-9) of monosaccharides under hydrolysis.
- (i) **Disaccharides:** These sugars produce two monosaccharides under hydrolysis, e.g. sucrose and maltose.
- Disaccharides: One molecule of disaccharide produces two molecules of monosaccharides on hydrolysis. For example maltose, lactose, sucrose.
- **Maltose:** On hydrolysis one molecule of maltose produces two molecules of glucose. The structure of maltose is as follows. It is reducing sugar as it reduces Fehling's solution and Tollen's reagent.



- **Sucrose:** One molecule of sucrose gives one molecule of each D-glucose and D-fructose under hydrolysis. It does not reduce Fehling's solution and Tollen's reagent, so it is a non-reducing sugar.



- (ii) **Trisaccharides:** These sugars produce three monosaccharides under hydrolysis, e.g. raffinose.
- (iii) **Tetrasaccharides:** These sugars produce four monosaccharides under hydrolysis.
- (c) **Polysaccharides:** These are the carbohydrates having very high molecular weight which produce more than ten monosaccharides on hydrolysis, for example starch and cellulose.

❖ **Starch:** It is the main storage polysaccharide of plants. It does not reduce Fehling's solution and Tollen's reagent. It does not form an osazone. It is a polymer of D-glucose and consists of two components, 10-20% amylose and 80-90% amylopectine.

❖ **Amylose:**

- It is water soluble fraction.
- It is a linear polymer of  $\alpha$ -D-glucose.
- The glucose units are linked to one another through  $\alpha$ -linkage where C1 of one glucose unit is linked with C4 of another glucose unit.

❖ **Amylopectine:**

- It is water insoluble fraction.
- It is a branched polymer of  $\alpha$ -D-glucose.

❖ **Cellulose:**

- It is the major structural polysaccharide in higher plants.
- It is probably the most frequently observed organic compound in nature.
- It is a straight chain polysaccharide which is composed of D-glucose units by  $\beta$ -glycosidic linkages in which C1 of one glucose unit is linked to C4 of another glucose unit.

### 3.12.3. Glycogen:

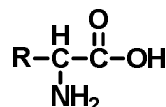
- It is a polysaccharide whose structure is very similar to that of starch.
- In this form animals store glucose for further use.
- Its best source is liver or muscle.

### 3.12.4. Proteins:

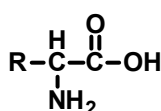
- These are long-chain polyamides which are obtained from  $\alpha$ -amino acids. The amide bond is formed by coupling of amine group of one  $\alpha$ -amino acid with the carboxyl group of another  $\alpha$ -amino acid.
- The amide bond between two  $\alpha$ -amino acids is called peptide bond.
- Amino acids are formed when proteins get hydrolyzed.

**3.12.5. Amino acids:**

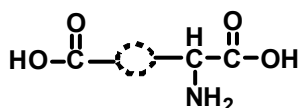
- Amino acids are those compounds containing one acidic carboxyl group (-COOH) and one basic amino group (-NH<sub>2</sub>).

**3.12.5a. Categories of Amino acids:**

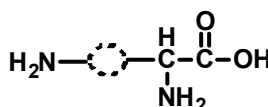
Amino acids are categorized as neutral- (which contains one amino group and one carboxyl group), acidic- (which contains one amino group and two carboxyl group) and basic (which contains two amino group and one carboxyl group)-amino acids.



neutral amino acid

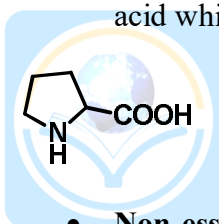


acidic amino acid



basic amino acid

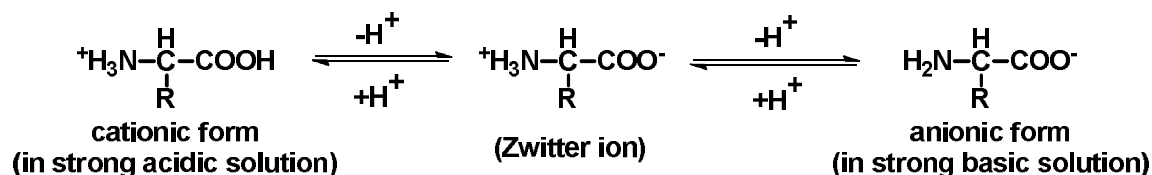
- All the amino acids generally contain primary amino group, but proline is an amino acid which has secondary amino group. The structure of proline is as follows



- Non-essential amino acids:** The amino acids which can be synthesized in the human body to make the proteins are called Non-essential amino acids.
- Essential amino acids:** Other amino acids which must be provided in the diet are called essential amino acids.

**3.12.5b. Amino acids as dipolar ions:**

- Amino acids have both acidic and basic group, hence they are amphoteric in nature.
- In dry solid state they exist as dipolar ions.



- **Isoelectric point:** Isoelectric point of amino acid is the pH at which there is no net charge that means the negative charge on the amino acid is exactly balances the positive charge on it.

**3.12.6. Peptides:** Peptides are amino acid polymers in which single amino acid units are linked together by amide bonds.

- **Residue:** Each amino acid units in a peptide is called residue.
- **Oligopeptide:** It is the peptide which contains about four to ten amino acid residues.
- By convention peptides are always written with the N-terminal amino acid (free  $-NH_2$  group) on the left and C-terminal amino acid (free  $-COOH$  group) on the right.
- The name of the peptide is generally written by applying three letter names for each amino acid.
- Thus, alanylserine is abbreviated as Ala-Ser and serylalanine can be abbreviated as Ser-Ala.
- **Sanger reagent:** 2,4-dinitrofluorobenzene is known as Sanger reagent which is used for the identification of N-terminal amino acids. A modern approach is the use of dansyl chloride (5-N-dimethylaminonaphthalene-1-sulphonyl chloride).

**3.12.6a. Structure of Proteins:** There are four levels of protein structures that are important for understanding the protein function.

**3.12.6a.I. Primary structure:** In this aspect the  $\alpha$ -amino acids are linked together by peptide bonds in a specific sequence.

**3.12.6a.II. Secondary structure:** The orientation of a protein chain in three-dimensional space is described by the secondary structure.

**3.12.6a.III. Tertiary structure:** The overall shape of a protein is defined by tertiary structure.

**3.12.6a.IV. Quaternary structure:** The spetial arrangement of the protein aggregates is or assembles is defined as the quaternary structure.

### **3.12.6b. Denaturation of Proteins**

A protein should be in tertiary structure to fulfill the biological function. When a protein is denatured by the treatment with acid, alcohol or heating, it gets unfolded and becomes biologically inactive because of the destruction of its tertiary structure.

**3.12.7. Lipids:** Lipids are nothing but the esters of long chain fatty acids and alcohols respectively.

- The higher members of carboxylic acids are known as fatty acids.
- Fats contain large proportion of saturated acids while oils contain large proportion of unsaturated acids.
- Oils can be converted into fats by hydrogenation.

**3.12.7a. Classification of Lipids:** *Lipids can be divided into three classes*

(1) Simple Lipids, (2) Compound Lipids and (3) Derived Lipids

(1) **Simple lipids:** They contain long chain fatty acids and all their acid derivatives. Oil and fats are simple lipids. These are esters of glycerol and three fatty acids that's why simple lipids are also known as triglycerides. The fatty acids further can be subdivided into two categories.....

(a) **Saturated fatty acids**

Lauric acid:  $\text{CH}_3(\text{CH}_2)_{10}\text{COOH}$ , Palmitic acid:  $\text{CH}_3(\text{CH}_2)_{14}\text{COOH}$  and Stearic acid:  $\text{CH}_3(\text{CH}_2)_{16}\text{COOH}$ .

(b) **Unsaturated fatty acids**

Oleic acids:  $\text{C}_{17}\text{H}_{33}\text{COOH}$ , Linoleic acid:  $\text{C}_{17}\text{H}_{31}\text{COOH}$  and Linolenic acid:  $\text{C}_{17}\text{H}_{29}\text{COOH}$ .

(2) **Compound Lipids:** These are the compounds which produce fatty acids, alcohols and other compounds on hydrolysis. These are also classified as phospholipids and glycolipids.

- **Phospholipids:** These are mixed glycerides of higher fatty acids and phosphoric acid, for example-lecithins and cephalins.
- **Glycolipids:** These are the esters of fatty acids with carbohydrates but there is no phosphorous.



(3) **Derived Lipids:** These are the substrates which are derived from simple and compound lipids. These contain fatty acids, fatty alcohols, mono- and di-glycerides, steroids and terpenes.

- **Functions of lipids:**

1. Simple lipids act as important source of energy.
2. Phospholipids act as structural materials of cells and tissues such as cell membrane.
3. Lipids are essential for the absorption of fat soluble vitamins such as A, D, E and K.
4. Simple lipids act as heat insulators and shock absorbers for living organisms.

**3.12.7b. Fats and Oils:** These are the triesters of glycerol and hence called as triglycerides. They undergo hydrolysis to afford one molecule of glycerol and three molecules of fatty acids.

- **Saponification:** The alkaline hydrolysis of fat or oil is known as saponification.
- **Acid value:** The number of milligrams of potassium hydroxide required to neutralize the free carboxylic acids present in one gram of fat or oil is known as acid value.
- **Saponification value:** The number of milligrams of potassium hydroxide required to saponify 1g of the fat or oil. The higher the molecular weight of the fat, the smaller is the saponification value.
- **Iodine number or value:** the degree of absorption of halogen by a fat or oil is proportional to the number double bonds present in carbon chain of fatty acid moieties. Thus this addition reaction is used as an index of the degree of unsaturation in a fat or oil. The index value is called iodine value or number.
- Greater the number of double bonds, in oil or fat, the greater will be the iodine value.

**3.12.7c. Mineral oils:**

- They are made up of saturated and unsaturated hydrocarbons and not esters/glyceraldehydes.
- They cannot be saponified.
- They are oils only in their physical appearance.
- They resemble oils in being insoluble in water.
- They are non-edible and used as domestic fuels and in auto-mobile.
- Paraffin oil is a typical mineral oil.



### 3.12.8. Nucleic acids:

- These are biologically important polymers found in all living cells. Nucleic acids are also referred as polynucleotides.
  - There are two types of nucleic acids (a) DNA (deoxyribonucleic acid) and (b) RNA (ribonucleic acid).
  - A nucleotide consists of three components.....
1. **Nitrogen containing heterocyclic base**, for example adenine (A), guanine (G), Thymine (T), cytosine (C) and uracil (U). Adenine and Guanine belong to the group of purine bases However, Cytosine, thymine and uracil belong to the group of pyrimidine bases.

Note: DNA contains adenine, guanine, cytosine and thymine whereas RNA contains adenine, guanine, cytosine and uracil.

2. **Sugars:** There are two types of sugars present in nucleic acids. Sugar present in RNA is D-ribose and in DNA is D-2-deoxyribose.
3. **Phosphate group:** These help to link nucleic acid polymers. The phosphate group is bonded to a hydroxyl group of sugar.

### 3.12.9. Nucleosides and Nucleotides:

**3.12.9a. Nucleosides:** A base-sugar unit, formed by the combination of a sugar (ribose or deoxyribose) and a nitrogen base is known as a nucleoside.

Adenosine (commonly known as adenosine) is an example of simple nucleoside formed by the combination of adenine (base) and D-ribose (sugar).

**3.12.9b. Nucleotides:** When one of the hydroxyl groups of the sugar part of the nucleoside is esterified with phosphoric acid, then a nucleoside is converted into a nucleotide.

Adenosine phosphate furnishes an example of simple nucleotide.

Nucleotides are joined together by phosphodiester linkage between 5' and 3' carbon atoms of pentose sugar.

**3.12.10. Terpenes or Terpenoids:** The term terpenoid is used for terpene like compounds, e.g. hydrocarbons or related oxygenated derivatives. Most natural terpenoids are those having molecular formula  $(C_5H_8)_n$ .

The term terpene is rejected due to the fact that the suffix “ene” is used to indicate the unsaturated hydrocarbons (alkenes), but the term terpene is not applicable for compounds such as alcohols, aldehydes or ketones. The term “terpene” is restricted to hydrocarbons of molecular formula  $C_{10}H_{16}$ .

**3.12.10a. Isoprene Rule:** Thermal decomposition of terpenoids give terpene as one of the products. “The skeleton structure of all naturally occurring terpenoids are built up of isoprene units”.

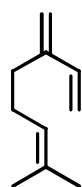
Isoprene rule states that the terpenoid molecules are constructed from two or more isoprene units. Alternatively this rule states that the terpenoid molecules are constructed of two or more isoprene units joined in a “head to tail” fashion.

**3.12.10b. Classification of terpenoids:** Terpenoids have been classified based on the number of  $C_5$  (or isoprene) units present in them. Thus these molecules are classified as follows which is given in tabular form.

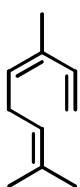
Class	No of carbon atoms	No of $C_5$	Example
Monoterpenes	10	2	$\alpha$ -pinene, citral
Sesquiterpenes	15	3	Farnesol, Eudesmol
Diterpenes	20	4	Vitamin A
Triterpenes	30	6	Squalene, Lanosterol
Tetraterpenes	40	8	Lycopene, $\beta$ -carotene
polyterpenes	$5n$	$n > 8$	Rubber

The terpenoids are further sub-divided into acyclic (open chain) and cyclic terpenoids, depending upon their open chain or cyclic structures.

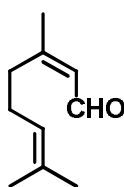
- **Acyclic monoterpenoids:**



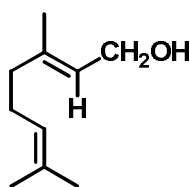
Myrcene



Ocimene

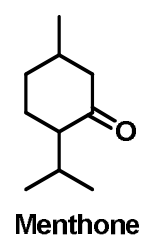
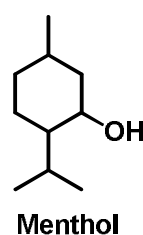
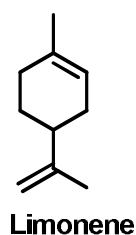
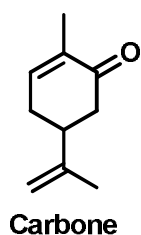
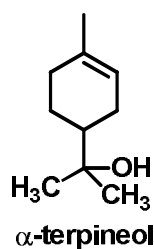


Citral

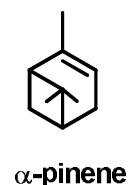
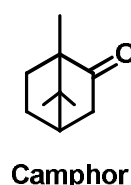
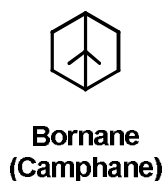


Geraniol

- **Monocyclic monoterpenoids:**



- **Bicyclic monoterpenoids:**



### 3.12.10c. Isolation of terpenoids

The extraction of essential oils (terpenoids) from the plant source is done by three methods

1. Steam distillation, 2. Extraction with solvents and 3. Fat adsorption method.

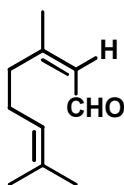
### 3.12.10d. General properties of terpenoids

- They are generally colourless pleasant smelling liquids.
- They are lighter than water.
- They are insoluble in water and soluble in organic solvents.
- They are steam volatile and generally optically active.
- They show chemical properties of double bond and functional groups present in them.

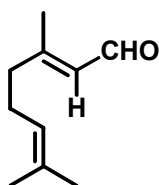
**3.12.11. Citral:** It is the most important member of the acyclic monoterpenoids. It is a pale yellow liquid having a strong lemon like odour.

It is obtained from lemon grass oil by the treatment with sodium bisulphate solution.

It is extensively used in perfume and flavor industry to stimulate lemon like odour and for the manufacture of vitamin A. It is also used for reduction of blood pressure.



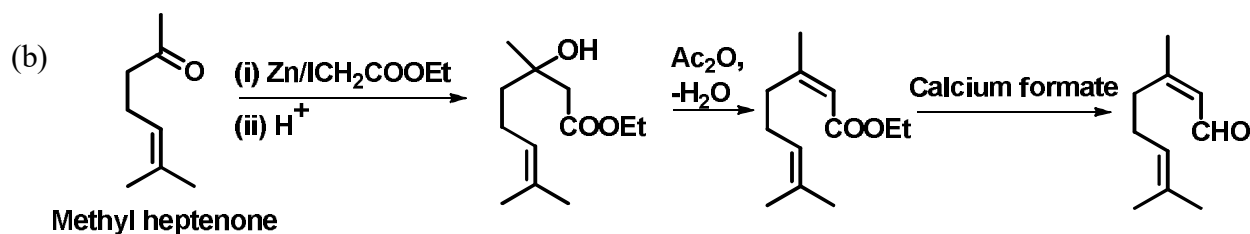
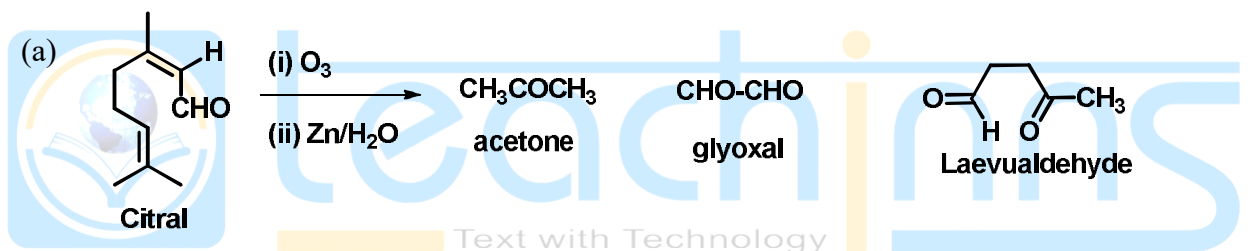
**Cis-citral; citral-b  
neral; Z-form**



**Trans-citral; citral-a  
geranial; E-form**

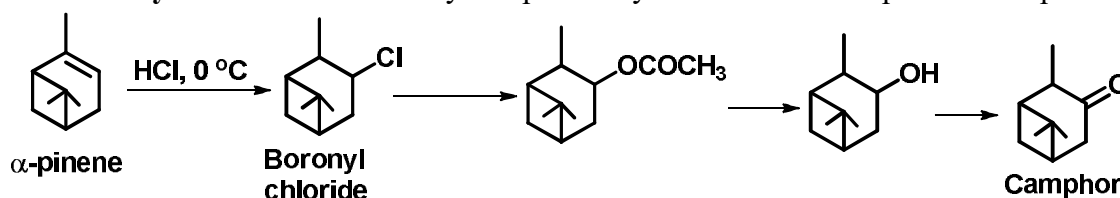
- **Structure of citral:**

The structure of citral is confirmed either by (a) ozonolysis or (b) on the basis of synthesis.



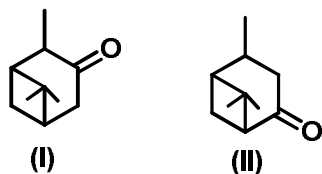
**3.12.12. Camphor:** It is obtained by the steam distillation of wood, leaves or bark of camphor tree. It has characteristic odour, and sublimates at room temperature.

**3.12.12a. Synthesis:** Commercially camphor is synthesized from  $\alpha$ -pinene as depicted below

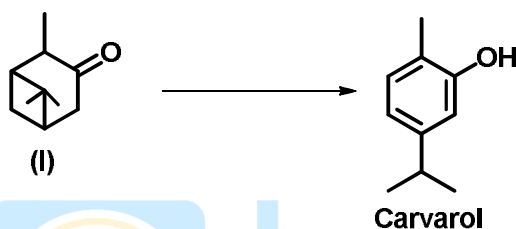


**3.12.12b. Structure of camphor:**

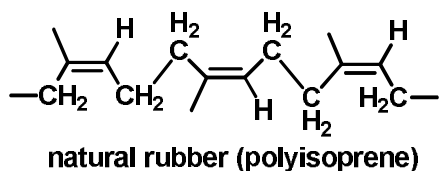
Camphor contains  $-\text{CH}_2\text{CO}$  group which is indicated by the formation of an oxime with nitrous acid. Hence, two structures are possible for camphor where only the position of keto group is different in the two structures.



However, the structure I is correct for camphor because carvarolis prepared when compound I is distilled with iodine as shown below.

**3.12.13. Polyterpenoids**

**3.12.13a. Rubber:** It is made up of isoprene units linked through head to tail fashion. Double bonds have cis-configuration, so rubber is cis-1,4-polyisoprene. These are weak due to cis configuration of double bonds.

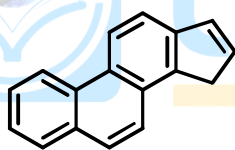


**3.12.13b.Carotenoids:** These are yellow or red pigments which are widely found in plants. Carotenoids are also known as lipochromes or chromolipids. They are fat soluble pigments. Chemically, they are polyenes. Their parent hydrocarbons have molecular formula  $C_{40}H_{56}$  and they have eight isoprene units. They are known as tetraterpenes.

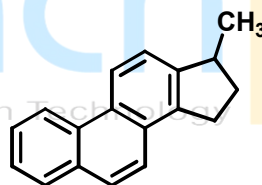
- Some carotenoids are known as carotenes. Other carotenoids which are oxygenated form of carotenes are called xanthophylls.
- They show deep blue colour with concentrated sulphuric acid and with a chloroform solution of antimony trichloride (Carr-Price reaction).
- Carr-price reaction is used for the estimation of carotenoids.
- There are some natural polyenes, which have less than 40 carbon atoms, but structurally related to carotenoids. These are called as “**apocarotenoids**”.

**3.12.13c.Steroids:** These are the members of a large class of organic compounds and widely found in plants and animals. They are characterized with the help of 1,2-cyclopentenophenanthrene.

- Steroids contain wide varieties of naturally occurring substrates like sterols, bile acids, sex hormone, contraceptive drugs etc.
- Upon selenium dehydrogenation at  $360^{\circ}\text{C}$  all the steroids give Diel's hydrocarbon.

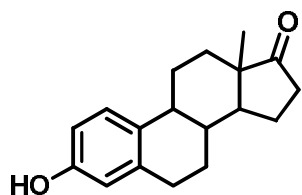


1,2-cyclopentenophenanthrene

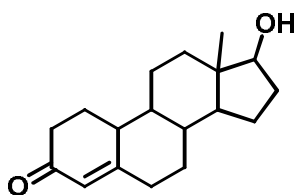


Diel's hydrocarbon

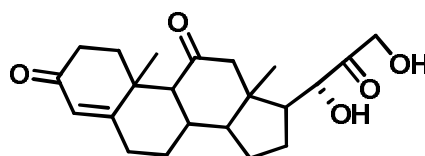
- Structure of some valuable steroids:



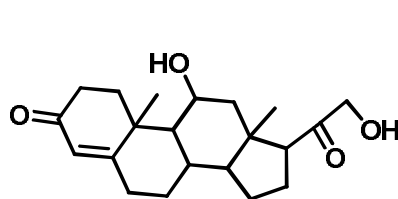
**Oestrone**  
(Female sex hormone)



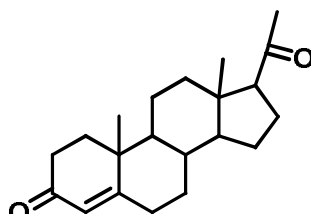
**Testosterone**  
(Male sex hormone)



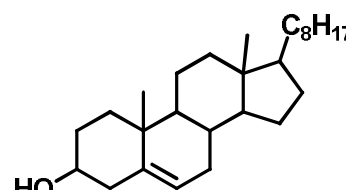
**Cortisone**



**Aldosterone**



**Progesterone**



**Cholesterol**

**3.12.14. Alkaloids:** These are an important class of basic organic compounds which occur in higher plants. They contain one or more nitrogen heterocyclic rings. They show pronounced physiological activities in animals and human system.

#### 3.12.14a. General properties of alkaloids:

- Most of them are crystalline solids and some of them are liquids, can volatilize without decomposition; e. g. coniine and nicotine.
- Most of the alkaloids have bitter taste and are optically active.
- Alkaloids are precipitated from their aqueous or acid solution by a number of substances such as picric acid, tannic acid, perchloric acid, potassium mercuric iodide.
- Generally, tertiary nitrogen atoms are present in the ring system.

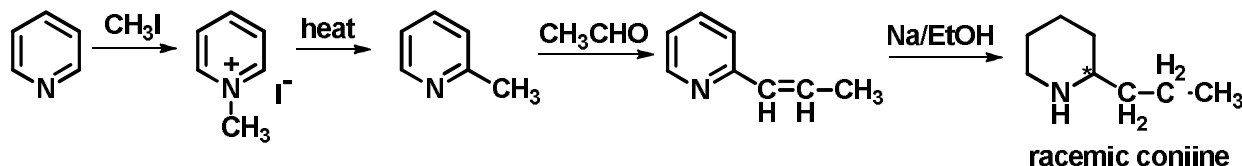
#### 3.12.14b. Classification of alkaloids:

This can be classified based on different groups which have been shown below

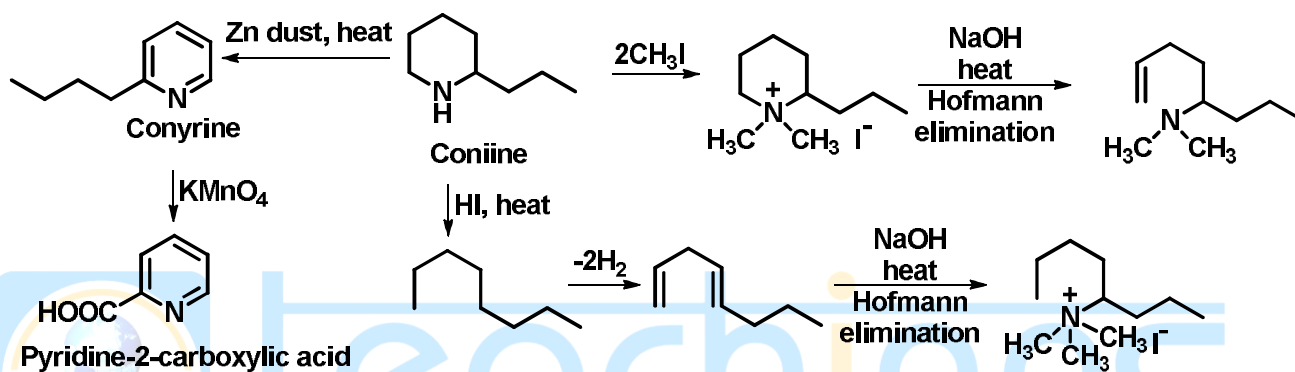
- Phenylethylamine group.
- Pyrrolidine group.
- Pyridine and piperidine group.
- Pyrrolidine-piperidine group.
- Quinoline group.
- Isoquinoline group.
- Phenanthrene group.



- ❖ **Coniine,  $C_8H_{17}N$ :** Naturally occurring coniine is a dextrorotatory molecule, whereas synthetic coniine is a racemic mixture of D- and L-coniine. It is liquid whose boiling point is high (166-167 °C). It has unpleasant taste and odour.

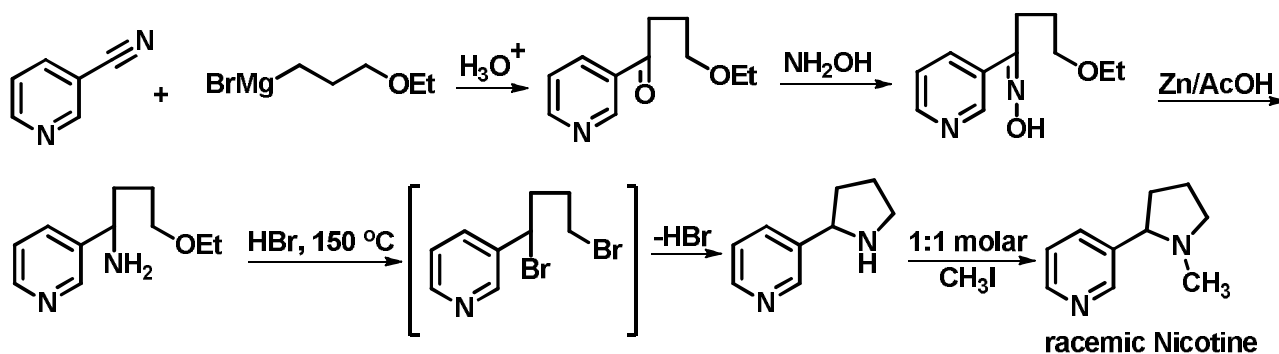


- Some important reactions of coniine are depicted below.....

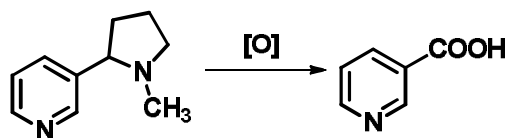


❖ **Nicotine,  $C_{10}H_{14}N_2$ :**

- It is the chief alkaloid of the tobacco plant.
- It is present as the salt of citric or maleic acid.
- It is liquid having very high boiling point.
- It stimulates the nervous system followed by depression.
- Its structure was confirmed by Craig's synthetic method.



- Nicotine under oxidation followed by heating at 187 °C affords nicotinic acid.



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