

# Tamil Nadu Agricultural University

**B.Sc. (Hons.) Agri. & B.S.(ABM)**



## SAC 355 Crop and Pesticide Chemistry (1+1)

### Theory Lecture Notes

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**SAC 355**  
**Crop and Pesticide Chemistry (1+1)**

**Lecture - 1**

**Chemical composition and nutritional quality of cereals and pulses - Rice, wheat, maize, minor millets, Red gram, blackgram and soybean. Starch synthesis and protein synthesis.**

In India, cereal production occupies 64 % and in Tamil Nadu it accounts for 45 % of the gross sown area. Cereals belong to the family gramineae (Poaceae). Cereals are the most important staple foods for mankind worldwide and represents the main constituent of animal feed. Most recently, cereals have been additionally used for energy production, for example by fermentation yielding biogas or bio-ethanol. The major cereals are rice, wheat, maize (corn), sorghum, barley, millet, oats and rye. Cereals account for one third of the calorific value and protein intake of human beings. Cereals produce dry, one seeded fruit called as kernel or grain in the form of caryopsis. A cereal grain is made up of hull / husk / bran, grain coat, embryo / germ and endosperm. The germ or embryo has higher oil content, crude protein, sugar and minerals and thus have high nutritive value. Endosperm is rich in starch but contains low proteins and fat. The composition of the cereal grains vary widely depending upon the genetic, soil, climatic and cultural factors. The details of various components of cereal grains are presented below:

**Carbohydrates**

Available carbohydrates mainly starch deposited in the endosperm. Cereal grain contain 67-79.1% carbohydrates, thus this is by far the most abundant group of constituents. The major carbohydrate is starch (55-70%) followed by others such as cellulose, hemicellulose, dextrin and soluble sugars. The carbohydrates insoluble in dilute acids and alkali is the crude fibre. The hulls and brans of the cereals are rich in cellulose, pentosans and ash constituents. The germ tissues have sucrose as the chief sugar with small amounts of trisaccharide sugars viz., raffinose.

**Proteins**

The average protein content of cereal grain covers a relatively narrow range (8-11%), variations however are quite noticeable. Cereals are low in protein and mostly simple proteins which yield  $\alpha$  - amino acids on hydrolysis. Conjugated proteins like nucleoproteins are present in the germ. Simple proteins found in the cereals are

- Water soluble proteins (Albumins)
- Salt soluble proteins (Globulins)
- Alcohol soluble proteins (Prolamines)

- Acids and alkali soluble proteins (Glutelins) – Abundant

Prolamines are characteristic of the Poaceae. The prolamine fractions of the different cereals have been given trivial names: gliadin (wheat), oryzin (rice), zein (maize), kafirin (millet, sorghum) and elusinin (ragi). The glutelin fraction of wheat has been termed glutenin. Nutritionally, the cereal proteins are not so high in biological value and are poor in one or more of essential amino acids.

### **Lipids**

Depending on cereal species average lipid contents of 2-7% in the grains are present. Lipids are mainly stored in the germ, to a smaller extent in the aleurone layer and to the lesser extent in the endosperm. Cereal lipids are present in the embryo of the seeds and they include fatty oils, phosphatides and sterols. Cereal lipids have similar fatty acid compositions, in which linoleic acid reaches contents of 39-69%, while oleic acid and palmitic acid make up 11-36% and 18-28%, respectively. The iodine value of cereal oils vary from 100 – 125 and are classified as semidrying oils. Iodine value is the number of grams of iodine required to be absorbed by 100 grams of fat or oil.

### **Enzymes**

The most important cereal enzyme is amylases. Other enzymes are proteases, lipases, oxidases, maltase, diastase etc.

### **Vitamins**

Cereals contain vitamins in concentrations ranging from below 1 to ca. 50 mg/kg, depending on the compound. Thus, cereals are a good source of vitamins from the B-group but low in vitamin C and D. The most important fat-soluble vitamins are the tocopherols (vitamin E), are found in large amounts in the unsaponifiable fraction of germ oils. Like the minerals, vitamins are concentrated in the outer layers of the grains, in particular in the aleurone layer as well as in the germ. Therefore, milling of cereals into white flour will remove most of the vitamins. Consequently, the use of whole-grain products or products enriched in vitamin-containing tissues will be of nutritional benefit for the consumer.

### **Minerals**

The mineral content of cereals ranges from ca. 1.0 to 3%. The major portion of the minerals (>90%) is located in the outer layers of the grains, namely in the bran, the aleurone layer and the germ. Consequently, products made from whole grains should increasingly be introduced into human nutrition to benefit from the mineral content of cereals. The dominant minerals are K, P and Mg. Other minerals like S, Cl, Ca and Na are also present in smaller amounts. Phosphorus

content is higher than that of Ca and is present as Ca or Mg salt of phytic acid. Silicon is present in higher proportion in rice and barley (4 -6 %). The elements found in trace amounts are Al, Cu, Fe, Li, Ni, Se, Sn, Ti and I<sub>2</sub>.

The members of cereal family are rice, wheat, maize, ragi, sorghum, cumbu etc and are detailed below:

#### Proximate composition of cereals (%)

Commodity	Quantity (%)				
	Protein	Fat	Fibre	CHO	Ash
Raw rice Home pounded	7.3	1.2	0.7	80.1	1.1
Raw rice milled	6.9	0.4	0.3	82.1	0.6
Parboiled rice Home pounded	8.5	0.6	-	77.4	0.9
Parboiled rice milled	6.4	0.4	-	79.1	0.8
Wheat	13.6	1.5	12.2	71.0	1.9
Maize	9.5-11	4.0	2.3	67.0	1.5
Sorghum	10.4	1.9	2.0	72.2	1.6
Ragi	7-11	1.3	3.6	76.3	2.7
Cumbu	11-13.5	5.0	1.2	67.5	2.7

#### Ultimate composition of cereals

Constituents	Amount (%)
N	0.5 -2
P	< 1
K	0.5 -2
Mg and S	< 1
Ca	1 -2
Fe, Zn, Cu and Mn	50 – 500 ppm
B and Mo	< 5 ppm

### Rice

Rice is predominantly grown in Asian countries. The paddy grain (caryopsis) consists of a loose outer husk enclosing the kernel.

### Carbohydrates

Starch is the major constituent of rice. Starch in glutinous rice varieties consists entirely of amylopectin (which is responsible for sticky quality). Small amounts of fructose, galactose and raffinose may be present in rice grains. Hemicellulose is made up of largely by arabinose and xylose (1:1) and small quantities of galactose, mannose and uronic acids are also present in it.

### **Proteins**

The protein content of rice varies from 6-9 % and one fourth of the protein is concentrated in the bran and polish. The glutelin of rice protein is called oryzenin, forms the major protein and is absent in bran. Oryzenin content is high in glutinous rice varieties. Prolamine and globulin is concentrated in the bran. Among cereal proteins, rice protein is biologically the richest because of its high true digestibility (88 %), high lysine content (4 %) and better protein utilization. Polypeptides and free aminoacids like alanine, tyrosine, threonine, methionine, proline, glutamic acid, aspartic acid and cystine are found in rice. The distribution of protein in the endosperm is an important factor deciding the nutritional quality of rice. The outer layers of the endosperm, which get detached during milling are rich in vitamins and proteins.

### **Vitamins**

Whole grain is a good source of vitamin B particularly thiamine (vitamin B1) and pantothenic acid (vitamin B5). Riboflavin is low and ascorbic acid (vitamin C) is practically absent. Fat soluble vitamins A and D is negligible but vitamin E (Tocopherol) is considerable. Milled rice is a poor source of thiamine and wide occurrence of beri-beri among rice eaters is mainly due to thiamine deficiency. Milling has an adverse effect on nutritional quality.

### **Minerals**

The coloured and coarse grained rice varieties are generally rich in P and Ca than the fine grained types. Rice, particularly the polished grain is poor in Ca and Fe. The Ca- P ratio is unfavourable for their effective utilization being 1:10 instead of 1:2. Some varieties have phosphorus content in phytate form. It also contains Na, K, S, Mg, Cl, Al and trace elements like Mn, Zn, Cu, B, Mo, V, I, F, Se, Ni and Ti. More than 65 % of the iodine is found in bran.

### **Enzymes**

The enzymes present in rice grains include  $\alpha$ -amylase,  $\beta$ -amylase, catalase, protease, lipase, phenolase, oxidase and peroxidase. Phosphatase, phytase and esterase is found in rice bran.

### **Pigments and alkaloids**

In coloured rice varieties monoglucosides of cyanidin and delphinidin are present. The dark puttu rice contains diglycosidic anthocyanin. Carotenoids, pectic substances and alkaloids are also

present. Rice contains several aromatic acids like citric, acetic, fumaric, succinic, oxalic, malic, ferulic, vanillic and paracoumaric acids.

### **Advantages of parboiling**

The advantages of parboiling are includes Grain becomes harder, Polishing is easy, Parboiled rice when washed does not loose (21 µg) much nutrients as raw rice (37 µg of thiamine) and parboiled rice can be preserved better. The only disadvantage is it involves additional process before polishing.

### **Puffed rice**

Paddy is cooked, dried and dehusked. Then it is fried in hot sand quickly. Because of this quick frying the moisture in the grain forces out and the grain is puffed. The extent of puffing depends on moisture content of the grain. Immediately after frying puffed rice is separated by sieving.

### **Wheat**

In 100 g, wheat provides 327 calories and is a rich source. Wheat endosperm contains chiefly of starch embedded in a protein matrix. Wheat is an important source of carbohydrates. Globally it is the leading source of protein in human foods, having a protein content about 9 -14 %, which is relatively high compared to other major cereals. Though they contain adequate amounts of the other essential amino acids, wheat proteins are deficient in the essential amino acid, lysine. Because the proteins present in the wheat endosperm (gluten proteins) are particularly poor in lysine, white flours are more deficient in lysine compared with whole grain. Albumins and globulins are present in small quantities (10 -15 %) while gliadin and glutenin constitute about 80-85% of the total protein. Gliadin (alcohol soluble) and glutenin (alkali soluble) together with other proteins and lipids when mixed with water form gluten, which is responsible for the elastic and cohesive properties of wheat flour. The biological value of wheat proteins is better than that of maize and sorghum but lower than that of rice. The minerals like P (288 mg), K (362 (mg), Selenium (70.7µg) and vitamin B1 (0.3 mg)and niacin 5.46mg)

Wheat flour lipids constitute about 2 % of the total flour and contribute to the dough properties and baking quality of the bread. It contains 2 % of the oil and is rich in tocopherols (vitamin E). The chemical composition of wheat is given below

### **Advantages of 70 % extraction**

- White in colour and hence preferred than brown bread
- Has low fat content and hence better keeping quality
- Has less phytate P and hence absorption of Ca and Fe is higher

## **Maize**

Starch is the predominant carbohydrate and the amylose content ranges from 20-36%. In waxy varieties, 100 % of starch exists as amylopectin. Sweet varieties contain a polysaccharide phytoglycogen. The protein content of maize is 11 % and the predominant protein found is prolamine which is known as zein. Zein of maize may be recovered from maize gluten by de-starching through acid or enzyme hydrolysis. It is a yellowish powder, stable under storage and is used as a substitute in making phonographic records. Maize protein is rich in leucine and low in lysine, tryptophan and methionine. Maize protein is unbalanced with respect to aminoacid composition and nutritional quality.

Maize is rich in P and Fe but is low in Ca. Phosphorus in the grain occurs mostly as phytin. Maize contains vitamins like thiamine, riboflavin, niacin,  $\beta$ -carotene, pantothenic acid, folic acid, choline, pyridoxine, biotin and vitamin E. Vitamin A content in yellow maize is high primarily due to the colouring substance called as cryptoxanthin. Yellow maize is rich in  $\beta$ -carotene. Very little vitamin C is present. Pellagra is a disease caused by deficiency of dietary niacin associated with maize diet. Ungerminated maize is devoid of  $\alpha$  - amylase and is a poor source of  $\beta$  - amylase. Phosphorylases, phytase, decarboxylase, dehydrogenase and invertase are the other enzymes present. Maize germ contains a semi drying oil with high linoleic acid.

## **Sorghum**

Sorghum contains vitamin A, thiamine, riboflavin and nicotinic acid and enzymes such as  $\alpha$  and  $\beta$  amylases, glucopyranosidase. Starch, sucrose and other sugars are present. Prolamine, glutelin, albumins and globulins are the common proteins present. The prolamine is commonly referred to as kafirin. High leucine concentration or imbalance in leucine / isoleucine ratio is responsible for pellagra disease among sorghum eating people. Genotypes with yellow endosperm contain the carotenoids viz., lutein, zeaxanthine and  $\beta$  carotene. Sorghum oil contains oleic and linoleic acids. The minerals like Ca (25 mg) and P (222 mg) present in sorghum.

Phenolic pigments referred to as tannins, are responsible for the low palatability and digestibility of sorghum products and for the off colour of starch. The alkaloid Hordenine found in grain sorghum may affect respiration at high doses. The leaves and stalks contain Dhurrin, is the cyanogenetic glucoside formed during germination, which releases hydrocyanic acid (HCN) and is toxic to animals. The maximum concentration is reached by about the third week of growth. Short duration varieties are suitable for feeding after 60 days and long duration varieties after 80 days. Abiotic stress, high N and low P favour the development of this glucoside.

## **Ragi (Finger millet)**

The nutritive value of ragi is greater than rice. The protein content is 7 - 11 % and white ragi contains 14 % protein. Elusinin is the characteristic protein (prolamine) of ragi and its biological value is high. Cystine, tryptophan and tyrosine are the important amino acids present. The minerals present are Ca (344 mg), P and Fe. The vitamins are A (0.48mg), B1 (0.33mg), B2 (0.11mg) and niacin (1.2mg).

### **Malting of ragi**

Malt is germinated cereal grains that have been dried in a process known as malting. The grains are made to germinate by soaking in water and are then halted from germinating further by drying with hot air. Finger millet has a good malting activity. The malted finger millet can be used as a substrate to produce for example gluten-free beer or easily digestible food for infants when they are sprouted, through alterations in flavor and texture. Often there are declines in stress and anti-nutritional factors, such as phytate (which interferes with the absorption of metal ions), oxalate, tannins (which inactivate many enzymes and reduce the digestibility of proteins), trypsin inhibitors and possibly other enzyme inhibitors and flatulence factors.

### **Cumbu (Pearl Millet / Bajra)**

Carbohydrates consist of starch with small amounts of sugars, pentosans and other hemicelluloses. Pearl millet contains carotene (vitamin A), thiamine, riboflavin and niacin. The proteins are composed of prolamines followed by globulins. The prolamine is high in tryptophan and cystine. Bajra is rich in Ca (42mg) and P (295mg).

### **Anti Nutritional Factors and its significance**

Millet is rich in minerals but the bioavailability of these minerals is low due to anti nutritional factors such as phytate, trypsin inhibitors and polyphenols (tannins).

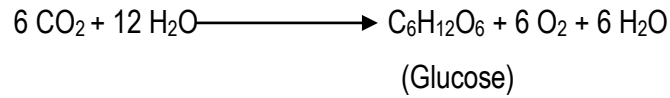
- **Phytic acid** ( $C_6H_{18}O_{24}P_6$ ) is also called Inositol hexaphosphate. Its salt, Phytate is the principal storage form of phosphorus which chelate divalent cations such as Ca, Mg, Zn and Fe reducing their bioavailability.
- **Trypsin inhibitors** are chemicals that reduce the availability of biologically active trypsin, an enzyme essential for the nutrition of many animals and human beings.
- **Tannins** are the polyphenolic compounds that bind to and precipitate proteins and organic compounds including acids and alkalis. They also chelate metals such as iron and zinc and decrease the absorption of these nutrients and inhibit the digestive enzymes.

The anti nutritional factors can be reduced by germination, roasting and fermentation of the grains. Eg. Sorghum contains two anti nutritional factors viz., tannins (polyphenolic compounds in the grain) and Dhurrin (a cyanogenic glucoside in aerial shoot and sprouted seeds).



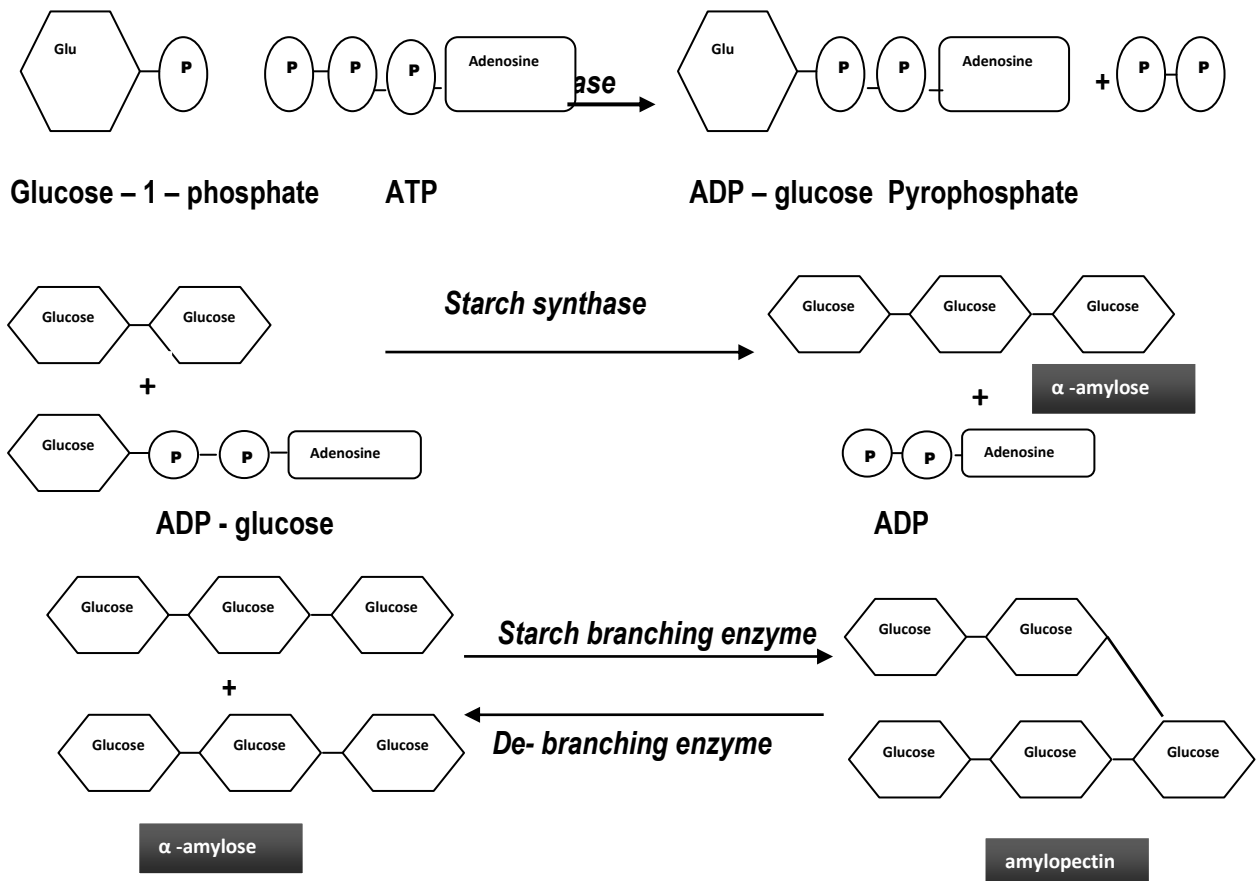
## Synthesis of starch

Starch is the nutritional polysaccharide and major storage carbohydrate found in the plants which are formed by photosynthesis. Photosynthesis is a process in which green plants convert the light energy from the sun into chemical energy with the evolution of O<sub>2</sub>. It is the process of reduction of CO<sub>2</sub> to carbohydrate and oxidation of water in the presence of sunlight and chlorophyll.



Plants produce starch by first converting glucose 1-phosphate to ADP-glucose using the enzyme ADP glucose pyrophosphorylase liberating pyrophosphate. This step requires energy in the form of ATP. The enzyme starch synthase uses ADP-glucose as a substrate and adds glucose units through 1,4-alpha glycosidic bond, liberating ADP and creating amylose. Starch branching enzyme introduces 1,6-alpha glycosidic bonds between these chains, creating the branched amylopectin. The starch debranching enzyme isoamylase removes some of these branches. Several isoforms of these enzymes exist, leading to a highly complex synthesis process.

### Pathway of starch synthesis



### Structure of starch

Starch consists of two components viz., amylose (15-20%), a long straight chain component and amylopectin (80-85 %), a branched chain polysaccharide. Amylose and Amylopectin can be differentiated by the following properties

Properties	Amylose	Amylopectin
Contents	15-20%	80-85%
Solubility in water	Highly soluble	Less soluble
Structure	Straight chain polysaccharide	Branched chain polysaccharide
Linkage	$\alpha$ -1,4 linkage	$\alpha$ -1,4 and $\alpha$ -1,6 linkage
Molecular weight	10,000 - 50,000	50,000 - 10,00,000
Reaction with Iodine	Blue colour	Red colour
End group	One end group for every 55-280 glucose units	One end group for every 24 -30 glucose units

### Utilization of starch

Starch is utilized during respiration and germination.

#### Respiration

During respiration most of the carbohydrates are used as the substrate. The first reaction involved in utilization is the conversion of starch into maltose, glucose and small quantities of dextrin. The glucose enters the glycolytic pathway. Energy of the biological oxidation is used for physiological and vital processes. The remaining energy is stored as ATP (high energy  $\text{PO}_4$  compound).

#### Germination

When seeds are placed in an environment favourable for germination, the rate of metabolism is accelerated. Hydrolysis, oxidation, desmolysis and synthesis are the reactions taking place during germination. During germination, the enzymes are activated and the insoluble reserve food material is converted to soluble and transportable compounds which are utilized by the embryo for the synthesis of compounds for new tissues.

### PULSES (Redgram, Blackgram and Soybean)

In Tamil Nadu, pulses are cultivated over an area of 6.37 lakh hectares with a total production of 24.6 lakh tones and productivity of 385 kg/ ha. Pulses are rich in protein and mineral constituents but low in nitrogen free extract (starch + dextrin + soluble sugars). The high protein content in legume is attributed to the fixation of atmospheric N in symbiosis with *Rhizobium*. The

proteins of pulses are chiefly simple proteins and the characteristic pulse protein is globulin. It accounts for 80 % of the pulse proteins and is dominated by the amino acid glycine. Other proteins like albumins and glutelins are also present. The important carbohydrate of pulse is starch.

### **Nutritional quality of pulses/importance of pulses**

Pulses are part of a healthy, balanced diet and have been shown to have an important role in preventing illnesses such as cancer, diabetes and heart disease.

- Pulses are low fat source of rich protein, with a high fibre content and low glycemic index
- Pulses typically contain about twice the amount of protein found in whole grain cereals like wheat, oats, barley and rice
- Pulses are very high in fibre, containing both soluble and insoluble fibres. Soluble fibre helps to decrease blood cholesterol levels and control blood sugar levels, and insoluble fibre helps with digestion and regularity.
- Pulses are also particularly abundant in B vitamins including folate, thiamin and niacin except riboflavin.
- Pulses provide important amounts of minerals include iron, potassium, magnesium and zinc.
- Finally, pulses are an important source of proteins and in most developing countries constitute the main source of protein for most populations.

### **Composition of pulses (%)**

<b>Pulse</b>	<b>Protein</b>	<b>Fat</b>	<b>Crude Fibre</b>	<b>NFE</b>	<b>Ash</b>
Red gram	22.3	1.70	5.80	57.2	3.60
Black gram	24.0	1.40	4.20	60.3	3.40
Green gram	24.0	1.30	3.80	56.7	3.60
Cowpea	24.6	0.70	3.80	55.8	3.20
Lablab	24.9	0.80	4.50	60.1	3.20
Soybean	43.0	20.0	3.70	21.0	4.60

### **Carbohydrates**

Pulses generally contain about 60–65% carbohydrates, slightly lower compared to cereals (70–80%). Pulse carbohydrates mainly contain monosaccharides, disaccharides, oligosaccharides and polysaccharides. The primary storage carbohydrate is starch, which constitutes a major fraction of the total carbohydrates of almost all the pulses. Some of the minor carbohydrates (oligosaccharide) are also present like raffinose, stachyose, verbacose etc. These are implicated in

gastro intestinal trouble and accumulate in the large intestine where natural gut microflora use these sugars. During cooking oligosaccharide content is reduced.

### **Proteins and Amino acids**

Proteins are complex, organic compounds composed of many amino acids linked together through peptide bonds. Pulses contain relatively high amount of protein and are an indispensable source of dietary protein. The quality of the protein is judged on the basis of the amino acids it contains. Proteins are located in the cotyledon and the embryonic axis of the seed, with small amounts present in the seed coat. The outer layer of the cotyledon in some pulses (chickpea, garden pea, pigeon pea and black gram) has higher protein content than the inner part of the cotyledon. The pulse contain average protein content is ranged between 22-43%. The most abundant storage proteins in pulse grains are the globulins (60-80%) and 15 - 20 % albumins and glutelins. Globulins are storage proteins and are mainly present in seeds. Albumins and glutelins are non storage proteins and present in membranes. Amino acids of pulses are glutamic acid and aspartic acid is the major amino acids in all the pulses and rich in lysine. Pulses are low in sulphur containing amino acids (methionine and cystine).

### **Lipids**

Present in small amount in the seeds and varies from 1 - 2 % except bengalgram which contains 6 %. Cowpea contains greater amount of total saturated fatty acids whereas black gram and soybean contains unsaturated fatty acids. There is no cholesterol in pulses.

### **Minerals**

Pulses are rich in minerals like Ca, Fe, P and K. All pulses are inferior to soybean with regard to Ca, Mg, P, Fe, Zn and Cu. Considerable quantities and bioavailability of the minerals are lost while cooking.

### **Vitamins**

Black gram is a greater source of thiamine, niacin, pantothenic acid and vitamin A. Vitamin content is more in the sprouted seeds than in the raw seeds. Milling does not effect the vitamin content in pulses.

The predominant members of the pulse family are detailed below:

### **Red gram**

The chief protein is globulin accounting for 22.3 %. The two isolates viz., cajanin and concajanin contributes to 58 and 8 per cent of the total N respectively. The protein is rich in tyrosine and fairly rich in cystine, argentine and lysine. The quality of red gram protein is inferior to that of Bengal gram protein.

## **Others (Green gram, Black gram, Cowpea, Lablab and Soybean)**

The protein contains two types of globulins viz.,  $\alpha$  and  $\beta$  globulins. These are rich in tyrosine and lysine.  $\beta$  - globulins are low in cystine content. Soybean contains 43 % protein and is a good source of lysine but deficient in methionine. Besides protein, soybean contains 20 % lipids and high content of minerals (4.6%).

### **Important aspects of pulses**

#### **1. Anti-nutritional factors in legumes**

In grain legumes anti-nutritional factors are widely distributed. They are naturally destroyed while cooking / boiling and do not cause any serious problems if it is consumed.

##### **a. Heat labile factors (Destroyed by heat)**

i) **Enzyme inhibitors** e.g Protease (Trypsin and chymotrypsin inhibitors) and amylase. Trypsin inhibitors reduce protein digestion and the availability of amino acids (methionine and cystine) consisting of sulphur in legume grains is low. Amylase inhibitors alter reactions to blood sugar and insulin by slowing down digestion and thus can be used for therapeutic purposes in diabetes.

ii) **Lectins (Hemagglutinins)** e.g. Phytohaemo glutenin.

One of their most important characteristics is that they prevent absorption of digestive end products in the small intestine.

##### **iii) Goitrogens**

Soybean, a kind of oil seed, contains glycosides called goitrogens. Consisting of sulphur, these glycosides cause the thyroid gland to grow by inhibiting the iodine intake of the thyroid gland. This toxic effect can be reduced with the addition of iodine to the diet.

##### **iv) Phytic acid and Phytoids**

Phytoid phosphorus accounts for almost 80 % of the total phosphorus in many legume seeds. Most of them are found on the outer layer of the aleurone or endosperm. Phytic acid causes the bioavailability of essential minerals to decrease and turn into insoluble compounds whose absorption and digestion is less in the small intestine.

##### **b. Heat stable factors (Not destroyed by heat)**

##### **i) Cyanogens Glycosides**

Cyanogen compounds of tall plants are of two types: cyanogen glycosides and cyanogen lipids. Both groups contain cyanohydrins and free carbonyl. Since glycosides, which consist of HCN (hydrocyanohydric acid), can come out as a result of hydrolysis, they are potentially toxic. Cyanide cannot be disintegrated with heat and since it separates from legumes during cooking or washing, it

will be beneficial to pour soaking water. It is known that broad beans and Lima beans are potential sources of cyanide.

## **ii) Toxic amino acids**

There are certain amino acids in legume plants that are not of protein nature and reduce nutritious value and cause toxic effects. These substances are commonly found in Lathyrus and broad beans. Dihydroxyphenyl alanine (DOPA) is the most common toxic amino acid found in legumes. It affects nerves and causes paralysis.

## **2. Cereal protein and Pulse protein – A comparison**

- Cereals contain 10 % protein whereas pulses contain 20 – 40 % protein
- Storage protein of cereals are soluble prolamines but legumes contain salt soluble globulins
- Storage proteins of cereals contain very little lysine and tryptophan but the proteins of pulses are low in methionine and cysteine
- Storage proteins of cereals occur in the endosperm and deposited in the endoplasmic reticulum. Synthesis of proteins in legumes takes place in cotyledons and deposited in vascular membranes.
- Pulses are deficient in sulphur containing aminoacids, pulse proteins have lower digestibility and sometimes cause flatulence.

## **3. Composition of protein**

All the proteins contain C, H, O and N. Most of them contain S and some contain P. Few contain Fe, Cu and Mn and are found only in prosthetic group. Proteins contain carbon (52 %), hydrogen (7 %), oxygen (23 %), nitrogen (16 %), phosphorus (1 %) and sulphur (1 %).

## **4. Functions of protein**

- Required for growth
- Required for the replacement of worn out tissues
- Essential for the synthesis of hormones and enzymes
- Required for the production of egg, milk, wool etc.,
- Acts as a source of energy.

## **5. Biosynthesis of proteins**

The process involves four major steps viz.,

- a. Nitrogen uptake
- b. Reduction of  $\text{NO}_3^-$  -N to  $\text{NH}_4^-$  -N
- c. Synthesis of amino acids and

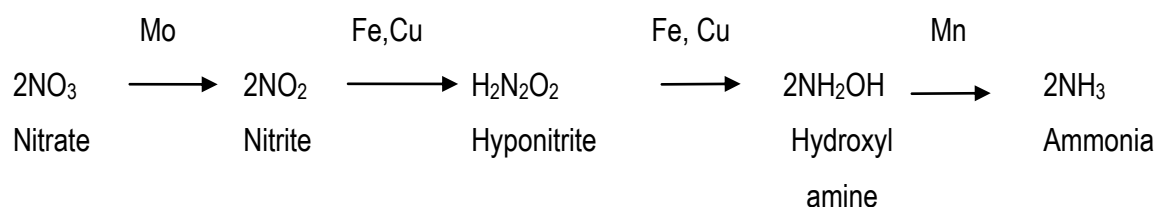
d. Condensation of amino acids to proteins

### a. Nitrogen uptake

Plants absorb nitrogen from the soil as  $\text{NH}_4$  or  $\text{NO}_3$  ions. Most of the plants prefer nitrate while some crops like paddy and potato absorb nitrogen in the  $\text{NH}_4$  form.

### b. Reduction of $\text{NO}_3$ - N to $\text{NH}_4$ -N

The first step is the formation of nitrite from nitrate which is catalyzed by the enzyme nitrate reductase for which Mo is the co factor. The enzyme nitrite reductase catalyses the reduction of  $\text{NO}_2$  to  $\text{NH}_3$  through intermediary steps



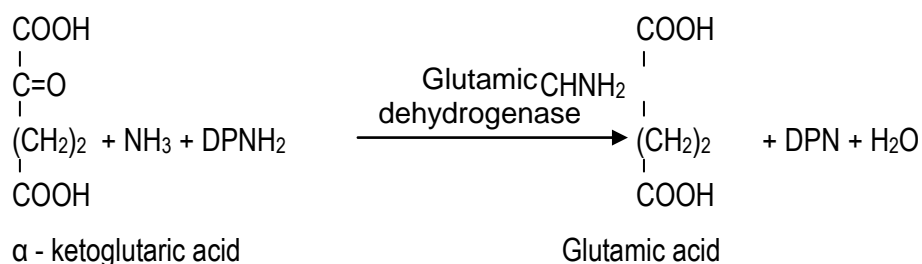
### c. Synthesis of amino acids

Amino acids are synthesized by the following processes viz, Reductive amination and Transamination

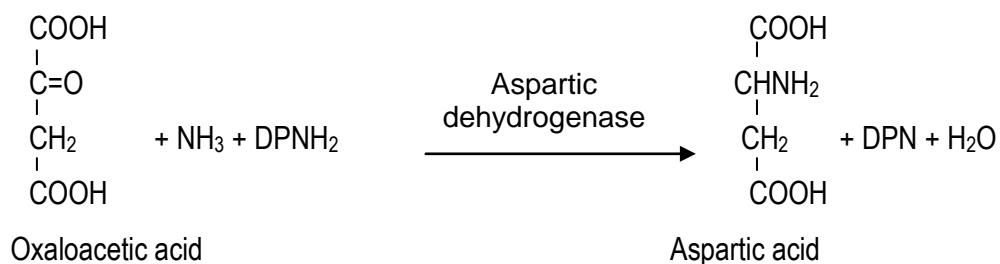
#### 1. Reductive amination

The ammonia formed by reduction of nitrate combines with keto acids like glutamic acid, aspartic acid and pyruvic acid formed during respiration (Kreb's cycle) to produce respective amino acids. Dehydrogenase enzymes are involved in reductive amination.

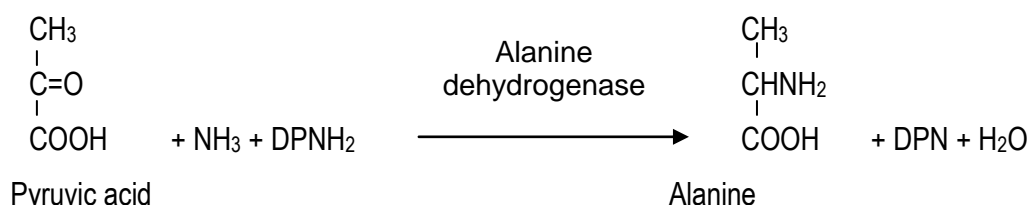
##### (i) Synthesis of glutamic acid



##### (ii) Synthesis of aspartic acid



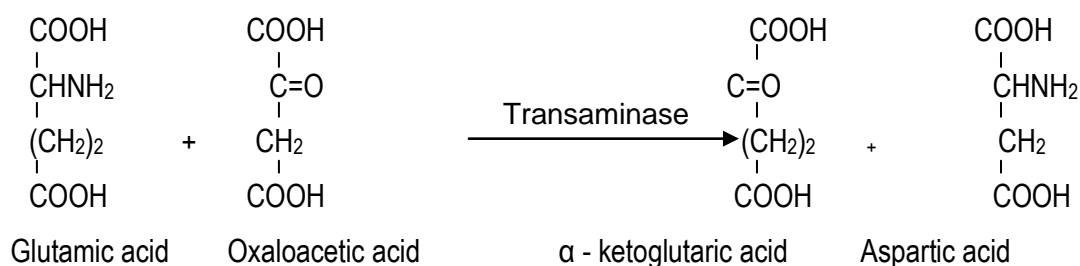
### (iii) Synthesis of alanine from pyruvic acid



## 2. Transamination

Glutamic and aspartic acids serve as precursors for the synthesis of other amino acids mediated by the enzyme transaminases. Most of the amino acids required for protein synthesis are obtained by transamination.

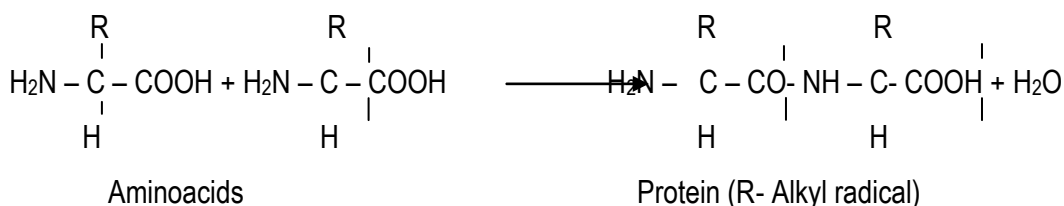
### Synthesis of aspartic acid



Thus the amino acids viz., alanine, glycine, valine, leucine, isoleucine, serine, threonine, phenylalanine, tyrosine, tryptophan, proline, cystine, cysteine, methionine, aspartic acid, glutamic acids, lysine, arginine and histidine are synthesized in plants.

### d. Condensation of amino acids

Proteins are synthesized by the condensation of amino acid molecules and they are held together by peptide linkage (-CO-NH).



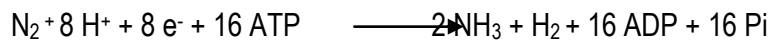
## 6. Improvement of cereal proteins

Cereals in general are limiting in lysine and threonine, white legumes are good sources. Hence legume proteins supplement cereal proteins effectively.

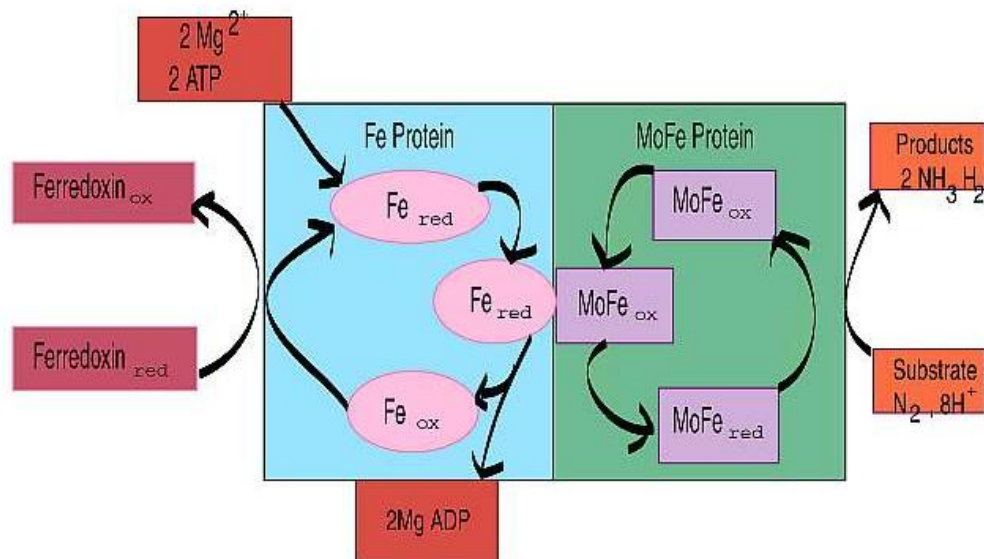
## 7. Biological Nitrogen Fixation

It is the process of conversion of atmospheric nitrogen into ammonia in the root nodules of higher plants catalyzed by the enzyme nitrogenase. Atmosphere is a large reservoir of nitrogen. Nitrogen molecule is highly inert and non reactive and hence requires lot of energy to break it. To reduce each mole of nitrogen 16-24 ATP molecules are required.





### Biological Nitrogen Fixation



The reaction is performed by prokaryotes using an enzyme complex nitrogenase. This enzyme consists of two proteins – an iron protein and a molybdenum iron protein. The reaction occurs when  $\text{N}_2$  is bound to the nitrogenase complex. The Fe protein is first reduced by the electrons donated by ferredoxin. Then the reduced Fe protein binds ATP and reduces the molybdenum-iron protein which donates electrons to  $\text{N}_2$  producing  $\text{HN}=\text{NH}$ . This process continues till  $\text{HN}=\text{NH}$  is reduced to  $\text{H}_2\text{N}-\text{NH}_2$  and then to  $\text{NH}_3$ .

### Nitrogen fixing bacteria

- Proteobacteria: *Rhizobium*, *Bradyrhizobium*, *Azospirillum*, *Azotobacter* and *Beijerinckia*
- Actinobacteria : *Frankia*
- Cyanobacteria : *Anabaena*, *Nostoc*
- Endospora : *Clostridium*

Nitrogen fixing bacteria may be symbiotic (Eg. *Rhizobium*) and non symbiotic (Eg. *Azotobacter* (Aerobic) and *Clostridium* (Anaerobic)). The important species of *Rhizobium* that fix atmospheric nitrogen in different crops are:

- *R. meliloti* - Alfalfa
- *R. leguminosarum* - Peas
- *R. phaseoli* - Beans
- *R. japonicum* - Soybeans
- *R. lupini* - Lupin
- *R. trifolii* - Clover

## **8. Tanins and their importance in pulses**

A tannin (or tannoid) is an astringent, polyphenolic biomolecule that binds to and precipitates proteins and various other organic compounds including amino acids and alkaloids. Most legumes contain tannins. Red-colored beans contain the most tannins and white-colored beans have the least. Peanuts without shells have very low tannin content. Chickpeas (garbanzo beans) have a smaller amount of tannins.

## **9. Complete and incomplete proteins**

There are two main types of protein: complete and incomplete. Complete proteins contain every essential amino acid. Incomplete proteins lack one or more of the essential amino acids. A complete protein will give your body access to all of the amino acids that it lacks the ability to make itself. This is important because the body needs every amino acid (essential and non-essential) to build and repair tissue. Since the body can make non-essential amino acids, it needs the essential amino acids from dietary sources. Eating complete proteins will ensure that your body has access to all the amino acids it needs.

## **10. Nutritional importance of germinated pulses**

1. Increases in protein quality
2. Increases in crude fibre content
3. Increases in essential fatty acids
4. Increases in vitamin content

During soaking the protease enzymes acts on the complex proteins and make it simple and available to the body. Fermentation decreases the phytate and trypsin inhibitors and enhances the ionisable iron content. Most reports agree that sprouting treatment of cereal grains generally improves their vitamin value, especially the B-group vitamins. Certain vitamins such as  $\alpha$ -tocopherol (Vitamin-E) and  $\beta$ -carotene (Vitamin-A precursor) are produced during the growth process.

## Lecture 2

### Chemical composition and nutritional quality of oil seed crops - Groundnut, sesame, sunflower, castor, coconut and palm

Oils extracted from plants have been used since ancient times and have been exploited in many ways. Predominantly, it is used as edible oil. It is also used in medicines and pharmaceuticals, industries, biodiesel, pet foods and component of many other products. Dietary fat, a concentrated source of energy, supplies about half of the calories and carries fat soluble vitamins. Its by-products are being used as feed, manures and find uses in many other industrial and domestic uses. With regard to the processes used to recover plant oils, it is practical to divide them into fruit and oilseed oils. While only two fruits are of economic importance in oil production (coconut and oil palm), the number of oilseed sources is enormous (soybean, peanut, rapeseed mustard, sunflower, safflower, sesame, linseed, castor and cotton seed are predominant). Oilseed crops are grown primarily for the oil contained in the seeds. The oil content of small grains (eg, wheat) is only 1-2%; that of oilseeds ranges from about 20% for [soybeans](#) to over 40% for [sunflowers](#).

The oilseed production in India is 3.0 million tonnes of which Tamil Nadu shares 1.14 %. In Tamil Nadu, the total oilseeds acreage is 5.56 lakh hectares. The major oilseed crops grown are groundnut (80%), sesame (0.1%), sunflower (3.6%), coconut (7.19%) and oil palm (0.004 %). Most fats and oils consist of triglycerides; which differ in their fatty acid compositions to a certain extent. All of the commonly used vegetable oils consist almost entirely of the triglycerides of long chain aliphatic acids. Most of these acids contain 17 carbon atoms plus the carboxyl group and they differs from oil to oil principally in the number of olefinic bonds.

#### Proximate composition of important oilseeds

Crop	Composition (%)				
	Protein	Fat	Fibre	NFE	Ash
Groundnut	26.2	50	2.10	1.70	2.80
Sesame	20.0	47.5	2.90	25.0	5.0
Sunflower	18.0	45.0	3.00	21.3	7.0
Coconut	4.50	42.0	3.60	13.0	1.0
Oil palm	1.90	58.4	3.20	12.5	1.0
Castor	17.88	46.65	14.99	12.61	2.73

## 1. Groundnut

Being an oil seed crop, it contains 40 to 54% oil. In addition to protein, groundnuts are a good source of calcium, phosphorus, iron, zinc and boron. The groundnuts also contain vitamin E and small amounts of vitamin B complex. Oil is edible and oil cake is used as a cattle feed. Groundnut flour is used in bread making. Nuts are rich source of fat, protein, vitamins B1, B2, nicotinic acid and vitamin E. Red skinned varieties are rich in vitamin B1 (1.14 mg) but 90 % (0.13mg) of which is lost during processing. Nuts are poor in vitamin A and completely lack vitamin C and are also a good source of lecithin (0.50 to 0.70 %).

### i. Proteins

Groundnut is a valuable energy giving food due to its high fat and protein content. Nearly 96 % of the nutrients are digestible. 100 g of groundnut is equivalent to 131.4 g of starch. The principal constituents of groundnut are globulin (18.3 % N) exists as arachin (2.50 %) and conarachin (8 %). Conarachin has a higher content of cystine, tryptophan and lysine. Methionine, threonine and isoleucine are limiting amino acids. Groundnut proteins are equivalent to milk proteins and superior to soybean proteins

### ii. Oil

Groundnut kernel contains 40 to 54 % oil. Its major component fatty acids are oleic acid (46.8% as olein), linoleic acid (33.4% as linolein) and palmitic acid (18.0% as palmitin). The oil also contains some stearic acid, arachidic acid, behenic acid, lignoceric acid and other fatty acids. Oil is used for the preparation of soaps, cosmetics and for medicines after sterilization at 150°C. It is also used as a substitute for olive oil, diesel oil, lubricant and an illuminant. Groundnut oil is of non-drying nature with an iodine value of 85 - 98.

### iii. Cake and haulms

Groundnut cake is used as important protein supplement in cattle and poultry rations and valuable nitrogenous manure. It's haulms are feed (green, dried or silage) to livestock. Seed coats are used in the manufacture of peanut butter.

#### Chemical composition of groundnut shell, haulms and oil cake (in %)

Characteristics	Shell	Haulms	Oil Cake
Cellulose	65.7	22.11- 35.35	-
Carbohydrates	21.2	38.06 - 46.95	22 - 30
Proteins	7.3	8.30 - 15.0	45 - 60
Minerals	4.5	1.39 - 2.88	4 - 5.7

Crude Fiber	-	22.11 - 35.35	3.8 - 7.5
Moisture	-	7.13 - 10.0	8 – 10

#### iv. Toxin

Aflatoxin-damp nuts (5%) if stored it will ferment and allow the development of poisonous moulds such as *Aspergillus flavus* in the kernels which is leading to contamination with aflatoxin it causes health hazard both for humans and animals (carcinogenic). Four mycotoxins viz., aflatoxin, citrinin, ochratoxin-A and zeavalenone occur naturally in groundnut of which aflatoxin is toxic and carcinogenic to animals and human beings.

## 2. Sesame

Glucose, sucrose, galactose are the major sugar fractions. Raffinose, pentosans and traces of starch are also present. The important minerals are Ca (1160mg/100g) and P ( 616 mg/100g) and the seeds are rich in thiamine and niacin. Vitamin A is present in traces. Sesame oil rich in vitamin E but is deficient in vitamin A. The details of the important constituents in the seeds are furnished below:

### i. Proteins

Gingelly contains globulins ( $\alpha$  and  $\beta$ ). The proteins are rich in sulphur containing amino acids, particularly methionine but deficient in lysine. They are good supplement to pulse protein which contains adequate amounts of lysine but lack S containing amino acids. Lysine deficiency may be one of the reasons for the low nutritional quality of sesame proteins.

### ii. Oil

Sesame oil is light to deep reddish brown in colour and oil content varies from 45 to 52 %. White seeded sesame has high oil content. Sesame oil is a semi drying oil with an iodine value of 104 - 113. Sesame oil contains more unsaturated fatty acids like oleic and linoleic acids (85%) and saturated fatty acids accounts for less than 20% of the total fatty acids like palmitic and stearic acids. Sesame oil is rich in vitamin E but is deficient in vitamin A. The oil also contains two active principles viz., sesamin and sesamolin. Sesamolin upon hydrolysis with mineral acids gives sesamol and samin.

Sesamol is a powerful phenolic anti oxidant and is responsible for the keeping quality of sesame oil. The high stability and resistance of sesame oil to oxidative rancidity is attributed to the sesamol released from sesamolin by hydrogenation, by acid or acid bleaching earth or other conditions of processing and storage. Sesame oil is used for cooking and is superior to groundnut oil. It is used in bakery and medicinal purpose. Oil cake is a good livestock feed and organic manure.

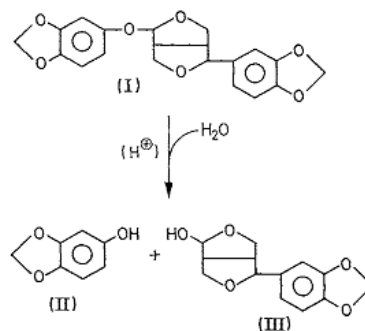


Figure: Sesamol (II) and samin (III) formation by sesamol (I) hydrolysis

### 3. Sunflower

#### i. Carbohydrates

The seeds contain 0.31 % mono-saccharides, 3.91 % saccharose and other di-saccharides and 0.73 % tri-saccharides. Starch and dextrans are absent. The seeds also contain lecithin, nuclein, organic acids like citric, tartaric and chlorogenic acids, cholesterol and phytin

ii. **Minerals:** The main mineral constituents of the ash are K, Ca, P, Mg and S.

#### iii. Proteins

Globulins are the major proteins (46 - 48 %) followed by albumins and glutelins. Alcohol soluble proteins are absent. The proteins are rich in argentine, leucine, isoleucine, methionine, threonine and valine. Lysine, tyrosine, tryptophan and cystine are present in small amounts.

#### iv. Oil

Sunflower oil is generally considered premium oil compared to most of other vegetable oil because of its light colour, bland flavor, high linoleic acid and absence of linolenic acids. Sunflower seed contains from 22 -36 % and kernel contains 45-55% of oil. The oil has good keeping quality. Refined oil is pale yellow in colour. The high iodine number (125-136) entitles it to be classified as a semi drying oil but the RM and Polenske values are <0.5 %. The fatty acids of the oil are saturated fatty acids (10%), Oleic acid (49.41%) and linoleic acid ( 40.48%).

The oil contains appreciable amounts of vitamin (A, D and E), sterols, terpenes and methyl ketones. It is used as a cooking and salad oil and marketed as Sanola. Sunflower oil is recommended for heart patients due to the presence of unsaturated fatty acids. Oil is used in the food, pharmaceutical and paint industries. The oil cake is rich in protein and is used as a livestock feed

#### v. Hulls

The hulls contain 35-55% seeds and are rich in K (23.7 % K<sub>2</sub>O) hence used as a fertilizer or for recovery of K<sub>2</sub>CO<sub>3</sub>. They are used as a bedding material for cattle and poultry. Hulls contain

35 % cellulose and are used in paper industry. The flower heads are rich in pectin (23 %) and is used as a cattle feed. The stalks are used as a fuel and its ash contains P, K and Ca.

#### **vi. Flowers and leaves**

The flowers furnish yellow dye. It also contains  $\beta$  – carotene, cryptoxanthine and lutein. The plant contains saponin and ascorbic acid, citric acid and malic acids are present in the leaves. Leaf extracts show antibacterial properties. Sunflower seeds are diuretic and expectorant.

### **4. Coconut**

#### **i. Proteins and sugars**

The proteins chiefly contain globulin and the dried copra contains 44 % carbohydrate comprising sucrose and cellulose. During early stages of maturity reducing sugars dominates in milk but with maturity, it has higher amounts of non reducing sugar viz., sucrose.

#### **ii. Oil**

The coconut kernel has 40 - 60 % oil and is colourless to pale yellow which solidifies at low temperature. The oil has low amount of unsaturated fatty acids like oleic and linoleic acids. Lauric acid is the predominant saturated fatty acid

<b>Fatty acids</b>	<b>Composition (%)</b>
Lauric acid	48
Myristic acid	16
Palimitic acid	9.5
Decanoic acid	8
Caprylic acid	7
Oleic acid	6.5
Others	5

Since the unsaturated fatty acids are less, it has a low iodine value (10 -23) and behaves like a fat in the winter season. The oil has a higher RM value. The characteristic odour of coconut oil is due to the presence of delta lactone and n-octanol. During deterioration, formation of methyl ketone of the above agents is responsible for foul odour.

Coconut oil is used in the manufacture of soap and margarine. Soap made of coconut oil is hard and stable due to low iodine value and high saponification number. Coconut oil soap is white in colour and produces excellent lather in hard and saline waters also due to the presence of saturated fatty acids. The oil is also used in cosmetics, textile, leather, paper, plastic and resin industries. Its cake forms about 32- 40 % of the coconut crush and is mainly used as a cattle feed.

### iii. Fibre

Brown fibre is extracted from ripe dry husk by mechanical defiltering process, which is used for brush making and mattress making. White fibre is extracted from green husk by bacteriological process of rotting. Coir pith contains 25 % lignin and 500 % moisture holding capacity which is used as a good mulching material and also in the reclamation of alkali soils. Coir pith has wide CN ratio and decomposes slowly in soil.

## 5. Oil Palm

Oil palm is the highest oil producer per unit area. It produces two kinds of oils viz., palm oil and palm kernel oil.

### Palm Oil

It is obtained from fleshy mesocarp of fruit which contain 45 to 50% oil. It is red in colour because of high beta carotene. It is semi-solid at room temperature and contains several saturated fats like glyceryl laurate (0.1%), myristate (1% ), palmitate (44 %), stearate (5%) and unsaturated fats like oleate (39%), linoleate (10%), and alpha-linolenate (0.3%). Like all vegetable oils, palm oil does not contain cholesterol, although saturated fat intake increases both LDL and HDL cholesterol. Palm oil has been found to be a reasonable replacement for trans fats. According to World Health Organization, consumption of palmitic acid increases the risk of cardio vascular diseases. Many processed food contains palm oil as the ingredient. It is used in the manufacture of biodiesel by trans-esterification.

### Palm kernel oil

Palm kernel oil is edible oil obtained from the kernel of oil palm. The endosperm contains 50 % oil. It is high in saturated fatty acids and is comparable to coconut oil. It is semi solid at room temperature. It is commonly used in commercial cooking because of its low cost and stability at high cooking temperature. Palm kernel oil is high in lauric acid which raises blood cholesterol levels. Palm kernel oil cake is used as a cattle feed. The compositions of various fatty acids in palm kernel oil are

Fatty acids	Composition (%)
Lauric acid (saturated)	48.2
Myrsitic acid (saturated)	16.2
Palmitic acid (saturated)	8.4
Capric acid (saturated)	3.4
Caprylic acid (saturated)	3.3
Stearic acid (saturated)	2.5



Oleic acid (monounsaturated)	15.3
Linoleic acid (polyunsaturated)	2.3

## 6. Castor

In India, it is the major non-edible oil produced which contributes 3-4% of the total oil seed production of the country. Castor oil is a vegetable oil obtained by pressing the seeds of the castor oil plant (*Ricinus communis*). It is a triglyceride in which approximately 90 percent of fatty acid chains are ricinoleates. Oleate and linoleates are the other significant components.

### Composition

The seeds are composed of about 25% husk and 75% kernel. The oil content of the seed varies from 45-55% and that of the kernel from 60-65%. The following percentage composition of castor seed.

Chemicals (%)	Whole seed	Kernel	Husk
Moisture	5.14	3.60	8.75
Protein	17.88	23.43	4.76
Oil	46.65	66.02	0.98
Carbohydrates	12.61	4.01	32.92
Fibre	14.99	0.70	48.69
Ash	2.73	2.24	3.89

The oil content of different varieties of bean ranges from 45-66%, It also contains moisture (4-8%), soluble carbohydrate, fibre, protein and minerals. Castor oil is well known as a source of ricinoleic acid (RA), a monounsaturated, 18-carbon hydroxylated fatty acid in addition to an olefinic linkage. Ricinoleic acid (12 hydroxy oleic acid) for about 90 % of the total fatty acid content produced upon saponification of castor oil. It is non-toxic, biodegradable and renewable resource, relatively high viscosity and specific gravity and more polar than most fats.

Average composition of castor seed oil / fatty acid chains (in%)	
Ricinoleic acid	90
Oleic acid	3
Linoleic acid	4
$\alpha$ -Linolenic acid	0.5-1

Stearic acid	1
Palmitic acid	0.5–1
Dihydroxystearic acid	0.3–0.5
Others	0.2– 0.5

The seeds contain ricinnine, a very mildly toxic alkaloid and ricin, an extremely poisonous protein. Ricin is found exclusively in the endosperm of castor seeds and is classified as a type 2 ribosome-inactivating protein. Type 2 ribosome-inactivating proteins such as ricin from castor oil are lectins, which irreversibly inactivate ribosomes, thus stopping protein synthesis and eventually leading to cell death. This makes ricin a potent plant toxin.

Castor beans, contain some allergenic (2S albumin) proteins as well as ricin; however, processed or refined castor oil is free from any of these substances and can be safely used in pharmaceutical applications. This can be attributed to its wide range of biological effects on higher organisms.

#### **Applications of castor oil and its derivatives**

It is one of the non-edible industrial oils used for a no. of products viz.

- Fuel and biodiesel
- Polymer materials
- Soaps, waxes, and greases
- Lubricants, hydraulic and brake fluids
- Organic Fertilizers. castor oil generates two main by-products: husks and meal
- Pharmacological and medicinal use.

### Lecture 3

## Chemical composition and nutritional quality of sugarcane - sucrose synthesis - post harvest changes in sugarcane & nutritional quality of forage crops

### Sugarcane

Sugarcane (*Saccharum officinarum*) family Gramineae (Poaceae) is widely grown in India. It provides employment to over a million people directly or indirectly besides contributing significantly to the national exchequer. Sugarcane growing countries of the world lay from tropical to subtropical zones. Sugarcane is grown even before vedic period and is the native of India. In India sugarcane is cultivated in an area of 47.74 lakh hectares with a production of 355 million tonnes. Uttar Pradesh is the major sugarcane growing state accounting for 48 % of the total area and 40 % of the total production. It is mainly used for the production of sugar and the byproducts of sugarcane include molasses, bagasse, filter mud, wax and cane trash which are having wide range of utility. White sugar recovered from sugarcane was 9.5 to 11.5 %. Molasses is used for alcohol production.

The chemical composition of ripened sugarcane is:

Constituents	Amount (%)
Water	70-75
Sugars (Glucose, fructose and sucrose)	12-15
Fibre	12-20
Nitrogenous substances	0.3 -0.4
Fats and waxes	0.15-0.25
Gums and pectin's	0.15-0.25
Free acids	0.08-0.12
Ash	0.3 -0.5
Organic matter	0.5-1.0

Energy wise white sugar and jaggery provides same calories viz., 242 KJ however, jaggery is rich in Ca (80 mg / 100 g) and Fe (2.64 mg / 100 g). The internodes of sugarcane are rich in sucrose while the rind is high in fibre. Sugarcane juice is opaque varying in colour from grey to dark green. The composition of the juice is as follows

Constituents	Amount (%)
Water	75-88

Sucrose	11.8-14.9
Reducing sugars	0.5-0.7
Ash	0.4 -0.6
Protein	0.16
Colloids	0.033-0.047
pH	5.4-5.7

## Sugars

Sugarcane juice contains three sugars viz., sucrose, glucose and fructose. The content of reducing sugars especially fructose decreases as the cane ripens. Hemicellulose, starch and pentosans are the other carbohydrates present. Based on sucrose content, the canes are classified as

- i. 12-15 % sucrose : Poor canes
- ii. 16 – 19 % sucrose : Fairly rich canes
- iii. > 20 % sucrose : Rich canes

The quantity of total solid (12-23) in a cane is estimated using hydrometer / brix meter.

## Nitrogenous substances

Proteins (albuminoids), amides, aminoacids, nitrates and ammonium salts are present. Asparagine and glutamine are the predominant amino acids in the juice. Other aminoacids include alanine, glycine, leucine, lysine, serine and tyrosine.

## Organic acids

The principal organic acid of cane juice is aconitic acid which constitutes 75 % of total carboxylic acid. Citric, malic and oxalic acids are also present in the juice.

## Minerals

Analysis of ash (0.4 -0.7 %) gives the following composition

Minerals	Quantity (%)
Silica	2.1 -5.3
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub>	5.2 -11.4
Cl	2.8 -5.1
SO <sub>4</sub>	35.0 -36.9
CaO	3.0 -5.6
MgO	1.2 -6.2
P <sub>2</sub> O <sub>5</sub>	10.8 -17.2

During maturity of cane, the ash, N and P decreases while the content of K and Ca increases. Analysis of ash in cane juice gives the calcium (18 mg), phosphorus (22 mg), potassium (22 mg), magnesium (13 mg) and iron (1.12 mg).

### **Vitamins**

Raw cane juice is not a rich of vitamins, it does contain a little vitamin A, some vitamin B (thiamine, riboflavin, niacin and biotin) and trace of vitamin D.

### **Starch**

Sugarcane juice contains 0.001 to 0.05 % of starch. The starch granules are found near the nodes of the cane, providing reserve food for germination.

### **Enzymes**

Hydrolyzing and color-producing enzymes are active in raw cane juice and both contribute to the formation of molasses. The cane plant contains the sucrose-hydrolyzing enzyme invertase and thus differs from the sugar beet, where it is absent. This enzyme is present in the juice and produces a simultaneous decrease of sucrose and an increase in reducing sugars. The color-producing enzyme systems are represented by an oxidase (laccase), a peroxidase and tyrosinase. These are oxidizing enzymes that produce phenols and quinones from aromatic compounds present in the plant juice which then react with ferric ion to produce dark colored complexes. Diastase and lactase are the other enzymes present.

### **Gums**

Sugarcane juice contains soluble gums which produce an undesirable effect during processing of the juice and sugar crystallization. Glucose, galactose, arabinose, xylose and rhamnose are the sugars obtained by the hydrolysis of gums.

### **Wax**

It is present as a whitish coating on the stalks mainly at the nodes.

### **Pigments**

The tannins and water-soluble anthocyanins pigments are called as saccharetin. Purple Mauritius cane contain a pigment Mauritin a pentose glucoside. Polyphenols (or) tannins present in the nodes also contribute to the colour of juice.

### **Byproducts of sugarcane**

The four main byproducts obtained from the sugarcane industry are cane tops, bagasse, press mud / filter muds and molasses.

- **Cane top** is used as an animal fodder.

- **Bagasse** is the fibrous residue of the cane stalk left after crushing and extraction of juice. It consists of fibres mostly cellulose, water and relatively small quantities of soluble solids - mostly sugars. Bagasse is used for the generation of steam and power, paper making and production of compressed fibre boards.
- **Pressmud** - During the process of juice clarification, CaO is added to prevent the inversion of sucrose which takes place in acidic condition and to coagulate the impurities. The treated juice then enters clarifiers in which organic substances such as chlorophyll, anthocyanin, waxes, gums, albumins, pectins as well as calcium phosphate formed from CaO coagulate to form flocks and precipitated as mud and removed from bottom. Mud slice contain sugar which can be recovered and the final product is filter cake. It is mainly used as organic manure and as a soil conditioner.
- **Molasses** is the final effluent obtained in the preparation of sugar by repeated crystallization. The main constituents are sucrose (32-36 %), glucose and fructose (20-30 %), H<sub>2</sub>O (20 %), minerals (9-11%) of which 4 % by weight is K<sub>2</sub>O. Sugars and other organic matter are used to augment the CHO content of animal feed. The potash in molasses make it a valuable by product for efficient plant growth. It is also used in the manufacture of industrial alcohol which is used as a fuel.

### **Maturity of cane**

The maturity of cane depends on sucrose content, brix and purity percentage. Matured cane should have 19-22 brix, 16 -18 % sucrose and 85 – 95 % purity. Another method to decide the maturity of cane is assessment of top bottom ratio. It is the ratio between the brix of the juice of the top half of the cane to bottom half of the cane. If the ratio is one or less the cane is said to be ripened.

### **Post harvest changes in sugarcane**

Post harvest deterioration of cane occurs mainly due to the delay in crushing of harvested canes. The delay could be during transportation or may be in the yard.

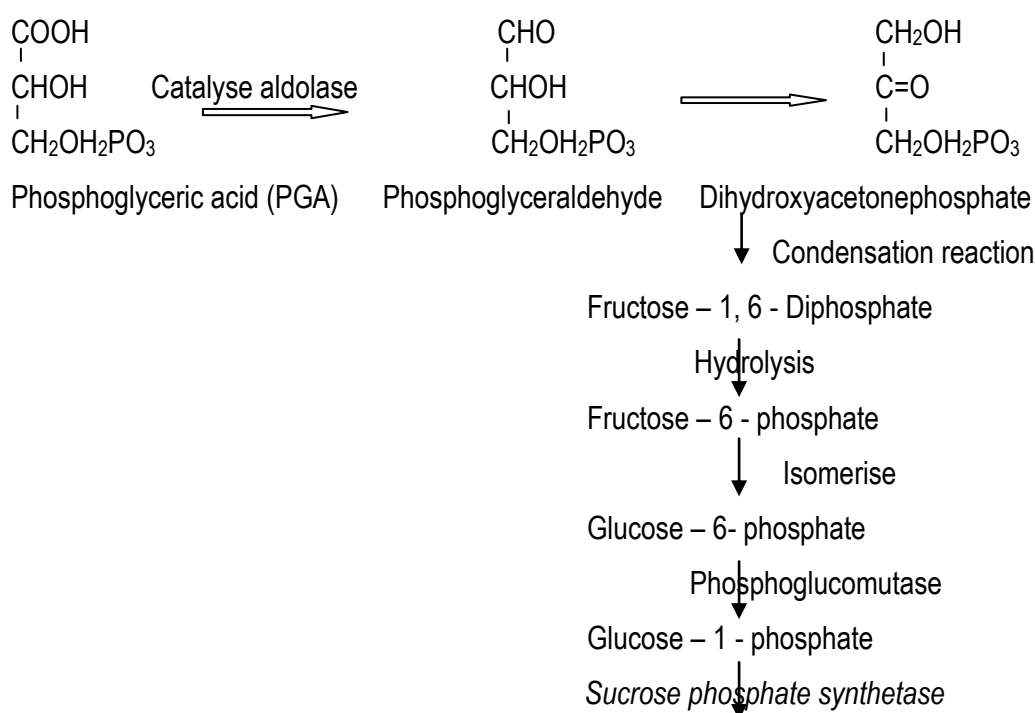
- Loss of moisture from the cane due to evaporation accounts for 1.5 -2 % for every 24 hours depending upon the weather conditions.
- Maximum deterioration of harvested cane occurs at 38 to 40 °C coupled with 15% moisture loss.
- Loss of sucrose per cent in juice is 0.10 to 0.20 units
- Increase in juice acidity, formation of gums and dextran adversely affecting the processing of juice.

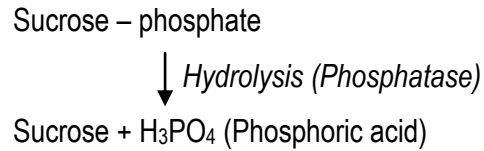
- Increase in fibre content leading to problems in juice extraction
- Increase in reducing sugars due to inversion of sucrose into glucose and fructose by the enzyme invertase and the sugar is called invert sugar.

After the harvest of cane, endogenous invertase enzyme gets activated and causes deterioration. Bio – deterioration is caused due to *Leuconostoc* sp. of bacteria. The moment cane is harvested, the *Leuconostoc* bacteria enters the cut ends and it has been found that within one hour after harvest, the bacteria can pass upto 20 cm in the stem from the cut ends. These organisms convert sucrose into dextran. A dextran level of above 500 ppm results in the formation of needle shaped sugar crystals with difficulties in the separation of molasses. The deterioration of juice quality is much faster when the canes are cut into bits.

### Biosynthesis of sucrose

During photosynthesis, sucrose is synthesized in the leaf cytosol from which it diffuses to the rest of the plant. Sucrose is a highly soluble disaccharide that provides a mobile energy source for all the plant cells. Sugar cane stores large amounts of sucrose in its leaves and stalk, whereas sugar beet stores it in roots. During photosynthesis phosphoglyceric acid (PGA) is the first stable compound formed in majority of crop plants. The PGA is converted into phosphoglyceraldehyde and then to glucose phosphate through a series of chemical reactions. The glucose and fructose phosphates are condensed in the presence of an enzyme sucrose phosphate synthetase to form sucrose phosphate which on hydrolysis yield sucrose and phosphoric acid. Sucrose thus formed is not utilized by the plants at once but  $H_3PO_4$  is reutilized.

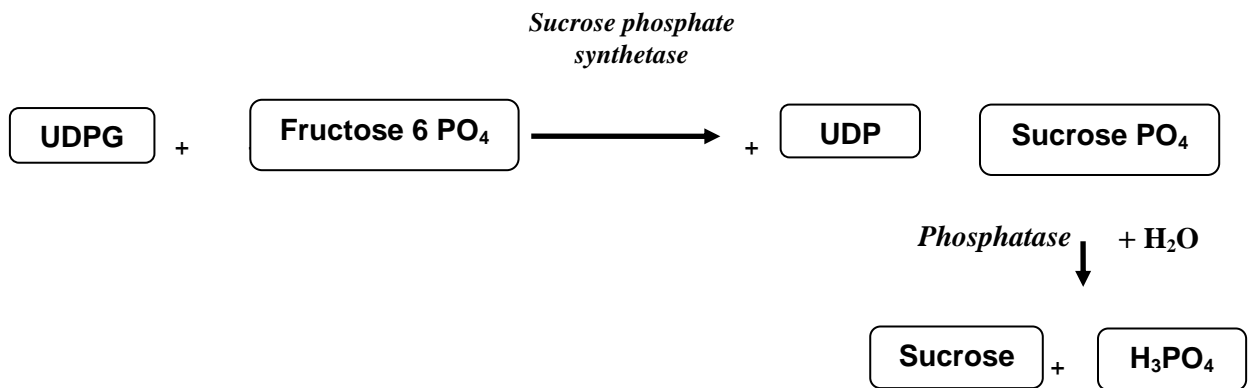




## Theories on Sucrose Synthesis

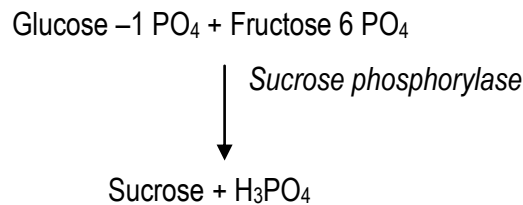
### I. UDPG (Uridine Diphospho Glucose) Theory

Fructose 6 PO<sub>4</sub> and UDPG are the precursors in sucrose synthesis. They combine under the influence of enzyme sucrose phosphate synthetase to form sucrose phosphate and UDP. Sucrose phosphate on hydrolysis yields sucrose and H<sub>3</sub>PO<sub>4</sub>.



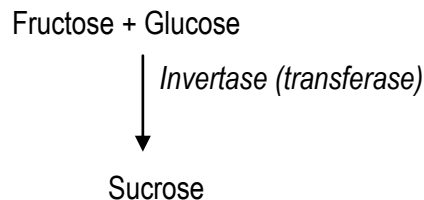
### II. Cori ester theory

Cori ester (Phosphoric ester of glucose – Glucose 1 phosphate) aids in sucrose formation.



### III. Involvement of Invertase enzyme

Invertase functions as a Transferase rather than acting as a hydrolase



Sugars thus formed are utilized in respiration and in body building. Excess sugar is stored in the form of sucrose. Sugar translocation takes place during day and night while sucrose synthesis takes place only during day time. During day time, the rate of synthesis exceeds the translocation capacity of phloem vessels and the excess sugar is converted to starch and other insoluble polysaccharides.



Sucrose content is more or less uniform along the stalk except the top and below ground butt which might be due to the immatured internode in the top and high fibre content in the lower butt. The maximum content of glucose is present in the topmost internode and decreases as they grow older. Sucrose accumulation is much affected by the water content of tissues.

### **Chemical composition and nutritional quality of forage crops**

Forage crops are, annuals, biennials or perennials grown to be utilized for grazing or harvested as whole crops to feed domestic animals. There are four categories of forages viz., cereals, legumes, grasses and trees.

#### **Cereals and grasses**

Cereals are rich in carbohydrates, fibre and poor in proteins and minerals. They contain 6 to 8% protein and 30-36% crude fibre.

#### **Legumes**

They are high in protein (14-20%) and minerals but less in carbohydrates. Crude fibre content is around 20-34%.

### **Criteria for suitability of a crop as a forage**

- Should contain greater total digestible nutrient (TDN)
- Should give more biomass yield
- Should be suitable for cultivation in all seasons.
- Crops should contain greater amount of nutrients and
- Biomass should be free from toxic elements.

### **Chemical composition**

- Green fodder contains about 70-75 % water while, dry fodder contains 1/ 10<sup>th</sup> of the total water.
- Nitrogenous substances include proteins, amino acids, amides, nitrogenous bases etc. The nitrate (NO<sub>3</sub>) content of forage crop should be less than 1% of dry weight.

### **Nitrogen free extracts (NFE)**

Total sugars are greater in young grasses. Water-soluble carbohydrates are more in grasses than in legumes, which make them highly suitable for silage. Crude fibre of forage consists of 85% cellulose and 12% lignin. Lignin content usually varies from 2 to 20%. On the cellulose framework, hemicelluloses and lignin are deposited. Crude fibre consists of two fractions viz.,

- \* NDF (Neutral Detergent Fibre) – is the sample residue left after treatment with neutral detergent (hemicellulose) which predicts uptake by animals

- \* ADF (Acid Detergent Fibre) – is the sample residue after treatment with acid detergent (cellulose, lignin and ash) which predicts digestibility.

### **Protein**

It occurs abundantly in leaves and other parts of plants, available as Amino acids like histidine, leucine, lysine, tryptophan and arginine. Forage crops generally contain 3-25 % crude protein. Crude protein is a mixture of true protein and non protein nitrogen. Quality wise the protein in grasses is inferior to legume protein.

### **Lipids / Ether extractives**

About 35% of crude fat is saponifiable matter in hays and fodders. As grass matures, both crude fat and total fatty acids decrease. Grass herbage usually contains 4 to 8% of lipid material. Fertilizer N at high rates increases fatty acids and sterols. Legumes appear to have similar lipid contents as in grasses.

### **Pectins**

It is a major constituent in grass amounting to < 1% and is located in the middle lamellae of cell wall.

### **Minerals**

Minerals such as P, K, Ca, Mg, S, Na, Cl, Fe, Mn, Cu, Zn and Co are generally present in forage crops. Molybdenum (Mo) at high level may interfere with copper (Cu) metabolism. In general legumes contain more of Iron (Fe), Magnesium (Mg) Cu and cobalt (Co) than grasses.

Legumes contain lesser cell wall material and dry matter content than the non-legumes at the same stage of maturity. The cell walls of legumes have considerably less hemicellulose content but are more lignified. Non-legumes have more cellulose and silica.

### **Organic acids**

The main organic acids present in grass herbage are malic, citric, quinic and succinic acids. NO<sub>3</sub> application increases the content of organic acids. Clovers and lucerne appear to contain greater quantities of organic acids than grasses. Carotene occurs in considerable quantity (20 to 40 mg/kg) in the dry matter and it decreases with maturity. Vitamin B complex is higher in legumes than in grasses.

### **Vitamins**

Vitamin D is present in sun-cured hays. Vitamin E content falls markedly with increasing maturity from 20 to 1.5 mg/100g and it is mostly present in leaves. Oestrogenic compounds which influence the reproductive behavior of animals are mostly present in legumes. Cyanogenic glucosides are the main source of goitrogenic activity. They are hydrolyzed in the rumen with the

release of hydrocyanic acid and which is converted into thiocyanate and inhibits the uptake of iodine by thyroid gland.

### Toxins

Oestrogens, coumarins, saponins, alkaloids, cyanogenic glucosides, NO<sub>3</sub>-N, oxalic acid, selenium and mimosine are the toxic substances present in forages. The toxic principles of the forage crops are presented below.

Toxic compounds and their effects in animals

Toxicants	Toxic principle	Effects on the animals
Oestrogen	Isoflavones in legumes Eg. Clover	Causes infertility
Coumarins	Dicoumarol is the oxidation product Eg. sweet clover	Reduces palatability, causes bleeding disease
Saponin	Sapogenins is the hydrolysis product E.g. Purple cockle	Excessive salivation, vomiting, damage to liver and kidney tissues
Alkaloids	Tryptomine, Perololine and Pyrrolizidine	Lesions in lungs and other organs. In severe cases results in death of animals
Cyanogenic glucosides	Release cyanide, nitrites and isothiocyanates. Dhurrin, a cyanogenic glucoside, is found in young seedlings of sorghum and Sudan grass. An enzyme, Dhurrinase acts on this glucoside and releases HCN	HCN reacts with haemoglobin to form methahemoglobin which reduces oxygen intake and results in mortality. HCN >100 ppm is unsafe to animals
Nitrate nitrogen	Reduced to nitrite nitrogen	Results in anoxia. Toxic level : 0.3 -0.4 %
Oxalic acid	Ca, Na and K oxalates interfere with Ca metabolism	Affects kidney and brain tissues. Toxic level : 3 %
Selenium	Found in Lucerne	Abnormal growth of muscles. S –application suppresses Se toxicity. Toxicity level- 4.0 ppm
Mimosine	Amino acid found in Leucaena.	Ill health, loss of hair, formation of goitre.

## Quality evaluation of forage crops

Quality of forage is evaluated by their nutritive value which includes digestibility, palatability and availability.

### Forage quality

Forage quality or feeding value could be defined as “biological assessment of the forage crop in terms of animal production”. Forage that is too fibrous for human, poultry and pigs are fed to cattle, buffaloes, camels, goats, sheeps, etc. The high level of fibre in forages is partially digested by the symbiotic bacteria living in the enlarged fore stomach of the ruminant. The criteria used in evaluating forage crops are

Total digestible nutrients = Digestible crude protein + Digestible crude fibre + DNFE

Digestible Nitrogen Free Extract = Digestible Fat x 2.25

The digestible ether extracts is multiplied by 2.25% because on oxidation of fat provides 2.25 times more energy as compared to carbohydrates.

$$\begin{aligned}\text{Nutritive ratio (NR)} &= \frac{\text{Digestible protein}}{\text{Digestible non protein compounds}} \\ &= \frac{\text{Digestible carbohydrates + fat}}{\text{Digestible crude protein}}\end{aligned}$$

**Net energy (NE)** is the energy required for mastication, digestion, assimilation. Net energy is the proportion of gross energy of feed that is used by the animal for maintenance and production.

**Digestible energy** is the gross heat of combustion of food minus the gross heat of combustion of faeces. Multiplying Digestible energy by a factor 0.82, metabolizable energy (ME) can be calculated.

**Metabolizable energy (ME)** is the difference of energy lost in urine and in combustible gases and the digestible energy.

Metabolizable energy = Heat in feed – (Heat lost in faeces + Heat lost in gases + Heat lost in urine)

**Digestible crude protein (DCP)** = (Feed N x 6.25) – N in faeces

% DCP + % DTP (Digestible Total Protein)

$$\text{Protein equivalent (PE)} = \frac{\text{Gain in body weight (g)}}{2}$$

$$\text{Net protein utilization (NPU)} = \text{PE} \times \text{DCE (Digestibility coefficient)}$$

$$\text{Protein efficiency ratio (PER)} = \frac{\text{Gain in body weight (g)}}{\text{Protein intake (g)}}$$

**Digestibility** : It refers to the extent to which any feed or feed component is digested by an animal. The quantity digested is termed as the digestibility coefficient.

### **Voluntary intake**

Voluntary intake is defined as the amount eaten during a period of time when the forage is offered adequately and is expressed as g/day. It is governed by nutritive value of forage pasture, **construction of leaf and stem**, amount of legumes in pasture, confinement of the animals to graze only in restricted areas, etc.

### **A. Cereal forages**

#### **I. Annuals**

##### **1. Fodder Sorghum**

Fodder sorghum is characterized by quick growth, high biomass and dry matter content with wider adaptability to stress. Single cut varieties are harvested at 50 % flowering and in multicut varieties, harvest is done after 55 DAS and subsequent cuts at 4 days interval.

Herbage quality depends mainly on the stage of growth at which the crop is cut and partly on the amount of fertilizer N applied. The percentage of crude protein and the carbohydrate value were highest at the boot leaf stage. Crude protein digestibility in silage is lower than that in green fodder.

The chemical composition (in % dry weight) of different forage crops

Forage crops	Constituent (%)				
	Crude protein	Crude fibre	NFE	Lipids	Total Ash
Sorghum	7.75	32.36	49.61	1.73	8.55
Maize	6.74	35.95	47.07	2.09	8.15
Cumbu napeir	10.2	30.5	41.0	2.1	16.2
Paragrass	3-16	28-34	40-57	0.9-3.9	-

Cowpea	15.77	20.11	30.43	2.39	16.94
Cluster bean	14-19	2.9	6.6	1.3-2.4	-
Lucerne	19.9	29.51	34.68	1.81	14.1
Desmanthus	15.6	34	46.7	3.0	6.4
Stylosanthus	14	31.2	48.6	2.4	7-14.2
Soobabul	26	20.4	-	-	11

### **HCN poisoning**

Cyanogenic glucosides called Dhuririn and Linamarin are present in sorghum. During mastication, the salivary enzymes combine with dhuririn and produce a glycone (methyl glucosinolates), which spontaneously dissociates to hydrogen cyanide and aldehyde. HCN affects palatability of fodder, prevents transport of oxygen in animal system and leads to the death of animals. The threshold content of HCN in sorghum is 100 ppm. In young herbage, the HCN content may be as high as 750 ppm or more, which is dangerous to animals. The crop should preferably be harvested after flowering but never before 40 to 50 days from the date of sowing. The leaves contain higher amounts of glucosides than stems. On dry weight basis, 500 ppm of HCN in leaf is dangerous to feed cattle. If sorghum is manured heavily with N fertilizers, free NO<sub>3</sub> accumulates quite considerably and causes poisoning in the livestock. The NO<sub>3</sub> is reduced to NO<sub>2</sub> by microorganisms in rumen and convert haemoglobin to methaemoglobin, which prevent transport and release of oxygen by the blood. High quality forage is obtained from sorghum and legume mixtures under good fertilizer management and package of practices.

### **2. Fodder maize**

Maize in India ranks fifth in total area and third in total production and productivity. For fodder purpose, it is harvested at pre flowering and at dough stage, the green ear and stover may be used as cattle feed.

## **II. Perennials**

### **3. Cumbu Napier Hybrid grass**

It has calcium (0.5%) and phosphorus (0.4%). Application of fertilizers to napier grass leads to the production of high amount of Na and NH<sub>4</sub> oxalate in the plant because of imbalance between anions and cations in the plant. On consumption of this grass, oxalic acid is produced in the animal system, which combines with Ca resulting in the formation of Ca-oxalate, which aids in kidney stone formation. Threshold value of oxalic acid is 3%. The oxalate content of some of varieties may be high (>3%) which can be mitigated if harvested at 45 to 60 days.

#### **4. Guinea grass**

It is palatable to all kinds of livestock. The crude protein ranges from 4 to 14% which declines with the age of herbage. The crude fibre content ranges from 28 to 36%. The content of ether extractives ranges from 0.6 to 2.8% and Nitrogen free extract ranges from 40 to 50%.

#### **5. Para Grass / Buffalo grass / Water grass**

The grass is poor in nutritive qualities. The total digestible nutrients range from 41 to 71%. The nutritive value of forage is improved if the grass is sown in mixture with legume. The calcium (0.35 to 0.8%) and phosphorus (0.32 to 0.76%) present.

#### **6. Doob grass (*Cynodon dactylon*)**

It is one of the most nutritious grasses. It is palatable and acceptable to all types of livestock. The dry matter constitutes 25 to 30% of fresh herbage. Crude Protein content slowly decreases with plant age and the leaf: stem ratio is high.

#### **7. Anjan grass / Kolukkattai grass (*Cenchrus ciliaris*)**

The crude protein content ranges from 3 to 16%. The calcium (CaO: 0.5 to 2%) and P content ranges from 0.4 to 1% which is in a well-balanced ratio. Ether Extractives: 1.72%, Crude Fibre: 30.54%, Ash: 16.08% and Nitrogen free extract is 43.3%. It is highly palatable and relished by animals.

### **B. Leguminous forage crops**

#### **I. Annuals**

##### **1. Fodder Cowpea**

The feeding value of fodder cowpea is high and comparable to lucerne. It is superior to soybean because of its low fibre content and minimum wastage in feeding livestock. It is used as fodder crop for green feeding, making hay, grazing and also for ensiling in mixtures with sorghum, maize or cereal fodders in order to enrich it with crude protein and mineral contents.

##### **2. Velvet bean**

It contains 15% crude protein which varies with the stage of harvest and has about 64% Total Digestible Nutrients. It is rich in minerals such as Ca, P, Fe and I.

##### **3. Cluster bean**

The HCN content of the forage ranges from 40 to 70 mg /100g in the early stages which decreases with advancement of crop period and is almost in traces at maturity. It is not harmful at fruiting stage. The forage is palatable and rich in crude protein and minerals. The digestibility coefficient of crude protein is high and varies from 70 to 85%.

#### **II. Perennials**

## 1. Berseem

It is highly nutritious, succulent and palatable fodder for all types of livestock especially for milch animals. It is rich in Ca and P. It has 20-24 % crude protein and 70 % dry matter digestibility. Harvested after 50-55 days of sowing and subsequently at 25-30 days interval.

## 2. Lucerne

It is a valuable leguminous fodder and hay crop. Grown as winter fodder crop in Rajasthan, Gujarat, parts of Tamil Nadu and Kerala. It is a perennial, drought tolerant forage legume. It contains 19.9 % crude protein with 72 % dry matter digestibility. Harvested after 55-65 days of sowing and subsequently at 30-35 days interval.

**It is rich in vitamins A and D. In leucerne hay, the fibre content is low but the protein and digestibility are very high. It is particularly rich in Ca (2.8% CaO) but poor in P (0.74% as P<sub>2</sub>O<sub>5</sub>). Like other leguminous crops, is a known source of phytoestrogens, including spinosterol. Grazing on alfalfa has been suspected as a cause of reduced fertility in sheep.**

## 3. Desmanthus / Hedge Lucerne/ Velimasal (*Desmanthus virgatus*)

It is a perennial leguminous fodder crop. It is grown mainly on hedges hence the name. It is rich in crude protein. For balanced nutrition three parts of grasses and one part of legume is recommended. Unlike *Leucaena*, *Desmanthus virgatus* does not contain mimosine and therefore can be fed safely to non-ruminants.

## 4. Stylosanthus / Muyalmasal

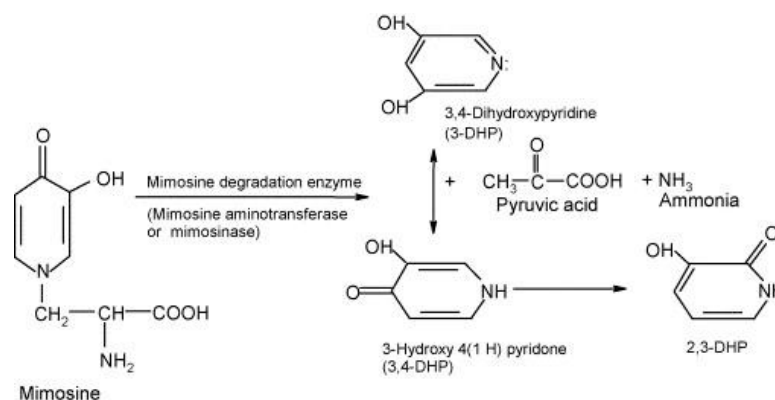
It is an herbaceous and dichotomously branched perennial leguminous fodder crop. It is rich in crude protein (12 – 18 %). It also contains essential amino acids with substantial amounts of glutamic acid, aspartic acid and leucine. The secondary metabolites viz., tannin is present to the extent of 13.2 g/kg DM. Highly nutritive and palatable so widely used as a feed for all types of animals as hay and silage.

## c. Tree fodder

### (i) *Leuceana* (Soobabul / Soundal)

It is a tree fodder and the foliage contains an uncommon amino acid-mimosine, which is toxic to non-ruminants at levels of 10% of diet. It is not fatal to ruminants since stomach micro-organisms convert mimosine to 3,4 dihydroxypyridine (DHP), which only on excessive and prolonged feeding results in ill health, poor growth, excessive salivation etc., Swollen thyroids (goiters) are common among cattle, for prolonged feeding on leuceana.





This is due to lesser production of thyroxine in thyroid gland. Wilting the forage for 4 to 6 hours in sun reduces its toxic effect considerably. Soaking of soababul in water for overnight reduces the toxicity. The leaflets contain 27 to 34% protein, which is of high nutritional quality. The fodder is a rich source of carotene and vitamin A. The calcium (2.36%) and phosphorus (0.23%).

Agathi, Acacia, Albizzia, Pongamia are also used as fodder for cattle and sheep.

#### Lecture -4

#### Chemical composition and nutritional quality of fruits - Mango, banana, papaya, grapes, guava, apple & pomegranate. Chemistry of post harvest changes in fruits

Fruits are a unique group of foods because of their wide variety of types, flavors, colors and textures. Fruits are abundant and cheap source of fibre. In Tamil Nadu, fruit cultivation spreads over an area of 3.90 lakh hectares with a total production of 79.65 lakh tones. At National level, Tamil Nadu ranks second in the productivity of fruits. The quality of processed fruit products depends on their quality at the start of processing; therefore, it is essential to understand how maturity at harvest, harvesting methods and post harvest handling procedures influence quality and its maintenance in fresh fruits between harvest and process initiation.

#### Contribution of fruits to human nutrition

- Most fruits are naturally low in fat, sodium and calories. None have cholesterol.
- Fruits are sources of many essential nutrients that are under consumed, including potassium, dietary fibre, vitamin C and folate (folic acid).
- Diets rich in potassium may help to maintain healthy blood pressure. Fruit sources of potassium include bananas and orange juice.

- Dietary fiber from fruits, as part of an overall healthy diet, helps reduce blood cholesterol levels and may lower risk of heart disease. Fibre is important for proper bowel function.
- Vitamin C is important for growth and repair of all body tissues, helps heal cuts and wounds, and keeps teeth and gums healthy.
- Folate (folic acid) helps the body form red blood cells.

### **General composition of fruits**

#### **Carbohydrates**

Carbohydrates and fats provide most of the calories the body requires for heat and energy. Fresh fruits vary greatly in their carbohydrate content, with a general range being between 10 and 25%. The structural framework, texture, taste and food value of a fresh fruit is related to its carbohydrate content. Sucrose, glucose and fructose are the primary sugars found in fruits. Sucrose content ranges from a trace in cherries, grapes and pomegranates to more than 8% in ripe bananas and pineapple. Such variation influences taste since fructose is sweeter than sucrose and sucrose is sweeter than glucose.

#### **Organic acids**

Organic acids are important intermediate products of metabolism. Most fresh fruits are acidic. Some fruits such as lemon and limes contain as much as 2-3% of their total fresh weight as acid. Malic and citric acids are the most abundant in fruits except grapes (tartaric acid) and kiwi fruits (quinic acid).

#### **Pigments**

Pigments, which are the chemicals responsible for skin and flesh colours, undergoes many changes during the maturation and ripening of fruits; these include loss of chlorophyll (green colour), synthesis and/or revelation of carotenoids (yellow and orange colours) and development of anthocyanins (red and purple colours), which are fruit specific.

#### **Phenolic compounds**

Total phenolic content is higher in immature fruits than in mature fruits and typically ranges between 0.1 -0.2 g per 100 g fresh weight. Fruit phenolics include chlorogenic acid, catechin, epicatechin, leucoanthocyanidins, flavonols, cinnamic acid derivatives and simple phenols. Enzymatic browning occurs due to the oxidation of phenolic compounds and is mediated, in the presence of O<sub>2</sub> by the enzyme polyphenoloxidase (PPO).

#### **Volatiles**

Volatiles are responsible for the characteristic aroma of fruits. They are present in extremely small quantities (<100 µg/g fresh weight). Volatile compounds are largely ester, alcohols, acids, aldehydes and ketones (low molecular weight compounds).

### **Vitamins**

The water soluble vitamins include thiamine, riboflavin, niacin, vitamin B6, folacin, vitamin B12, biotin, pantothenic acid and Vitamin C. Fat soluble vitamins include vitamins A, D, E and K.

### **Minerals**

Important fruit minerals include base forming elements (Ca, Mg, Na and K) and acid forming elements (P, Cl and S). Minerals present in micro quantities include Fe, Cu, Co, Mo, Zn, I and Mn. Potassium is the most abundant mineral found in fruits. Calcium is second most important mineral constituent followed by magnesium and phosphorus.

Chemical composition of different fruit crops

<b>Constituents</b>	<b>Mango</b>	<b>Banana</b>	<b>Papaya</b>	<b>Grapes</b>	<b>Guava</b>	<b>Apple</b>	<b>Pomegranate</b>
Moisture (%)	90	75	88	81	83	86	78
Energy (KJ) (kcal)	250 (60)	371 (89)	179 (43)	288 (69)	285 (68)	218 (52)	346 (83)
Protein (%)	0.82	1.10	0.50	0.72	2.55	0.26	1.67
Fat (%)	0.38	0.33	0.26	0.16	0.95	0.17	1.17
CHO (%)	15	23	10.82	18.1	14.32	13.81	18.7
Ascorbic acid (mg)	36.4	8.7	62	3.2	228	4.6	10.2
Potassium (mg)	168	388	182	191	417	107	236

### **1. Mango**

Mango is known as the king of fruits. Mango provides 60 calories per 100 g of fruit. Mango is an excellent source of bioactive compounds such as provitamin A carotenoids, vitamin C, folate and phenolics as well as dietary fibre, essential to human nutrition and health and that can easily be degraded during processing and storage. Vitamin C concentration was higher in the peel than in the edible portion. Chlorophyll, carotenes, anthocyanins and xanthophylls are all present in the fruit, although chlorophyll disappears during ripening, whereas anthocyanins and carotenoids increase with maturity. The major constituents of the pulp are water, carbohydrates, organic acids, fats, minerals, pigments, tannins, vitamins, and flavor compounds. The soluble sugars of the fruit pulp

consisted mainly of glucose, fructose, maltose and sucrose. Essential amino acids like alanine, aspartic acid, lysine, leucine, cystine, valine, arginine, phenyl alanine and methionine are present. Tannin present in the flesh (0.16 %) and skin (0.1 %) is responsible for astringency. Total carotenoids and  $\beta$ -carotene remained very low initially and increased gradually as the fruits approached maturity and ripening. Vitamin C registers a sharp fall on ripening. Green mangoes contain folic acid to an extent of 36 mg / 100 g. Mangoes also contain pectin which lowers the risk of gastrointestinal tract cancer. Mango contains a unique xanthonoid called mangiferin

The increase in flavor and aroma during fruit ripening is owing to the production of a complex mixture of volatile organic molecules mainly belonging to terpene, furanone, lactone and ester classes. In India, Alphonso is one of the most popular cultivars. In Alphonso mango, the lactones and furanones are synthesized during ripening; whereas terpenes and the other flavorants are present in both the developing (immature) and ripening fruits.

## **2. Banana**

Banana is a rich source of energy. Raw bananas (not including the peel) are 75% water, 23% carbohydrates, 1% protein and contain negligible fat (0.33%). Banana provides 89 calories per 100 g of fruit. The fruit contains 3% of soluble dietary fibre helping in bowel movements. It contains health promoting flavanoid, polyphenolic anti oxidants such as lutein, zeaxanthin,  $\alpha$  and  $\beta$  carotene, vitamin B<sub>6</sub> and vitamin C. Fresh bananas provide minerals like magnesium, phosphorus, manganese and is a good source of potassium (358 mg / 100 g). The primary component of the aroma of fresh bananas is isoamyl acetate (also known as banana oil), which, along with several other compounds such as butyl acetate and isobutyl acetate, is a significant contributor to banana flavor.

## **3. Papaya**

Papaya fruit is very low in calories (43 calories/100 g) and contains no saturated fats / cholesterol. It is a rich source of phyto-nutrients, minerals and vitamins. It also contains good amount of soluble dietary fibre that helps in normal bowel movements. Fresh, ripe fruit has the highest vitamin-C content. It is also an excellent source of Vitamin-A (1094 IU/100 g) next to mango and contains flavonoids like  $\beta$ -carotene, lutein, zeaxanthin and cryptoxanthin. Consumption of natural fruits rich in carotenes has been known to protect the body from lung and oral cavity cancers.

The fruit is also rich in many essential B-complex vitamins. Fresh papaya contains a good amount of potassium (182 mg per 100 g) and calcium (20mg) which helps in controlling heart rate and blood pressure counteracting the effects of sodium. Papaya skin, pulp and seeds contain a

variety of photochemical including carotenoids and polyphenols as well as benzyl isothiocyanates and benzyl glucosinates with skin and pulp levels that increase during ripening. Papaya seeds also contain the cyanogenic substance prunasin. In traditional medicine, papaya seeds are anti-inflammatory, anti-parasitic analgesic, and they are used to treat stomachache and ringworm infections. Papain prepared from the dried latex of immature fruits is a proteolytic enzyme used in meat tenderizing, manufacturing chewing gum, degumming natural silk and to give shrink resistance to wool.

#### **4. Grapes**

##### **Sugars**

Glucose and fructose account for 12 -27 %. Other sugars like sucrose, raffinose, stachyose, maltose and galactose are present in small amounts. Most of the sugars in the berries are manufactured in leaves.

##### **Organic acids**

The principal organic acids found in grapes are tartaric, malic acids accounts for over 90% of the total acids presents and to a small extent citric also present. During the early period of berry growth, concentration of both acids increases in the fruit. With the onset of ripening, as the sugar accumulates in the fruit, the acid concentration decreases. Generally the reduction in malic acid is greater and consequently, at maturity, the fruit contains more tartaric acid than malic.

##### **Tannins**

These are complex esters of phenolic acids occurring primarily in skin, stem and seeds of grapes. It is present to the tune of 0.1 % and its content influences the palatability of grapes and their products. The tannins give an astringent taste.

##### **Nitrogenous compounds**

Total nitrogen in crushed grape ranges from 10-200 mg / 100 ml. Ammonium cations and organic compounds such as amino acids, amines, peptides, nucleic acids and proteins constitute the major part of nitrogenous compounds.

##### **Minerals**

The minerals constitute 0.20 -0.60 % of fresh weight and include Ca, Cl, Mg, K, P and S.

##### **Vitamins**

Good amount of vitamin A is retained in dehydrated grapes. Natural raisins do not contain vitamin A. Thiamine, riboflavin, pyridoxine, pantothenic acid, nicotinic acid, inositol, biotin and folic acids are present. Vitamin C content is 13.5 mg / 100 ml of juice.

##### **Pectin**

During ripening, protopectin is converted to pectin and the berries soften as a result of middle lamellar pectate. Vinifera grapes contain smaller amount of pectin compared to American grapes which form stable jelly.

### **Colour**

The grape pigments include five anthocyanins (cyanidin, delphinidin, petunidin, malvidin and peonidin) are modified by glucose molecule attachment. The yellow pigment of both white and red grape is quercetin, a flavone and its glycoside – quercitrin, a flavanol. The anthocyanin content varies from 2500–3000 mg /kg. Brightness makes table grapes more attractive.

### **Flavour**

Certain volatile compounds are directly associated with the flavor and aroma of many fruits. Major volatiles in grapes (max 1000 µg/l) are: Terpens, free and glycosidated forms, nor-isoprenoids and thiols.

### **Enzymes**

Polyphenol oxidase is the main oxidizing enzyme of grapes and is confined to the skin. Other enzymes like phenolase, phosphatase and proteinase are found in skin and to a lesser extent in pulp. These enzymes accelerate oxidative browning and discoloration.

Grape seed oil contains tocopherols (vitamin E) and high contents of phytosterols and poly unsaturated fatty acids such as linoleic acid and oleic acid.

## **5. Guava**

Guava is rich in dietary fibre and vitamin C, with moderate levels of folic acid (49 µg), thiamine, riboflavin and vitamin A. It contains much iron but 80 % is in the seeds which is not utilizable. It is also a good source of potassium (260mg) calcium (18 mg) and phosphorus (40 mg). Pink fleshed cultivars are poor in vitamin C content than the white fleshed ones. Changes in polyphenols during ripening, loss of astringency during ripening of fruits and this is connected with the increased polymerization of tannins particularly leucoanthocyanidins. Guava leaves contain both carotenoids and polyphenols like (+)-galocatechin and leucocyanidin.

## **6. Apple**

Apples are low in calories; 100 g of fresh fruit slices provide only 52 calories. They, contain no saturated fats or cholesterol. The fruit is rich in dietary fibre. The ripe flavor of apple is due to ethyl-2-methyl butyrate. Amino acids like aspartic, glutamic acids and alanine are present in apple. It contains malic acid (0.3 -1.0 %). Additionally, they are also good in tartaric acid that gives tart flavor to them. The fruit contains good quantities of vitamin-C and beta-carotene. It is a good

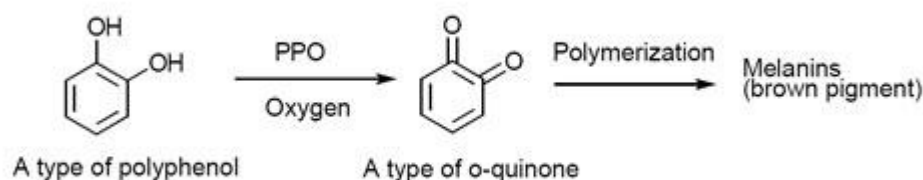
source of B-complex vitamins such as riboflavin, thiamin, and pyridoxine (vitamin B-6). It also contains small amount of minerals like potassium (107 mg), phosphorus and calcium.

### Phytochemicals

Apples are a rich source of antioxidants like flavonoids and polyphenolics. Some of the important flavonoids are quercetin, epicatechin and procyanidin found in the skin, core and pulp of the apple, they have unknown health values in humans. One of the most common anthocyanin pigment is cyanidin, which in the form of cyanidin-3 glucoside, is the pigment responsible for red coloration in apple skin.

### Enzymatic browning

Sliced apples turn brown with exposure to air due to the conversion of natural phenolic substances into [melanin](#). This is called enzymatic browning. More technically, an enzyme called polyphenol oxidase (PPO) (also known as tyrosinase) catalyzes the reaction of phenolic compounds (monophenol) to o-quinones causing the pigment to turn darker and therefore brown.



### Toxicity of seeds

The seeds of apples contain small amounts of amygdalin, a sugar and [cyanide](#) compound known as a [cyanogenic glycoside](#). Ingesting large amounts of apple seeds can cause adverse reactions.

## 7. Pomegranate

The fruit juice easily ferments and is used in the production of wine. The bark of the stem and root contains a number of alkaloids belonging to pyridine group. Seed contains 15 % oil. The fruit is moderate in calories; 100 g provides 83 calories, more than [apples](#). It contains no cholesterol or saturated fats. Pomegranate seeds are a rich source of dietary fiber (4g/100g) which is entirely contained in the edible seeds. It is suggested for weight reduction and cholesterol controlling programs.

### Juice

The most abundant phytochemicals in pomegranate juice are polyphenols, including the hydrolyzable tannins called ellagitannins formed when ellagic acid and/or gallic acid binds with a carbohydrate to form pomegranate ellagitannins, also known as punicalagins (polyphenolic anti-

oxidant). The oxygen radical absorbance capacity (ORAC) is 2341  $\mu\text{mol TE}/100\text{ g}$ . The red color of juice can be attributed to anthocyanins such as delphinidin, cyanidin and pelargonidin glycosides. Generally, an increase in juice pigmentation occurs during fruit ripening.

It is a good source of antioxidant vitamin-C, providing 17% of daily requirement. Regular consumption of pomegranate has also been found to be effective against prostate cancer, benign prostatic hyperplasia (BPH), diabetes and lymphoma. It is also a good source of many vital B-complex groups of vitamins such as pantothenic acid (vitamin B-5), folates, pyridoxine and vitamin K, and minerals like calcium, phosphorus, potassium and magnesium.

### **Chemistry of post harvest changes in fruits**

[Fruits](#) and [vegetables](#) contain 65 to 95 percent water. When food and water reserves are exhausted, produce dies and decays. The rate at which a food and water reserves are used up increases the rate of loss of product also increases. As per the estimates of Indian Council of Agricultural Research, about 12.5 - 18 % of the fruits and vegetables in India suffer post harvest losses.

### **Compositional changes**

The fresh young developing fruits contain very little sugar and the large amount of starch, acids and phenolics make them inedible. As the fruits approach maturity, flesh cells enlarge considerably and sugar content increases while starch, acid and phenolic contents decrease. In addition, certain volatile compounds develop, giving the fruit its characteristic aroma. Chlorophyll degradation (loss of green colour) and synthesis of carotenoids (yellow and orange colour) and anthocyanins (red and purple colour) take place both in the skin and the flesh with fruit ripening. All fruits soften as they ripen due to changes in cell wall composition and structure.

### **Carbohydrates**

Starch occurs as small granules within the cells of immature fruits. Starch is converted to sugar as the fruits mature and ripens. The transformation of insoluble pectins into soluble pectin is controlled, for the most part, by the enzymes pectinesterase and polygalacturonase.

### **Proteins**

Fruits contain less than 1% protein. Enzymes, which catalyze metabolic processes in fruits, are proteins that are important in the reactions involved in fruit ripening and senescence. Some of the enzymes important to fruit quality include the following

Enzyme	Action
Polyphenol oxidase	Catalyze oxidation of phenolics; resulting in formation of brown polymers



Polygalacturonase	Catalyze hydrolysis of glucosidic bonds between adjacent polygalacturonic acid in pectin; results in tissue softening
Pectinesterase	Catalyze de-esterification of galacturoans in pectin; may result in tissue firming
Lipoxygenase	Catalyze oxidation of lipids; results in off-odour and off- flavour production
Ascorbic acid oxidase	Catalyze oxidation of ascorbic acid; results in loss of nutritional quality
Chlorophyllase	Catalyze removal of phytol ring from chlorophyll; results in loss of green colour

### **Lipids**

Lipids constitute only 0.1-0.2% of most fresh fruits. Lipids are important because they make up the surface wax, which contributes to fruit appearance and cuticle, which protects the fruit against water loss and pathogens.

### **Organic acids**

Organic acid content usually decreases during ripening due to the utilization of organic acids during respiration or their conversion to sugars.

### **Pigments**

Pigments, which are the chemicals responsible for skin and flesh colours, undergoes many changes during the maturation and ripening of fruits; these include loss of chlorophyll (green colour), synthesis and/or revelation of carotenoids (yellow and orange colours) and development of anthocyanins (red and purple colours), which are fruit specific.

### **Phenolic compounds**

Astringency is directly related to phenolic content and it usually decreases with fruit ripening because of conversion of astringent phenolic compounds from the soluble to the insoluble non-astringent form.

### **Volatiles**

An increase in volatile compounds gives characteristics flavor of a fruit during ripening.

### **Vitamins**

Fat soluble vitamins are less susceptible to postharvest losses. Ascorbic acid is most sensitive to destruction to adverse handling and storage conditions.

## **Minerals**

Mineral nutrients move into the fruit most rapidly during the earlier stages of development at a time when xylem water flow is dominant. As fruit approaches maturity, surface to volume ratio declines, the skin becomes less permeable to water loss and large amounts of assimilates are imported via phloem connection.

## **Quality of fruits**

The quality of processed fruit products depends on their quality at the start of processing; therefore, it is essential to understand how maturity at harvest, harvesting methods and post harvest handling procedures influence quality and its maintenance in fresh fruits between harvest and process initiation. Quality attributes of fresh include appearance, texture, flavour and nutritive value. Appearance factors include size, shape, colour and freedom from defects and decay. Texture factors include firmness, crispness and juiciness. Flavour components incorporate sweetness, sourness (acidity), astringency, bitterness, aroma and off-flavours. Nutritional quality is determined by a fruit's content of vitamins (A and C are the most important in fruits), minerals, dietary fibre, carbohydrates and proteins. Losses in fresh between harvest and processing may be quantitative (water loss, physical injuries, physiological breakdown and decay) or qualitative (loss of acidity, flavor, colour and nutritive values).

## **Post harvest changes**

Fruits after harvest lead an independent life as they are removed from the parent plants and the normal supply of water, minerals and other organic molecules are completely cut off. The harvested fruits do not have any significant photosynthetic process but they carry out all other processes such as,

1. Physiological processes eg. Maturity and ripening
2. Biological processes eg. Transpiration, respiration, ethylene etc
3. Environmental processes eg. Temperature, relative humidity, air movement and atmospheric composition.

### **1. Physiological changes**

#### **a. Maturity**

The post harvest quality and storage life of fruits is controlled by maturity. Maturity can be described as the attainment of a particular size or stage after which ripening takes place. Ripening means the qualitative changes in fruits after maturity, as a result of which it becomes edible. Maturity is one of the primary factors affecting fruit composition, quality and storage life. Various maturity indices such as number of days from fruit set, visual indicators (size, shape, colour and

appearance), texture, specific gravity, starch content, soluble solids, sugar: acid ratio and oil content are used to determine the maturity of fruits.

For example in mango variety Alphonso takes 110 to 125 days after fruit-set for surface colour to change from dark green to olive green and flesh colour from white to pale yellow. It was also observed that fruits having specific gravity above 1.04 were partially ripe and below that were green at the time of harvest. The maturity of pineapple is characterized by rapid decline in shell pH and marked increase in flesh brix and titrable acidity. Starch is absent in mature orange fruits.

## **b. Ripening**

Ripening is a physiological process by which fruits attain their desirable flavor, quality, colour, palatable nature and other textural properties that makes it acceptable for consumption. These quality changes are accompanied by respiratory changes in the fruit and compositional changes such as transformation in pigments, pectins, carbohydrates, acids, phenolics, etc. Colour change in fruit is due to degradation or breakdown of chlorophyll and consequent unmarking of carotenoid pigments in case of oranges.

Fruit softening is caused by the break down of insoluble protopectin and formation of soluble pectin. During ripening, there is a decrease in starch and increase in fructose, glucose and sucrose resulting in sweetness of the fruit. Ripening also decreases the organic acids and phenolics to reduce the acidity and astringency and makes it more acceptable. An increase in volatile compounds gives the characteristic flavour of a fruit during ripening. The most striking change during ripening of banana, are the hydrolysis of starch and accumulation of sugar. In mango, the peel colour changes from dark green to olive green and flesh colour from white to pale yellow.

### **Chemical changes during ripening in mango and banana fruits (Thomas, 1978)**

<b>Compounds (g/100g)</b>	<b>Mango</b>		<b>Banana</b>	
	<b>Raw</b>	<b>Ripe</b>	<b>Raw</b>	<b>Ripe</b>
Starch	10.00	-	20.60	1.20
Glucose, fructose	1.80	6.00	0.24	15.34
Sucrose	1.80	9.70	0.62	2.60
Organic acids	3.40	0.38	0.40	0.30
Vitamin C (mg/100g)	88.00	36.00	15.00	12.00
Carotenoids (mg/100g)	0.95	15.80	0.20	0.36

## **2. Biological processes**

### a. Transpiration or Moisture loss

Water loss is the main cause of deterioration because it results not only in direct quantitative losses (loss of soluble weight), but also losses in appearance (wilting and shriveling), textural quality (softening, flaccidity, limpness, loss of crispness & juiciness) and nutritional quality.

Transpiration rate is influenced by internal or commodity factors (morphological and anatomical characteristics, surface to volume ratio, surface injuries and maturity stage) and external/environmental factors (Temperature, relative humidity, air movement and atmospheric pressure). Transpiration is a physical process that can be controlled by applying treatments to the commodity (eg wax, surface coating/wrapping with plastic films) or manipulation of the environment (RH and control of air circular).

### b. Respiration

Respiration is a continuing process in a plant and cannot be stopped without damage to the growing plant or harvested produce. Respiration is the process by which stored organic materials (CHO, proteins and fats) are broken down into simple end products with a release of energy. Oxygen (O<sub>2</sub>) is used in this process and carbon dioxide (CO<sub>2</sub>) is produced. The loss of stored food reserves in the commodity during respiration hastens senescence as the reserves that provide energy to maintain the commodity living status are exhausted. When the air supply is restricted, [fermentation](#) instead of respiration can occur. Poor ventilation of produce also leads to the accumulation of [carbon dioxide](#). When the concentration of carbon dioxide increases, it will quickly ruin the produce.

During respiration, the sugar disappears with the uptake of O<sub>2</sub> and production of CO<sub>2</sub> and H<sub>2</sub>O. A great deal of energy is liberated as heat at the time of respiration. The initial phase of respiration is production of pyruvic acid from glucose, a phase known as glycolysis. The terminal phase of respiration is the conversion of pyruvic acid into CO<sub>2</sub> and H<sub>2</sub>O, which is strictly aerobic. In most of the fruits, the rate of respiration increases rapidly with ripening. The sudden upsurge in respiration is called the turning point in the life of fruits. After this, senescence and deterioration of the fruit begins. The fruits belonging to this type of respiratory process are called climacteric fruits. In non-climacteric fruits, there appears to be a simple gradual decline in respiration. [Climacteric fruits](#) are able to continue ripening after being picked, a process accelerated by [ethylene](#) gas. Non-climacteric fruits can ripen only on the plant and thus have a short shelf life if harvested when they are ripe.

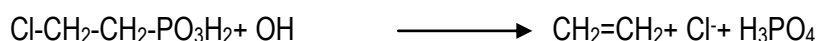
Climacteric fruits	Non-Climacteric fruits
Respiration rate increases with ripening	Respiration rate decreases with ripening

Continue ripening after harvest	Ripe only on plant
Long shelf-life	Short shelf-life
Ethylene gas accelerate the ripening	Not accelerated except degreening of citrus and pineapple
Eg. Banana, papaya, mango, sapota	Eg. Pineapple, grapes, lemon

The rate of respiration is a good index of the post-harvest life of fruit. To extend life of the fruit, respiration rate should be reduced. Once harvested, carbohydrates utilized during respiration cannot be replaced and the calorific value of the fruit is reduced.

**c. Ethylene** (C<sub>2</sub>H<sub>4</sub> or CH<sub>2</sub>=CH<sub>2</sub>)

It is known as the ripening hormone. The methionine (amino acid) is the immediate precursor of ethylene production in fruit tissue. The methionine is first converted into S-adenosyl – L- methionine (SAM) by SAM synthetase enzyme. The SAM is then converted to 1-aminocyclopropane-1-carboxylic acid (ACC) by the enzyme ACC synthase. The final step is ACC is converted to ethylene in the presence of enzyme ACC oxidase and requires oxygen. Ethylene, is produced by unripe fruit in minute quantities (0.01- 0.05 parts per million) but at the beginning of ripening there is a dramatic rise in ethylene production to levels frequently a thousand fold greater than that in unripe fruit. During the ripening of Alphonso mango generates ethylene gas in the range of 0.02 to 0.18 ppm. Mature unripe fruits are stimulated to ripen if treated with very low concentration of ethylene gas of about 0.1 ppm. Ethephon (2-chloroethyl phosphonic acid, Trade name: ethrel), is ethylene releasing compound. Ethephon is breaks down into ethylene, phosphate and a chloride ion.



Application of ethephon imparts attractive colour to mangoes and increases their commercial value but reduces the ascorbic acid content. Citrus fruits are degreened with Ethephon, which actually widens carotenoid synthesis, apart from hastening chlorophyll degradation. Application of ethylene at 0.10 ppm or higher to green bananas accelerates the onset of the climacteric stage. Advancement of ripening by application of Ethrel has also been observed in many fruits by various workers. Ethylene is 100 times more effective than acetylene. Fruits ripened by calcium carbide has attractive colour but it has health concerns due to traces of arsenic and phosphorous.

Natural ethylene produced by fruits can lead to in- storage losses. For example, ethylene destroys the green colour of plants. Leafy vegetables will be damaged if stored with ripening fruit and this can cause early ripening of climacteric fruit during transport.

### **Environmental factors**

#### **Temperature**

Temperature is the most important environmental factor that influences the deterioration rate of harvested fruits. For each increase of 10 C above the optimum temperature, the rate of deterioration increase by two fold or threefold. The temperature also influences how ethylene, reduced oxygen and elevated carbon dioxide levels affect the commodity. The growth rate of pathogen is greatly influenced by temperature.

#### **Relative Humidity (RH)**

The rate of water from fruits depends upon the vapour pressure deficit between the commodity and the surrounding ambient air, which is influenced by temperature and RH. Low RH results in unacceptable moisture loss, while humidities close 100% may result in excessive growth of microorganism and surface cracking.

#### **Air movement**

Air circulation rate and velocity can influence the uniformity of temperature and RH in a given environment and consequently, rate of water loss from the commodity.

#### **Atmospheric composition**

Reduction of O<sub>2</sub> and elevation of CO<sub>2</sub>, whether intentional or untentstional, can have a beneficial or harmful effect on deterioration.

## Lecture 5

### Chemical composition and nutritional quality of vegetables: Tomato, bhendi, brinjal, moringa, greens, cauliflower, radish and peas

Fresh vegetables endowed with almost all of the nutritional principles that our body requires. The health benefits of vegetable nutrition are enormous. They are good source of vitamins, minerals, antioxidants and dietary fiber. Vegetables, like fruits, are low in calories and fats but contain good amounts of vitamins and minerals. All the Green-Yellow-Orange vegetables are rich sources of calcium, magnesium, potassium, iron, beta-carotene, vitamin B-complex, vitamin-C, vitamin-A, and vitamin K.

As in fruits, vegetables too are home for many antioxidants. These health benefiting phyto-chemical compounds firstly; help protect the human body from oxidant stress, diseases, and cancers, and secondly; help the body develop the capacity to fight against these by boosting immunity. Additionally, vegetables are packed with soluble as well as insoluble dietary fiber known as non-starch polysaccharides (NSP) such as cellulose, mucilage, hemi-cellulose, gums, pectin, etc. These substances absorb excess water in the colon, retain a good amount of moisture in the fecal matter, and help its smooth passage out of the body. Thus, sufficient fiber offers protection from conditions like chronic constipation, hemorrhoids, colon cancer, irritable bowel syndrome, and rectal fissures.

#### 1. Tomato

Tomato is one of the most popular and widely grown vegetables in the world ranking second in importance. It is popular because it supplies vitamin C, adds colour and flavor to foods. Tomato is consumed in diverse ways, including raw as an ingredient in many dishes, sauces, salads and drinks. Green tomatoes are used for pickles. Tomato seed contains 24 % oil which is extracted from the pulp. The composition of tomato per 100 g of edible fruit is as follows:

Constituents	Content	Constituents	Content
Moisture	: 93.1 g	Vitamin A	: 320 I.U
Protein	: 1.9 g	Thiamine	: 0.07 mg
Fat	: 0.1 g	Riboflavine	: 0.01 mg
Mineral matter	: 0.6 g	Nicotinic acid	: 0.4 mg
Fibre	: 0.7 g	Vitamin C	: 31 mg
Carbohydrates	: 3.6 g	Calcium	: 20 mg
Sodium	: 45.8 mg	Magnesium	: 15 mg

Potassium	:	337 mg	Chlorine	:	38 mg
Copper	:	0.19 mg	Phosphorus	:	36 mg
Sulphur	:	24 mg	Iron	:	1.8 mg

Tomatoes are one of the low-calorie vegetables containing only 18 calories per 100 g. They are also very low in fat and have zero cholesterol levels. Tomato fruit is a reservoir of a diverse range of antioxidant molecules, such as carotenoids, flavonoids, phenolic acids and ascorbic acid. They also good sources of dietary fibre, minerals and vitamins. The antioxidants present in tomatoes are found to prevent cancers, Total-ORAC (Oxygen Radical Absorbance Capacity) is 367  $\mu\text{mol TE}/100\text{ g}$ . Lycopene, a flavonoid antioxidant, is the unique phytochemical present in tomatoes (2573 $\mu\text{g}/100\text{g}$ ). Lycopene is the most abundant carotenoid present in ripe red tomatoes, comprising up to 90% of the pigments present. Zea-xanthin is another flavonoid compound present abundantly in this vegetable which helps to protect the eyes. In addition, it also contains anti-oxidants such as  $\alpha$  and  $\beta$ -carotenes (550  $\mu\text{g}/100\text{g}$ ), xanthins and lutein (123  $\mu\text{g}/100\text{g}$ ).

Flavonoids and phenolic acids are the two major classes of phenolics, which are relevant to the appearance, taste and flavor of food products as well as to their health promoting properties. It contains very good levels of vitamins A and C. Fresh tomato is rich in potassium. 100 g contains 237 mg of potassium and 5 mg of sodium. Contains moderate levels of vital B-complex vitamins such as folates, thiamine, niacin, riboflavin and some essential minerals like iron, calcium, manganese and other trace elements. Tomato has rich medicinal value. The pulp and juice promote gastric secretion and serve as blood purifier and intestinal antiseptic. Leaves, stems and green unripe fruits contain toxic alkaloid is tomatine (Glycoalkaloid). Tomatine content in small hard tomato is 300 mg / 100 g of edible portion and that of larger green fruits is 150 mg / 100 g.

## 2. Bhendi (Okra)

They are rich sources of dietary fibre, minerals, and vitamins. The composition of bhendi per 100 g of edible fruit is as follows

Constituents	Content	Constituents	Content
Moisture	: 89.6 g	Vitamin A	: 88 I.U
Protein	: 1.9 g	Thiamine	: 0.07 mg
Fat	: 0.2 g	Riboflavine	: 0.1 mg
Mineral matter	: 0.7 g	Nicotinic acid	: 0.60 mg
Fibre	: 1.2 g	Vitamin C	: 13 mg



Carbohydrates	: 6.4 g	Calcium	: 66 mg
Sodium	: 7 mg	Magnesium	: 43 mg
Potassium	: 103 mg	Iron	: 1.5 mg
Copper	: 0.19 mg	Phosphorus	: 56 mg
Sulphur	: 30 mg		

The pods provide very low calories (30 calories per 100 g) besides containing no saturated fats or cholesterol. The rich fibre and mucilaginous content in okra help in smooth peristalsis of digested food particles. Okra mucilage refers to the thick and slimy substance found in fresh as well as dried pods. Mucilaginous substances are chemically acidic polysaccharides associated with proteins and minerals. Although nature of the polysaccharides varies greatly, galactose (25%), rhamnose (22%), galacturonic acid (27%) and amino acids (11%). The pods contain high amounts of vitamin A and flavonoid anti-oxidants such as beta carotenes, xanthin and lutein. It is one of the green vegetables with highest levels of these anti-oxidants. The flowers contain two flavonol pigments viz., gossypetin ( $C_{15}H_{10}O_8$ ) and quercetin ( $C_{15}H_{10}O_7$ ) in the form of their glucosides. Gossypetin is the major component. Anthocyanin present in flower is cyaninidin comprised 28.5% of the flavonoid content of red flower.

Fresh pods are the good source of folates providing 22% of Recommended Daily Allowance (RDA) per 100 g. Folate increases the growth and development of the fetus brain. It is also rich in B-complex group of vitamins like niacin, vitamin B-6 (pyridoxine), thiamin and pantothenic acid. The pods also contain good amounts of vitamin K and a good source of minerals such as iron, calcium, manganese and magnesium. Okra seed is mainly composed of oligomeric catechins (2.5 mg/g of seeds) and flavonol derivatives (3.4 mg/g of seeds), while the mesocarp is mainly composed of hydroxycinnamic and quercetin derivatives (0.2 and 0.3 mg/g of skins). Its ripe seeds are roasted and ground to form a caffeine free substitute for coffee. Fibre formation in the fruit starts from 6<sup>th</sup> day of fruit formation and a sudden increase in fibre content from the 9<sup>th</sup> day is observed.

### 3. Brinjal (Egg plant)

Brinjal has been a staple vegetable in our diet since ancient times. In general, oblong fruited cultivars are rich in total water soluble sugars, whereas long fruited cultivars contain large amounts of free reducing sugars, anthocyanin, phenol and glycoalkaloids (solasodine). The composition of brinjal per 100 g of edible fruit is as follows:

Constituents	Content	Constituents	Content
Moisture	: 92.7 g	Vitamin A	: 124 I.U

Protein	: 1.4 g	Thiamine	: 0.04 mg
Fat	: 0.3 g	Riboflavine	: 0.11 mg
Mineral matter	: 0.3 g	Nicotinic acid	: 0.09 mg
Fibre	: 1.3 g	Vitamin C	: 12 mg
Carbohydrates	: 4.0 g	Calcium	: 18 mg
Sodium	: 3 mg	Magnesium	: 16 mg
Potassium	: 229 mg	Iron	: 0.9 mg
Copper	: 0.17 mg	Phosphorus	: 47 mg
Sulphur	: 44 mg	Chlorine	: 52 mg

Eggplant is very low in calories and fats but rich in soluble fibre content. 100 g provides just 24 calories but contributes about 9% of RDA (recommended daily allowance) of fibre. Effective to control high blood cholesterol. The peel or skin (deep blue/purple varieties) has significant amounts of phenolic flavonoid phyto-chemicals called anthocyanins (Nasunin) which act against cancer, aging, inflammation, and neurological diseases. Polyphenolases have been reported in brinjal. The oxygen radical absorbance capacity (ORAC) is 993  $\mu\text{mol TE}/100\text{ g}$ . It is one of the low glycemic index (GI) vegetables. GI is a number associated with a particular type of food that indicates the food's effect on a person's blood glucose level. It contains many essential B-complex groups of vitamins such as pantothenic acid (vit B5), pyridoxine (vit B6), thiamin (vit B1) and niacin (B3). It is a good source of minerals like manganese, copper, iron and potassium. Manganese is used as a co-factor for the antioxidant enzyme, superoxide dismutase.

Bitterness in brinjal is mainly because of glycoalkaloid called solasodine. High amount of glycoalkaloid produces a bitter taste and off flavor. Discolouration in brinjal fruit is attributed to high polyphenol oxidase activity. The browning of eggplant flesh results from the oxidation of polyphenols, such as the most abundant phenolic compound in the fruit is chlorogenic acid. Green cultivars have better processing facilities than purple cultivars.

#### **4. Moringa (Drum stick)**

The leaves, flowers and fruits are used in culinary preparations. Moringa leaves are an excellent source of protein 100 g of fresh raw leaves carry 9.8 g of protein or about 17.5% of daily required levels. Fresh leaves rich source of vita A and good sources of minerals Dry, powdered leaves indeed are an excellent sources source of several quality amino acids. The calcium in moringa leaves is bound as crystals of [calcium oxalate](#) which may inhibit calcium availability to body. The pods are particularly high in vitamin C, but are also a good source of [dietary fibre](#), [potassium](#),

[magnesium](#) and [manganese](#). The greens, as well as pods, also contain good amounts of many vitamin B-complex.

The chemical composition of pod and leaves is:

Constituents	Pod	Leaves
Moisture	86.9 %	75.9 %
Carbohydrates	8.53 %	8.28 %
Protein	2.5 %	9.40 %
Fat	0.1 %	1.7 %
β Carotene	110 µg	6780 µg
Thiamine	0.05 mg	0.06 mg
Riboflavin	0.07 mg	0.05 mg
Vitamin C	141 mg	220 mg
Calcium	30 mg	185 mg
Iron	5.3 mg	7 mg

Its leaves, when eaten in large quantities, may cause stomach upset, gaseous distension and loose stools due to their laxative properties. The seed yields 38-40% edible oil known as 'oil of ben' used for lubricating delicate machines and as a biofuel. The seed cake remaining after oil extraction may be used as a fertilizer or as a flocculent to purify water. Moringa seeds contain dimeric cationic proteins, which absorb and neutralize colloidal charges in turbid water, causing the colloidal particles to clump together, making the suspended particles easier to remove as sludge by either settling or filtration. Moringa is used to combat malnutrition, especially among infants and nursing mothers. Moringa root contains alkaloid spirochin, which is a potential neuro-paralytic toxin.

## 5. Greens

The leaves and tender stems of *Amaranthus* are rich in proteins, minerals, vitamins A, C and Fe. The composition of greens is as follows.

Moisture	: 85.7 %	Vitamin A	: 9200 I.U
Protein	: 4.0 %	Thiamine	: 0.03 mg
Fat	: 0.5 %	Riboflavine	: 0.10 mg
Mineral matter	: 2.7 %	Nicotinic acid	: 1 mg
Fibre	: 1.0 %	Vitamin C	: 99 mg
Carbohydrates	: 6.3 %	Calcium	: 3.97 mg
Sodium	: 230 mg	Magnesium	: 247 mg
Potassium	: 341 mg	Iron	: 25.5 mg

Sulphur : 61 mg      Phosphorus : 83 mg

### **Cruciferous vegetables**

Many commonly consumed cruciferous vegetables come from the Brassica genus, including cabbage, cauliflower, broccoli, Brussels, turnips etc. Cruciferous vegetables are unique in that they are a rich source of sulfur containing compounds called glucosinolates, that impart a pungent aroma and a spicy (bitter) taste. Glucosinolates can be classified into three categories based on the chemical structure of their amino acid precursors; aliphatic glucosinolates (eg. Glucoraphanin), indole glucosinolates (eg. Glucobrassicin) and aromatic glucosinolates (eg. Gluconastrutin). Glucosinolates and their breakdown derivatives (metabolites) especially isothiocyanates and indole-3-carbinol, exert a variety of biological activities that may be relevant to health promotion and disease prevention in humans.

The hydrolysis of glucosinolates which is catalysed by a class of enzyme called myrosinase, leads to the formation of breakdown compounds such as thiocyanates, isothiocyanates, indole-3-carbinol, oxazolidine-2-thiones, epithionitrile and nitrile. Indole-3-carbinol (an indole) and sulforaphane (an isothiocyanate) have been most frequently examined for their anticancer effects. These are defensive compounds against pathogen, insects and herbivores. These compounds are powerful antioxidants and known to help protect against breast, colon and prostate cancer as well as it reduces LDL (low density lipoprotein) levels in the blood. When raw cruciferous vegetables are chopped during the cooking process, glucosinolates are rapidly hydrolysed by myrosinase, generating metabolites that are then absorbed in the proximal intestine. A neutral pH may favour the formation of isothiocyanates from glucosinolates. Once absorbed, isothiocyanates such as glucoraphanin derived sulforaphane, are conjugated to glutathione in the liver and then sequentially metabolized.

Glucobrassicin, the glucosinolate precursor to indole-3-carbinol (plant sterol) is found in substantial quantities in a number of cruciferous vegetables. Typical levels in vegetables such as cabbage, cauliflower, Brussels sprouts and turnips range from 0.1 to 3.2 mmol/kg fresh plant weight. Indole-3-carbinol, which appears to function as an anti-estrogen agent. Di-indolyl-methane (DIM) is a compound derived from the digestion of indole-3-carbinol, found in cruciferous vegetables such as broccoli, Brussels sprouts and cabbage. DIM is a lipid soluble compound found to be effective as immune modulator, anti-bacterial and anti-viral compound.

Apart from these phytochemicals, all these vegetables are rich in carotenoids (beta-carotene, lutein and zeaxanthin), vitamins like C, K, B2, B6 and folic acid. Also found in them are

minerals such as potassium, magnesium and the potent antioxidant selenium. They are also a rich source of soluble fiber and plant based Omega 3.

Cabbage and other cruciferous vegetables contain small amounts of thiocyanate, a compound associated with goiter formation when iodine intake is deficient. Excessive consumption of cabbage may lead to increased intestinal gas which causes bloating and flatulence due to the trisaccharide (raffinose), which the human small intestine cannot digest.

The composition of cabbage and cauliflower is as follows:

Parameters	Cauliflower	Parameters	Cauliflower
Moisture	91.7 %	Phosphorus	2.71 %
Carbohydrates	4.9 %	Iron	205 ppm
Protein	2.4 %	Copper	15 ppm
Fat	0.2 %	Iodine	218 ppm
Minerals	2 -3 %	Calcium	0.73 %
Fibre	1.0 %	Vitamin A	400 I.U
Potassium	3.58 %	Vitamin B1	27.1 I.U
Sulphur	1.07 %	Vitamin C	148.2 mg

### **Cauliflower**

It is very low in calories (26 cal/100 g). Its florets contain about 2 g of dietary fibre per 100 g providing about 5% of recommended value. Fresh cauliflower is an excellent source of vitamin C; 100 g provides about 48.2 mg or 80% of daily recommended value. It contains good amounts of many vital B-complex groups of vitamins such as folates, pantothenic acid (vitamin B5), pyridoxine (vitamin B6), thiamin (vitamin B1), niacin (B3) as well as vitamin K. It is also good source of minerals such as manganese, copper, iron, calcium and potassium.

### **Radish**

Radish, like other cruciferous and Brassica family vegetables Radish is one of very low calorie root vegetables (16 cal per 100 g). Characteristic pungent flavor is due to the presence of volatile (isothiocyanate anti-oxidant compound called sulforaphane) and the colour of the pink is due to the presence of anthocyanin pigments. Studies revealed that the sulforaphane has cytotoxic effects on cancer cells. Thiocyanate content increases with increasing sulphate level in soil solution. It is a good source of vitamin C (15-40 mg / 100 g of edible portion) and minerals. Pink skinned radish is richer in ascorbic acid than white skinned one. The chemical composition of radish is as follows:

Constituents	Radish roots		Radish tops
	White cultivar	Pink cultivar	
Moisture	94.4 %	90.8 %	90.30 %
Carbohydrate	3.40 %	6.80 %	3.4 0%
Protein	0.70 %	0.60 %	2.70 %
Fat	0.10 %	0.30 %	0.60 %
Fibre	0.80 %	0.60 %	0.90 %
Minerals	0.60 %	0.90 %	2.10 %
Calcium	30 mg	50 mg	310 mg
Phosphorus	25 mg	20 mg	60 mg
Iron	0.60 mg	0.50 mg	16.10 mg
Vitamin A	5 I.U	5 I.U	18.6 I.U
Thiamine	0.02 mg	0.06 mg	0.03 mg
Riboflavin	0.04 mg	0.02 mg	0.16 mg
Nicotinic Acid	0.50 mg	0.40 mg	0.30 mg
Vitamin C	15 mg	17 mg	103 mg

Radishes are an excellent source of antioxidants, electrolytes, minerals, vitamins and dietary fiber. Fresh roots are rich in vitamin C; provide about 15 mg or 25% of RDI (Reference Daily Intake) of vitamin C per 100 g. They contain adequate levels of folates, vitamin B-6, riboflavin, thiamin and minerals such as iron, magnesium, copper and calcium. They contain many phytochemicals like indoles which are detoxifying agents and zeaxanthin, lutein and beta carotene, which are flavonoid antioxidants. Their total antioxidant strength, measured regarding oxygen radical absorbance capacity (ORAC value) is 1736  $\mu\text{mol TE}/100\text{ g}$ . The leaves of radish are a good source for protein extraction on a commercial scale and the radish seeds are a potential source of non drying fatty oil used in soap making, and illuminating.

### Peas

Highly nutritive, contains high percentage of digestible proteins along with carbohydrates, vitamins (A and C) and minerals (Ca and Fe). It is a vegetable of low glycemic index. The composition of peas is as follows:

Constituent	Content	Constituent	Content
Moisture	: 74.7 %	Vitamin C	: 40 mg
Carbohydrate	: 14.45 %	Calcium	: 25 mg

Protein	:	5.42 %	Phosphorous	:	108 mg
Fat	:	0.4 %	Potassium	:	244 mg
$\beta$ carotene	:	449 $\mu$ g	Iron	:	1.47 mg
Riboflavin	:	0.1 mg	Folates	:	65 $\mu$ g
Thiamine	:	0.26 mg	Vitamin K	:	24.8 $\mu$ g

Peas are relatively low in calories compared to beans, and cowpeas. 100 g of green peas provide 81 calories and no cholesterol. Fresh pea pods are excellent source of folic acid. 100 g provides 65  $\mu$ g or 16% of recommended daily levels of folates. Fresh green peas are very good in ascorbic acid (vitamin C). Contains 40 mg/100 g or 67% of daily requirement of vitamin C. Peas contain phytosterols especially  $\beta$ -sitosterol which help to lower cholesterol levels in the body. Garden peas are also good in vitamin K. 100 g of fresh leaves contains about 24.8  $\mu$ g of vitamin K. It contains phyto nutrients saponin viz., Pisum saponin – I and II. It also contains omega – 3 fats in the form of alpha linolenic acid (ALA). Fresh green peas also contain adequate amounts of anti-oxidants flavonoids such as carotenes, lutein and zeaxanthin as well as vitamin-A. In addition to folates, peas are also good in many essential B-complex vitamins such as pantothenic acid, niacin, thiamin, and pyridoxine. They are rich source of many minerals such as calcium, iron, copper, zinc, and manganese.

## Lecture-6

### **Chemical composition of spices and condiments (Turmeric, chillies, pepper, ginger, onion, garlic), Beverages (tea & coffee) and Tuber crops (Potato & Tapioca)**

Spices and condiments have played a dramatic role in civilization and in the history of nations. The delightful flavour and pungency of spices make them indispensable in the preparation of palatable dishes. In addition, they are reputed to possess several medicinal and pharmacological properties and hence find position in the preparation of a number of medicines. Spices impart aroma, colour and taste to food preparations and sometimes mask undesirable odours. Volatile oils give the aroma and oleoresins impart the taste. Aroma compounds play a significant role in the production of flavourants, which are used in the food industry to flavour, improve and increase the

appeal of their products. They are classified by functional groups, e.g. alcohols, aldehydes, amines, esters, ethers, ketones, terpenes, thiols and other miscellaneous compounds.

A spice is a dried [seed](#), [fruit](#), [root](#), [bark](#), or [vegetative substance](#) primarily used to add flavour and [coloring](#) to a food. Sometimes a spice is used to hide other flavours. Eg. Coriander, Ginger. It posses antimicrobial, antioxidant and antibacterial properties.

A condiment is an edible substance or food adjuncts added to impart a particular flavor, enhance its flavour, or to complement the dish by enhancing the taste. Eg. Chilli, Black pepper

## 1. Turmeric

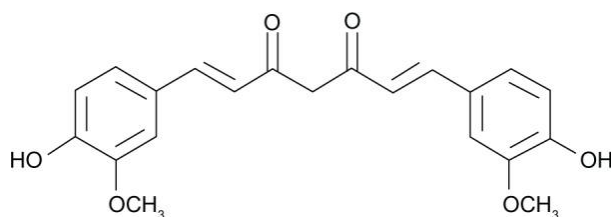
Turmeric (*Curcuma longa*) is a rhizomatous herbaceous perennial plant of the ginger family; Zingiberaceae. It is used in India for more than 1000 years in Ayurvedic medicine. It has anti-inflammatory, antioxidant, antitumour, antibacterial and antiviral activities.

### Chemical composition

Turmeric powder is approximately 60-70% carbohydrates, 6-13% moisture, 6-8% protein, 5-10% fat, 3-7% dietary minerals, 3-7% essential oils, 2-7% dietary fiber and 1-6% curcuminoids. It is also rich in essential vitamins like B6 (90 mg/100g) and C (43 mg/100g) and also good source of minerals like potassium (2525 mg/100g), iron (230 mg/100g), magnesium (48 mg/100g), sodium (38 mg/100g) and calcium (18 mg/100g).

### Turmeric oil

Dried rhizomes and leaves are used industrially to extract the volatile oil. Generally, the oil is extracted by steam distillation. Dried rhizomes contain 5-6% and leaves contain about 1.0-1.5% oil. The peculiar turmeric aroma is imparted by ar-turmerone, the major aroma principle in the oil. The components of the volatile oil are mono and sesquiterpenes like alpha and beta pinene, alpha phellandrene, camphor, camphene, zingiberene, alpha and beta curcumenes. The rhizomes contain curcuminoids (2.5–6%) and are responsible for the yellow colour. The main constituent of the curcuminoids is curcumin. Curcumin is the main active ingredient in turmeric. Turmeric contains phytochemical compounds of diarylheptanoids curcumin along with other constituents (demethoxy curcumin and bisdemethoxy curcumin) known as curcuminoids. Curcumin constitutes about 0.30 to 5.4% (3.14% on average) of powdered turmeric, having variations in content among the species of *Curcuma longa*.





## 2. Chillies

These are the green or dried ripe fruits of *Capsicum annuum* and sometimes *Capsicum frutescens*. Pungency and colour determines the quality of the product. The composition of green chilli is as follows

Constituent	Content	Constituent	Content
Moisture	- 85.7 %	Sodium	- 6.5 mg
Carbohydrate	- 3.0 %	Sulphur	- 34 mg
Protein	- 2.9 %	Chlorine	- 15 mg
Fat	- 0.6 %	Iron	- 1.2 mg
Minerals	- 1.0 %	Riboflavin	- 0.39 mg
Fibre	- 6.8 %	Nicotinic acid	- 0.9 mg
Calcium	- 30 mg	Thiamine	- 0.19 mg
Magnesium	- 24 mg	Vitamin A	- 292 I.U
Potassium	- 217 mg	Vitamin C	- 111 mg
Phosphorus	- 80 mg	(mg of the content is per 100 g)	

Chillies contain capsaicin ( $C_{18}H_{27}O_3N$ ) which is a condensation product of 3-hydroxy-4-methoxy benzylamine and decylenic acid. Capsaicin is the active ingredient that gives peppers their pungency. Capsaicin content of red chilli is 0.34 %. The unique capsicum carotenoids are capsanthin, capsorubin and cryptocapsin. The major red colour in chilli due to the presence of capsanthin and capsorubin, while the yellow-orange colour is from  $\beta$ -carotene and violaxanthin.



Capsanthin, the major carotenoid in ripe fruits, contributes up to 60% of the total carotenoids. Capsanthin and capsorubin increase proportionally with advanced stages of ripeness, with capsanthin being the more stable of the two. The other pigments are zeaxanthin and cryptoxanthin. Dry chillies also contain xanthophylls. The fixed oil content varies from 9-20 % while it has relatively low volatile oil content ranging from 1-2.6 %. Fresh chili, red and green, are rich source of vitamin-C and A. Chillies are also good in B-complex group of vitamins such as niacin, pyridoxine (vitamin B6), riboflavin and thiamin (vitamin B1). Chillies contain a good amount of minerals like potassium, manganese, iron, and magnesium. Scoville scale: measurement of

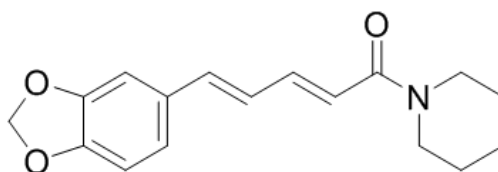
the pungency (spicy heat) of chili peppers as Scoville heat units (SHU). Capsaicin: 16,000,000 SHU.

### 3. Pepper

There are two types of pepper namely black pepper (prepared from dried immature berries, strong pungent) and white pepper (prepared by removal of mesocarp of matured berries, mild pungent). The composition of black pepper is

Constituent		Content (%)
Moisture	:	8.7 – 21.7
Total N	:	1.55 – 2.67
Starch	:	28 -49
Crude fibre	:	8.7 - 18
Crude piperine	:	2.8 -9
Volatile oil	:	2 -3.8
Ash	:	2.6 -5.6

Black pepper contains about 2.0–2.6% volatile oil and about 6–13% oleoresin. Pepper is valued for its pungency and flavour, which is attributed by the alkaloid piperine along with its isomer chavicine and the volatile oil. Piperine is the major constituent of pepper oleoresin.

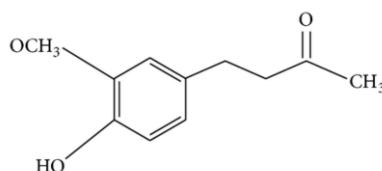


Black pepper oil contributes towards the aroma, which varies between 2 and 5 % in the berries and oleoresin contributes towards the overall taste. The main constituent of oils are monoterpene hydrocarbons such as pinene ( $\alpha$  and  $\beta$ ), limonene, sabinene, myrcene and the major sesquiterpene hydrocarbon is  $\beta$ -caryophyllene. These active principles in the pepper may increase the digestion power by stimulating gastro-intestinal enzyme secretions. Black pepper contains a good amount of minerals like potassium, phosphorus, calcium, zinc, manganese, iron, and magnesium. They are also an excellent source of many vital B-complex groups such as pyridoxine, riboflavin, thiamin and niacin besides many anti-oxidant vitamins such as vitamin-C and A. They are also rich in flavonoid polyphenolic anti-oxidants like carotenes, cryptoxanthin and zea-xanthin. Peppers are known for its anti-inflammatory, carminative and anti-flatulent properties.

### 4. Ginger

Ginger is used in medicine as carminative and aromatic stimulant to gastro intestinal tract. It is used as analgesic, sedative, antipyretic and antibacterial. Ginger rhizome contains steam volatile oil, pungent compounds, resin, proteins, cellulose, pentasans, starch and mineral matter. Crude fibre content is 10 %. Pungent principle is 1-3 % in freshly prepared dried ginger. Starch comprises 40-60 % of the rhizome on dry weight basis. Essential oil is 3% (Sesquiterpenoids with Zingiberene).

The characteristic fragrance and flavor of ginger result from volatile oils that compose 1-3% of the weight of fresh ginger, primarily consisting of zingerone, shogaols and gingerols. Zingerone is produced from gingerols during drying, having lower pungency and a spicy-sweet aroma. The aroma and flavour of ginger are determined by the composition of its steam volatile oil, which is comprised mainly of sesquiterpene hydrocarbons, monoterpene hydrocarbons and oxygenated monoterpenes. The monoterpene constituents are believed to be the most important contributors to the aroma of ginger and they tend to be relatively more abundant in the natural oil of the fresh (green) rhizome than in the essential oil distilled from dried ginger.



## 5. Onion

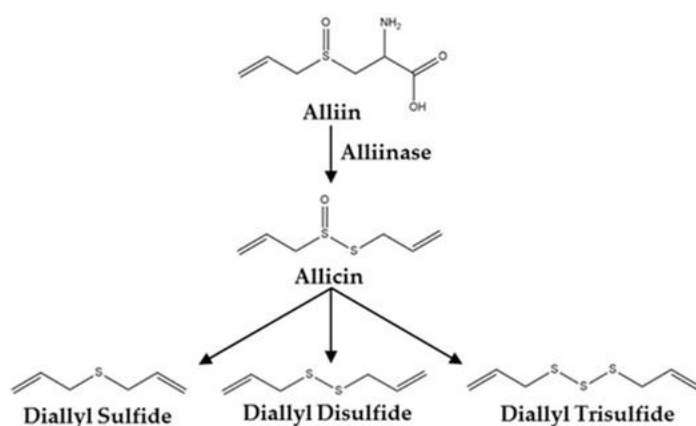
Most onion cultivars are about 89% moisture, 9% carbohydrates (including 4% sugar and 2% dietary fibre), 1% protein and negligible fat. Onions contain low amounts of essential nutrients and have an energy value of 166 kJ (40 Calories) in a 100 g. As onions are sliced, they release a class of enzymes, allinases, which break down amino acid sulfoxides, generating sulfenic acids. A specific sulfenic acid (1-propenesulfenic acid) formed when onions are cut, is rapidly rearranged by a second enzyme, called lachrymatory factor synthase (LFS), to produce syn-propanethial-S-oxide. It is a member of a class of organosulfur compounds, is a liquid that acts as a lachrymatory agent (triggers tearing and stinging on contact with the eyes). Sharp, pungent smell of onion is due to its sulfur compound, allyl propyl disulfide. Thiosulfinates are the primary flavour and odour producing molecules in an onion. These compounds are not present in intact bulbs, but are formed via enzymatic reaction from sulfur amino acids.

- Onions are a rich source of chromium, a trace mineral that helps tissue cells respond appropriately to insulin levels in the blood. It thus helps facilitate insulin action and control sugar levels in diabetes.

- They are also a good source of antioxidant flavonoid quercetin, which is found to have anti-carcinogenic, anti-inflammatory and antidiabetic functions.
- They are also good in antioxidant vitamin-C and mineral manganese. Onions are also good in the B-complex group of vitamins like pantothenic acid, pyridoxine, folates and thiamine

## 6. Garlic

Garlic is a rich source of carbohydrates, protein and phosphorus. Ascorbic acid content is high in green garlic. It contains a colourless, odourless water soluble amino acid alliin which is responsible for the broad spectrum of anti bacterial activity. When fresh garlic is chopped or crushed, the enzyme alliinase breaks down alliin to produce allicin ( $C_6H_{10}OS_2$ ), which is an ester.



Allicin is responsible for the aroma of fresh garlic. The allicin generated is unstable and quickly changes into a series of other sulfur-containing compounds such as diallyl disulfide and diallyl trisulfide, are major contributors to the characteristic odour of garlic. Allicin is part of a defense mechanism against attacks by pests on the garlic plant. Allicin possess antibacterial anti oxidant and antifungal properties. It contains 0.1 % volatile oil. The chemical composition of raw garlic is:

Constituent		Content (%)
Moisture	:	59
Carbohydrates	:	33
Protein	:	6.0
Fat	:	<1
Dietary fibre	:	2
Calcium	:	0.03
Phosphorus	:	0.31
Iron	:	0.001

The constituents of the oil are diallyl disulphide, diallyl trisulphide, allyl propyl disulphide, diethyl disulphide etc. With anti oxidant properties, it promotes the heart and immune systems by enhancing the immune cell activity and maintains healthy blood circulation. It helps the body to inhibit the growth and reproduction of germs. One milligram of allicin is equal to 15 standard units of penicillin. Garlic can also reduce cholesterol. Garlic's strong- smelling sulfur compounds are metabolized, forming allyl methyl sulfide (AMS) and cannot be digested and is passed into the blood.

### **Why Spices and Condiments in diet?**

- Spices and condiments contain plant-derived chemical compounds having disease preventing and health promoting properties. They are known for its anti-inflammatory, carminative and anti-flatulent properties.
- They have anti-clotting action, prevent clogging of platelets in the blood vessels, thus helps easing blood flow, preventing stroke and coronary artery disease.
- The active principles increase the digestion power by stimulating gastro-intestinal enzyme secretions.
- Decoction of certain spices is taken for the treatment of colds, influenza, mild fevers, indigestion, stomach upset, and painful menstruation.
- They also have natural anti-helminthes (control worm infestation) function
- The essential volatile oils act as a rubefacient increasing the flow of blood to make the skin feel warmer. It is a popular home remedy for arthritis and sore muscles, used either as a poultice or in hot baths.
- Their essential oils are used in aromatherapy as well as de-odorants in the perfume industry.
- They contain a good amount of minerals like potassium, manganese, iron and magnesium.

### **Beverages: Coffee and tea**

It is liquid preparation from leaves/beans which acts as stimulant.

#### **1. Coffee**

The important constituent, which acts as stimulant in body, is caffeine, the alkaloid which is also present in tea and cocoa to a smaller extent. Leaves and beans of coffee contain caffeine ( $C_8H_{10}N_4O_2$  - 1, 3, 7 trimethyl xanthine) and its content varies with species and varieties (*Coffea arabica*- 1.2 to 1.8% and *C. robusta* - 2 to 2.6%). Coffee seeds contain 1–2% of caffeine and traces of theophylline and theobromine. Some species like Madagascar coffee is free from caffeine content. Roasting brings rupture of oil canal in bean resulting in escape of oil as evidenced by oily coat on roasted bean. The nicotinic acid derivative trigonelline is present in green seeds to the

extent of about 0.25–1%; during roasting, this is extensively converted into nicotinic acid (vitamin B3). During roasting, citric and malic acids are partly degraded into aconitic and fumaric acids.

Caffeine undergoes little loss during roasting but considerable formation of gases especially CO<sub>2</sub> occurs. Part of which is held in the bean itself giving it slightly a puffed up appearance as compared with raw bean. Total oil content in the raw bean is 12 to 13% of which volatile oil escape during roasting. Aroma and flavour associated with roasted bean is mainly due to the presence of essential oil called caffiol, which is a water soluble infusion.

#### Composition of Coffee

Constituent	Raw bean	Roasted bean
Moisture (%)	8.75	3.75
Ash (%)	4.41	4.49
Oil (%)	12.96	13.76
Caffeine (%)	1.87	1.81
Crude fibre (%)	20.7	14.7
Protein (%)	9.5	12.9

#### Nutritional significance of coffee

Coffee consumption reduces the risk of prostate cancer, Alzheimer's disease, dementia, Parkinson's disease, heart disease, diabetes mellitus type 2, non-alcoholic fatty liver disease, etc. Specifically, the antidiabetic effect of caffeine has been attributed to caffeic acid and chlorogenic acid. The presence of antioxidants in coffee has been shown to prevent free radicals from causing cell damage. Roasted coffee has a stronger antioxidant effect than green coffee.

However coffee consumption makes anemic by interfering with iron absorption due to the presence of polyphenols, more specifically in mothers and infants. Drinking caffeinated coffee can cause a temporary stiffening of arterial walls. Coffee may aggravate gastroesophageal reflux disease, migraines and cause anxiety and sleep disturbances.

## 2. Tea

Tea is an aromatic beverage commonly prepared by pouring hot or boiling water over cured leaves of the tea plant, *Camellia sinensis*. The most important constituents, which make tea as a beverage, are polyphenols, caffeine and essential oil (caffeine is also called theanine). Cell sap contains higher amount of potassium.

#### Phenols

The most important and characteristic component in the cell sap is polyphenol, which undergoes a series of changes when the leaf is macerated during curing of tea. A group of natural phenols called flavonoids contribute to better health. The phenols occurring in tea are catechin which constitutes 25 % of fresh tea leaves. The four types of catechin are catechin, epicatechin, galocatechin and epigallocatechin. Other phenolic compounds are theaflavins and tannins which contribute to bitterness and astringency of steeped black tea.

The polyphenol and caffeine content is highest in buds and top leaf and successively diminish in lower leaves. Good quality tea is a product of good leaf with higher polyphenol and increased enzyme activity. Tea grown under shade has decreased polyphenol content.

### **Pigments**

Chlorophyll of leaves enters into chemical reaction and decomposes during process of fermentation. The red and yellow pigments of tea leaves are derived from anthocyanins and flavones. Black tea is made from withered, rolled, fermented and dried tea leaves. In black tea manufacture, polyphenol (tannins) are oxidized by enzymes in the presence of air, the bruised condition of old leaves and all sap is brought to the surface. Tannin is oxidized and reduced in quantity. Manufactured tea contains only 4.5% tannin as against 13 to 14% tannins present in fresh leaves.

Green tea is made from tea leaves which are steamed and dried the leaves to prevent oxidation and does not undergo withering and fermentation. Green tea avoids the above procedure and tannin is not lost to some extent. Too long soaking of tea leaves in hot water dissolves greater proportion of tannin and makes tea bitter in taste. All beverage crops contain xanthine compound, which is responsible for imparting particular flavour. Processing helps in getting maximum flavour. Most polyphenols in green tea are flavan-3-ols (catechins). Processing can be done by fermentation and heating / roasting treatment.

### **Fermentation**

After the harvest, the leaves turn progressively darker due to break down of chlorophyll and release of tannins. This enzymatic oxidation process is called as fermentation in which the plant's intracellular enzyme causes the tea to darken. During oxidation, colorless catechins (up to 40% in dried leaf) are converted into intensely colored theaflavins and thearubigins. Both of these groups contribute towards the orange-red colouration of tea, as well as to the taste. Oxidative degradation of leucine, isoleucine and valine takes place. Most polyphenols in black tea are theaflavins-bitterness and astringency of steeped black tea-due to increased oxidation of leaves.

### **Nutritional significance of tea**

Tea contains a large number of bioactive chemicals, including flavonoids, amino acids, vitamins, caffeine and several polysaccharides. Green and black tea may give protection against cancer, and the catechins in green tea are effective in preventing obesity-related cancers. Both green and black tea gives protection against cardiovascular disease.

## Tuber crops

### Potato

Potatoes are one of the richest sources of starch, vitamins, minerals and dietary fibre. 100 g provides 70 calories, very little fat (0.1 g per 100 g) and no cholesterol. They are very good natural sources of both soluble and insoluble fibre. The fibre content aids in slow digestion of starch and absorption of simple sugars in the gut. Potatoes are often broadly classified as high in the glycemic index (GI). The composition of potato is as follows:

Constituent	Content	Constituent	Content	
Moisture	: 80 %	Sulphur	: 95 mg	
Carbohydrates	: 18 %	Copper	: 0.23 mg	
Protein	: 2.1 %	Vitamin A	: 139 I.U	
Fat	: 0.1 %	Thiamine	: 0.1 mg	
Fibre	: 4 %	Riboflavin	: 0.02 mg	
Minerals	: 0.8 %	Nicotinic Acid	: 0.8 mg	The
Calcium	: 14 mg	Vitamin C	: 19.7 mg	tubers are
Phosphorus	: 57 mg	Oxalic acid	: 14 mg	one of the
Iron	: 1.0 mg	Potassium	: 421mg	richest
				sources of B-

complex group of vitamins such as pyridoxine (vitamin B<sub>6</sub>), thiamine, niacin, pantothenic acid and folates. Fresh potato along with its skin is good source of antioxidant vitamin; vitamin-C. 100 g of fresh tuber provides 19.7 mg of vitamin C. They also contain adequate amounts of many essential minerals like iron, manganese, magnesium, phosphorous, copper and potassium. Red and *russet potatoes* contain good amount vitamin A, and antioxidant flavonoids like carotenes and zeaxanthins. Recent studies revealed that flavonoid antioxidant; quercetin present in potatoes has anti-cancer and cardio-protective properties. Potato contains toxic compounds known as glycoalkaloids, of which the most prevalent are solanine and chaconine. These alkaloids present in the greatest concentrations just underneath the skin and may increase proportionately with age. Cooking at high temperature destroys these toxic compounds (10 -20 mg / kg). Maximum limit is 200 mg / kg. Often



you may across greening discoloration with sprouts over their surface, is an indication of old stock and sign of formation of toxic alkaloid solanine.

### **Tapioca**

It is a starch extracted from cassava plant (*Manihot esculenta*). It is a staple food for millions of people in tropical countries, it provides only CHO food value, low in protein, vitamins and minerals. In other countries, it is used as a thickening agent in various manufactured foods

### **Nutritional value**

- Tapioca predominantly consists of carbohydrates, with each cup containing 23.9 grams for a total of 105 calories; it is low in saturated fat, protein and sodium.
- Cassava roots are very rich in starch & contain small amounts of ca (16 mg), p (27 mg) & vitamin C (20.6 mg) per 100 g
- However, they are poor in protein and other nutrients.
- In contrast, cassava leaves are a good source of protein (rich in lysine), but deficient in methionine and tryptophan.
- Raw cassava is 60% water, 38% carbohydrates, 1% protein
- Cooked cassava starch has a digestibility of over 75%.
- Cassava, also has antinutritional and toxic factors.
- Of particular concern are the cyanogenic glucosides of cassava (linamarin and lotaustralin).
- On hydrolysis (linamarase) these release hydrocyanic acid (HCN).
- The presence of cyanide in cassava is of concern for human and for animal consumption.
- It is a paralytic disease associated with several weeks of almost exclusive consumption of insufficiently processed bitter cassava.
- Cassava tubers and hay are used worldwide as animal feed.
- Cassava hay contains high protein (20–27% crude protein) and condensed tannins (1.5–4 percent CP).
- It is valued as a good roughage source for ruminants such as cattle.

## Lecture 7

### Alkaloids in medicinal plants (Cinchona, Gloriosa, Coleus & Aloe vera)

Alkaloids are organic nitrogenous bases found mainly in plants, but also to a lesser extent in microorganisms and animals. In addition to nitrogen, alkaloids contain carbon, hydrogen, oxygen and sulfur. One or more nitrogen atoms are present, typically as primary, secondary, or tertiary amines and this usually confers basicity to the alkaloid, facilitating their isolation and purification since water-soluble salts can be formed in the presence of mineral acids (acid-base reaction). Alkaloids have a wide range of pharmacological activities including antimalarial (e.g. quinine), antiarrhythmic (e.g. quinidine) and antihyperglycemic (e.g. piperine). Many have found use in traditional or modern medicine, or as starting points for drug discovery.

#### 1. Cinchona

A considerable number of alkaloids have been characterized in cinchona bark, four of which account for some 30–60% of the alkaloid content. These are quinine, quinidine, cinchonine, cinchonidine, dihydroquinine and dihydroquinidine. Quinine is a major alkaloid is used for its anti-malarial action and anti-pyretic. Quinidine, cinchonine, and cinchonidine also have antimalarial properties, but these alkaloids are not as effective as quinine. In addition to its use in pharmacy, quinine, quinidine and their derivatives are utilized in insecticide formulations for the preservation of fur, feather, wool and textiles. The alkaloids also used in organic chemistry as organocatalysts in asymmetric synthesis. The alkaloids are often present in the bark in salt combination with quinic acid or a tannin material called cinchotannic acid. Cinchotannic acid decomposes due to enzymic oxidation during processing of the bark to yield a red pigment.

#### 2. Gloriosa

Gloriosa is a medicinal plant and all parts of the plant contain an alkaloid colchicine and related ones called gloriosine. The colchicines content in rhizome varies from 0.15 to 0.3% and in the seed varies from 0.7 to 0.9%. Rhizomes and seeds also contain isoperlolyrine and related tropolane alkaloids. Alkaloids are toxic if ingested, enough to cause human and animal fatalities, and if contact with the stems and leaves can cause skin irritation. All parts of the plant, (stem, leaves, flowers, fruits & tubers) are poisonous, but tubers are extremely poisonous. It induces polyploidy in plants.

The chemical constituents of glory lily are as follows.

Plant Part	Chemical constituent
Plant	Cornigerine, 3-demethyl-N-formyl-N-deacetylblumicolchicine,

	3-demethyl-g-lumicolchicine, 3- demethylcolchicines.
Young leaf	Cholidonic acid
Flower	Luterlin and its glucosides, lumicolchicine
Fresh tubers, roots and seeds	Colchicine, Superbine

### Medicinal properties in Siddha and Ayurveda

Plant Part	Uses
Tubers	Intermittent fevers, wounds, antifertility purpose, Gonorrhea and Leprosy
Roots	Abortifacient, Expectorant, Purgative, effective against insect bite, rheumatism and paralysis
Leaves	Effective against asthma, arthritis and lice

### 3. Coleus

Coleus is a perennial branched aromatic herb belonging to the family *Lamiaceae*. The active phytochemical present in coleus root is diterpenoid compound is forskolin (Coleus is the only source). Coleus has 68 chemical components including coleoside, cedrol, coleonic acid etc. It is used to treat disorders like high blood pressure, chest pain (angina) and as well as respiratory disorders such as asthma. The adverse reactions of forskolin include restlessness, coughing and gastro intestinal disturbances.

Coleus was used traditionally as a digestive aid to treat bloating and flatulence. This herb has also been used to treat pathogenic infections. The plant may be useful in treating glaucoma and skin problems. It can be used in weight loss because it can help to break down stored fat and inhibit the synthesis of adipose tissue. It affects the thyroid glands resulting in increased hormone production.

### 4. Aloe vera

*Aloe vera* is a succulent plant. The alkaloid content varies from 1-5 %. Typical phytochemicals is aloin and also glucomannans, salicylic acid and sterols. Extracts from *Aloe vera* are widely used in cosmetics and alternative medicine industries, being marketed for having rejuvenating, healing or soothing properties. *Aloe vera* is used extensively as an herbal remedy for treating human illnesses. *Aloe vera* gel is used as an ingredient in commercially available lotions, yogurt, beverages, and some desserts, although at certain doses, it has toxic properties when used either for ingested or topical applications. *Aloe vera* is used in multipurpose skin treatment which

may be due to the presence of saponin, a chemical compound that acts as an anti-microbial agent and hence used in wound healing.

Aloin, a compound found in the exudate of some Aloe species, was the common ingredient in laxative products in US during 2003, but FDA has banned its use. Aloe vera leaves also contain phytochemicals as acetylated mannans, polymannans, anthraquinone C-glycosides, anthrones, anthraquinones, such as emodin, and various lectins. These compounds are found to have purgative, anti inflammatory, anti viral and anti tumour activities. Aloe vera is used in anti diabetic drugs. Although the plant may have therapeutic effects, the pyrrolizidine alkaloids and anthraquinones can cause adverse reactions in human beings.

## **Lecture 8**

### **Pesticides- Définition, Classification and Trends in pesticide use**

#### **Pesticide**

Pest+i (many words are formed with connecting i) +cide, L-cida, it is from Latin word caedere means to kill, therefore the meaning of pesticide is to kill the pest. Pesticides are chemical substance or a mixture of chemical substances used for killing, repelling, mitigating, preventing, or even regulating pests, diseases/weed with a view to minimise the damage caused to crops, animals and indirectly on human health. The 19th century marked the dawn of manufactured chemical pesticides, when chemicals began to be extracted from their botanical sources and were purified in laboratories.

Agrochemicals: A chemical that is used in farming to enhance growth and yield of crops apart from chemicals that destroys pests and diseases. It Includes plant nutrients like fertilizers as well as other alternate chemicals like plant growth regulators, pheromones, attractants, repellents and bio-organism.

#### **Characteristics of an ideal pesticide**

- Broad spectrum activity
- Non toxic to mammals and plants
- Low toxicity to beneficial insects
- Good compatibility with other agrochemicals
- Low persistence
- Eco-friendly (environmental safety)
- Easily available formulation
- Low production cost

### **Classification of pesticides**

- Based on their use
- Based on target organism
- Based on chemical nature
- Based on mode of entry
- Based on mode of action

#### **A. Based on their use**

- Crop
- Veterinary
- Public health
- Stored grain
- Household insecticide

#### **B. Classification based on target organism**

Insecticides	Substances that prevent, destroy or kill the insects Eg. Malathion
Fungicides	Substances that prevent, destroy or inhibit the growth of fungi/ diseases in crops Eg. Mancozeb
Herbicides	Substances that prevent or inhibit the growth of unwanted plants/weeds. Eg. Butachlor
Rodenticides	Substances that inhibit, destroy or kill the rodents. Eg. Zinc phosphide
Acaricides	Substances that control mites, ticks, etc. Eg. Dicofol
Nematicides	Substances that control nematodes. Eg. Carbofuran
Molluscicides	Substances that prevent, repel, destroy or inhibit the growth of the Phylum – Mollusca. (Snails and slugs). Eg. Metaldehyde
Chemostreilants	Substances used to sterilize the insect pests. Eg. TEPA, Aphomide
Defoliants	Substances that cause the plant leave to die and fall away Eg. Gramoxone
Desiccants	Substances used to remove moisture from plants and make them to dry

	Eg. Penta Chloro Phenol
Attractants	Substances used to attract the pests. Eg. Methyl eugenol
Repellants	Substances that repels the pest from a treated plant. Eg. Citronella oil
Fumigants	Gaseous toxicants. Eg. Methyl bromide
PGR	Substances that accelerate or retard the growth. Eg. IAA
Sex attractants	Substances that attract the opposite sex. Eg. Gyplure
Pheromones	Chemical excreted in to the external environment by an animal and they elicit a specific response in receiving the individual of the species.
Algicides	Substances used for the destruction of algae and aquatic vegetation. Eg. Phygon
Bactericides	Substances used for the control of plant pathogenic bacteria. Eg. Streptomycin
Antiseptics	Substances used for protection of non-metals from micro- organisms. Eg. Zinc oxide

However, out of these, insecticides, fungicides and herbicides are most widely used.

C. Based on chemical nature

#### **i) In-organics**

#### **ii) Organics**

##### **a. Natural**

##### **1. Hydrocarbon oils**

2. Animal origin
3. Plant origin

##### **b. Synthetic organic compounds**

1. Insecticides
  - i. Organochlorines (OC)
  - ii. Organophosphorus (OP)
  - iii. Carbamates
  - iv. Synthetic Pyrethroids (SP)
2. Fungicides
3. Herbicides
4. Nematicides
5. Acaricides
6. Rodenticides

#### **i. Inorganics**

Comprise compounds of mineral origin and elemental sulphur. These are chemicals used during prewar periods. eg. Arsenic compounds (Lead arsenate, calcium arsenate) fluorine compounds (Sodium fluoride, sodium fluoro aluminate, sodium fluosilicate), sulphur, lime, barium carbonate, thallium sulphate and zinc phosphide. However, except sulphur and zinc phosphide others are not in use now.

## **ii. Organics**

### **a. Natural**

#### **1. Hydrocarbon oils**

The constituents of the oils are solely of hydrogen and carbon. Mineral (petroleum) oils and coaltar oils are recognised. Among coaltar oils, creosote oil and green oil or anthracene are useful for insecticidal purpose. Oils in their natural state are toxic to plants. They are used as solvents or diluents.

#### **2. Animal origin**

A toxin isolated from the marine annelids *Lumbriconereis heteropoda* and *L. brevicirra* has been found to possess insecticidal properties. The toxin is known as "Nereistoxin". It acts as a nerve poison and used against various lepidoptera. eg. Cartap (Padan).

#### **3. Plant Origin**

Toxicants derived from plants are used in insect control and among them, nicotine, pyrethrum, rotenone, derris, ryania, acorus and neem are well known.

### **b. Synthetic Organic Compounds**

These dominate the field of pest control today and a rigid classification of the many synthetic pesticides is rather difficult. However, they can be assigned to certain broad groups such as: Insecticides, fungicides, herbicides, nematicides, acaricides and rodenticides. The insecticides includes

#### **Organochlorines (OC)**

The basic constituents of these compounds are carbon, hydrogen and chlorine and certain compounds have oxygen and sulphur also. They are potent nerve poisons with quick knock down effects. They remain in the foliage and soil for longer periods and undergo slow degradation. Eg. DDT, HCH, aldrin, dieldrin, heptachlor, endrin and endosulfon. Organochlorine compounds are phytotoxic to cucurbits. Endosulfan is highly toxic to fish.

#### **Organophosphorus (OP)**

Insecticidal activity of OP compounds is attributed to their capacity to inhibit cholinesterase in insect's nerve tissue. Poisoning due to OP toxicants give rise to typical cholinergic symptoms. In insects they cause hyper activity, tremors, convulsions, paralysis and death Eg. Dichlorovos (DDVP), Phosphamidon, Monocrotophos, Chlorpyrifos, Quinalphos etc.

#### **Carbamates**

They are the esters of carbamic acid. They act more as nerve poison inhibiting cholinesterase mediated synaptic transmission. Carbaryl is an important member of this group. Others include carbofuran, aldicarb, oxamyl and methomyl.

### **Synthetic Pyrethroids**

These have good knock down effect in insects and are relatively less toxic to higher animals. Repeated use causes resurgence of insects. Eg. Cypermethrin, Decamethrin, Fenvalerate, Permethrin.

## **D. Based on mode of entry**

Based on the manner in which toxicants are administered to the insects and their mode of entry into the body, the insecticides are classified into.

### **i. Stomach poison**

The toxicant applied on the leaves and other parts of plant body, when ingested acts in the digestive system of the insect and kills it by deranged metabolism. The stomach poison should be palatable to the pest and should kill the insect quickly. Most organochlorines and organophosphorus compounds act as stomach poisons.

### **ii. Contact poison**

A toxicant, which kills the insect by means of contact or absorption in the cuticle and penetration in the body, is a contact poison. It may be directly applied on to the body of the insect as a spray or dust and entry through the cuticle and tracheae. All insecticides like organochlorines, organophosphates, carbamates and synthetic pyrethroids act as contact insecticides.

### **iii. Systemic poison**

Chemicals when applied to the plant or soil are absorbed by foliage or roots and translocated to various parts of the plant in lethal amount and insects particularly the sucking insects get poisoned and killed are called as systemic insecticides. Eg. Methyl demeton, dimethoate, phosphomidan, phorate, carbofuran and aldicarb.

### **iv. Fumigant**

Fumigants are respiratory poisons and act in gaseous phase. These are applied in vapour state and their entry is through trachea of the insect and brings about its death. All kinds of insects can be controlled irrespective of their feeding habits. Eg. Hydrogen cyanide, Aluminum phosphide.

## **E. Based on mode of action**

Based on the ways in which the chemicals act upon the system of an insect to cause its death, they may be classified as,

### **i. Physical poison**



It exerts a physical effect rather than a biochemical effect and kills the insects by asphyxial effect (suffocation) as with heavy oils and tar oils or by affecting a loss of body moisture from the insect by inert dust. They cause loss of body moisture from insects by two types of action. Abrasive dusts Eg. Aluminium oxide cause water loss by lacerating the epicuticle; Water adsorbents like charcoal remove water as a consequence of their hygroscopic properties.

#### **ii. Protoplasmic poison**

It is associated primarily with precipitation of protein. The cellular protoplasm of midgut epithelium is destroyed. Eg. Nitrophenols, Nitroresols.

#### **iii. Respiratory poison**

It is associated with blocking of cellular respiration by combining with cytochrome oxidase and other oxidases containing Fe and inhibits their catalytic action. Eg. HCN, H<sub>2</sub>S.

#### **iv. Nerve poison**

The action of these poisons appears to be associated primarily with their solubility in the tissue lipids and inhibition of acetylcholine esterase in insects and warm-blooded animals. Eg. OC, OP and botanical insecticides.

### **Toxicity**

The toxicity of a pesticide is its ability of a chemical to bring about changes in biological systems of the animal or plants. Toxicity or poisoning may be acute or chronic toxicity.

**Acute poison:** Poisoning occurs all of a sudden at once. It manifests in upsetting the vital activities with possible lethal accounts.

**Chronic poison:** Chronic poisoning is the result of repeated action of small amounts of pesticide and manifests itself in slowly developing malfunction of vital activities. It provides protracted mild forms of symptoms.

**Measurement of Toxicity:** Animals like rats, rabbits and mice are used to test pesticide toxicity. Due to some differences between the ways human and animals body work, toxicity studies are just guidelines for estimating and comparing toxic effects of pesticides.





### **Lethal Dose (LD<sub>50</sub>)**

The amount of poison which will kill one-half or 50 percent of a group of experimental animals is known as LD<sub>50</sub> value and is expressed as mg/kg of the body weight (b.wt.) of the animal. Smaller the LD<sub>50</sub> value more toxic is the chemical. Dermal toxicities are slightly less than the oral values while intravenous toxicities are higher than the oral figures.

### **Lethal Concentration (LC<sub>50</sub>)**

The  $LC_{50}$  is the concentration of pesticide which is lethal to 50% of a population of test animals and it is a measure of acute inhalation toxicity (e.g. inhalation for 4 hours).  $LC_{50}$  values for pesticides in air are expressed as mg/L or parts per million (ppm).

**Pesticide toxicity classification based on hazards- BIS classification (Bureau of Indian standards)**

Depiction				
Colour of the lower triangle	Bright red (Poison)	Bright yellow (Poison)	Bright blue (Danger)	Bright green (Caution)
Toxicity class	Extremely toxic	Highly toxic	Moderately toxic	Slightly toxic
$LD_{50}$ (oral) mg/kg	1-50	51-500	501-5000	> 5000
$LD_{50}$ (dermal) mg/kg	1-200	201-2000	2001-20000	> 20000

**Trends in pesticide usage**

Worldwide approximately 9,000 species of insects and mites, 50,000 species of plant pathogens, and 8,000 species of weeds damage crops. Insect pests cause an estimated 26% of loss; plant pathogens cause a 26% loss and weed causes 33% loss (Pimentel, 2009). Pesticide hence became indispensable in agricultural production.

**Reasons for use of pesticides**

- To ensure better protection at harvest against unpredictable losses caused by pest and diseases
- To improve both qualitative and quantitative of food
- To decrease the extent of vector born and other disease in human and animals

**World scenario**

More than 2.6 million tones of active ingredients of pesticides are used world wide. Roughly 85 % of this consumption is used in agriculture. About three - quarters of pesticides are used in developing countries, mostly in Europe and Japan. Fruits and vegetables consume the highest amount of pesticides (26%) in the world, followed by cereals (15 %),

maize (12 %), rice (10 %) and cotton (8.6 %). Estimates reveal that only 25 -30 % of the total cultivated area is under pesticide cover.

#### **Changes in pesticide consumption world wide (% to the total)**

<b>Category</b>	<b>1960</b>	<b>1970</b>	<b>1980</b>	<b>1990</b>	<b>2000</b>	<b>2005</b>	<b>2012</b>
<b>Insecticides</b>	36.5	37.1	34.7	29.0	27.9	25.0	29.5
<b>Herbicides</b>	20.0	34.8	14.0	44.0	47.5	48.0	47.5
<b>Fungicides &amp; Bactericides</b>	40.0	22.2	18.8	21.0	19.6	24.0	17.5
<b>Others</b>	3.5	5.9	5.5	6.0	5.0	3.0	5.5
<b>Total</b>	100	100	100	100	100	100	100

It is evident that the proportion of herbicides in pesticide consumption increased rapidly from 20 % in 1960s to 47.5 % in 2012. But the proportion of consumption of insecticides and fungicides declined. In developed countries, out of the total pesticide consumption, 36 % are herbicides, 25 % are insecticides and 10 % are fungicides. But in developing countries, insecticides constitute a major portion of pesticide consumption but only 12 % herbicides are used. The per hectare consumption of pesticides in India is amongst the lowest in the world and currently stands at 0.6 kg/ha against 5-7 kg/ha in the UK and at almost 20 times ~ 13 kg/ha in China .

#### **Pesticide consumption (Kg/ha) comparison**

<b>Country</b>	<b>Consumption (kg/ha)</b>
Taiwan	17
China	13
Japan	12
USA &	7

Korea	
France & UK	5
India	0.6
World average	0.50

### Indian scenario

India is one of the largest producers of pesticide in Asia and ranks 4th in world after USA, Japan and China. At present there are 287 pesticides registered for use in agriculture and public health while 18 pesticides have been refused registration. Due to their deleterious effects, 34 pesticides have been banned and 8 pesticides have been withdrawn. India's consumption of pesticides is only 2% of the total world consumption. The consumption of pesticides in India has increased from 2,353 metric tones (MT) in 1950s to 75,000 MT in 1990s. Thereafter the consumption steadily declined to 57,000 MT in 2017 primarily due to (i) banning of high persistent organochlorine insecticides such as DDT, aldrin, heptachlor etc., (ii) introduction of new generation pesticides such as neo-nicotinoid, that are effective at doses as low as 20 g a.i/ ha.

#### Pesticide registered in India under section 9(3) of the Insecticides Act, 1968 (as on 26/02/2018)

Details	Number
Pesticides registered	287
Pesticides banned For manufacture, import and use	28
Pesticides/Pesticides formulations banned for use but allowed for export	2
Pesticides formulations banned for manufacture, import and use	4
Pesticides refused for registration	18
Pesticides withdrawn	8

The Indian crop protection market is dominated by Insecticides, which form almost 65% of domestic crop protection chemicals market. Fungicides and herbicides are the largest growing

segments accounting for 15 and 16% respectively of total crop protection chemicals market respectively. Currently bio- pesticides constitute only 3% of Indian crop protection market. The per hectare consumption of pesticide in India is very low compared other developed countries which can be attributed to the fragmented land holdings, low level of irrigation, dependence on monsoons, lack of awareness among the farmers etc., Of the total pesticide consumption 42% is on cotton-crop, followed by rice (22%), vegetables and fruits (14 %) and pulses (4%), however there is a slow change in the above trend because of transgenic conditions. During 2016-17, Maharashtra, Uttar Pradesh and Punjab are top three states contributing to 52.17% of pesticide consumption in India. Among Indian states Maharashtra (23.88%) highest pesticides consuming state followed by Uttar Pradesh and Punjab.

#### **Tamil Nadu scenario**

State's consumption of technical grade pesticides which was 10,926 MT during 1984-85 has been brought down to 2,335 MT in 2010s. During 2016-17 state consumption of technical grade pesticide was 2000 MT with 3.57% and Tamil Nadu stands at seventh position. The use of bio-pesticides and bio control agents were encouraged.

### **Lecture 10**

**Pesticide formulations- Dusts, wettable powders and flowables, sprays –Emulsion concentrates – water soluble liquids - granules, fumigants and aerosols - characteristics and uses**

#### **Pesticide formulation**

The term 'Pesticide formulation' denotes both a process and a product. Pesticide formulation is the process by which the active ingredients are made ready to use by mixing with liquid or dry diluents either by grinding or by addition of emulsifiers, stabilizers and other adjuvants to form a commercial product.

Pesticide formulation is a physical mixture of one or more biological active chemicals (a.i-active ingredients) with inert ingredients in a definite proportion so as to make it more effective, safe, economical and easy to use.

Pesticides come in various formulations. It's due to variations in the active ingredient's solubility, ability to control the pest and ease of handling and transport.

#### **Why pesticide to be formulated/advantages**

1. **Ease of application:** Formulating a pesticide allows a small quantity to be mixed with a large quantity of carrier so that the pesticide can be applied more uniformly to a large area.
2. **Improved pesticide performance:** Formulating a pesticide aids in application, aids in mixing, improves coverage and aids in uptake.
3. **Stability of product:** Formulating a pesticide provides better stability in shipping and a longer shelf life.
4. **Safety:** Formulating a pesticide dilutes the active ingredient and its acute toxic effect; the user is exposed to lower concentrations.
5. **Compatibility:** Formulating a pesticide aids mixing with carriers.

#### **Considerations in formulation selection**

- Percent of active ingredient
- Ease in handling and mixing
- Personal safety risk
- Effectiveness against the pest
- Crop growth habits and stage of pests
- Availability of equipment or machinery
- Environmental concerns (drift, runoff, wild life)
- Possible injury to crop/phyto-toxicity
- Cost

#### **Different types of formulations**

##### **I. Dry/solid formulations**

- Dust (D)
- Wettable Powder (WP)
- Water Soluble Powder (WSP/SP)
- Dry flowables (Water Dispersible Granule-WDG)
- Granules (G)
- Others- Seed disinfectants

##### **II. Wet/liquid formulations**

- Emulsion Concentrate (EC)
- Oil concentrate
- Wet flowable (Suspension Concentrate-SC)

- Others- microemulsion (ME), suspoemulsion (SE)

### III. Gaseous formulation

- Fumigants (FU)

### **(I) Dusts (D) or dustable powder (DP)** Free flowing powder suitable for dusting

Dusts are very finely ground mixture of the active ingredient combined with or without inert diluents like saw dust, talc, clay, powdered nut hulls. They are used dry and never mixed with water. The particle size is <200 mesh (75µm) preferably 30-50 microns. The toxicant can be classified as

- Undiluted toxic agent (Calcium arsenate, sodium fluoride, ground pyrethrum)
- Toxic agent with an active diluents (Rotenone with sulphur)
- Toxic agent with an inert diluent (Lindane with pyrophyllite)
- Inert dusts (silica)

The concentration of toxicant present in the dust formulation ranges from 0.1 to 25 per cent ( Eg. Malathion 5% DP and Carbaryl 10% DP). Dusts are easy to handle. Best results are obtained if applied early in the morning when the plants are wet with dew. Even slight wind may cause drift of dust to other fields.

#### **Preparation of Dust**

The preparation of dust formulation includes three separate steps

- i. Pre-blending of toxicant and carrier
- ii. Pulverization of the mix and
- iii. Post-blending of the pulverized mix

#### **Manufacture of dusts**

The manufacturing of dust formulation involved two different methods. They are

- a. Ball mill method
- b. Solvent Mix method / Toxicant spray method

##### **a. Ball mill method**

The active ingredients (solid or semi solid) and fillers like soap stone, talc or pyrophyllite are readily ground in a ball mill, mixed well and used directly. During grinding, heat develops which melts the pesticide and imparting a fine coating on the inert material. In this method, the active ingredients are uniformly distributed and an efficient formulation is obtained. Finer the grinding, more effective is the dust. Lumps formed are removed by introducing a jet of air which takes away the finer particles upstream and the heavier ones fall back in the ball mill.

##### **b. Solvent mix method**

This method involves moving column of carrier and spraying the insecticidal solution over it and saturating the solution. The solvent is then evaporated leaving behind the impregnated dust.

#### **Criteria for the selection of diluents**

- Diluents should be free from impurities like mica, Fe, acidity and alkalinity
- Hydrophilic minerals like kaolin, bentonite should not be used for humid climate as it will lead to caking

#### **Properties of dusts**

- **Particle shape**

Dust particles may be spherical, polyhedral, tubular or irregular. Platy particles adhere well.

- **Particle size**

Particle size is expressed in terms of sieve size. The size varies from macroscopic to colloidal range. When size is decreased volatilization and decomposition increases due to increased surface area. Small particles are more readily consumed by chewing insects. Very fine powders have slow settling, low carrying power and increased drift.

- **Bulk density**

It is an indication of fluffiness. A good diluent is one which has a bulk density of 0.3 g / cc. Lighter materials remain in the air for a longer time while heavier materials fall rapidly.

- **Particle density**

It is the actual density of the solid particles without air spaces between them. It affects feeding in the duster. It influences carrying power, segregation and settling of dust.

- **Electrostatic charge**

It is produced due to the friction between particles and the dusting equipment. Materials with high silica give positive charge to the blower and negative charge to the dust stream. Electrostatic charges affect the attraction of dusts to the plan surfaces and dust distribution.

- **Flowability**

It indicates the feed rate of dusting equipment. The angle of slope which is a measure of flowability is measured by allowing the dust to fall through a funnel upon a disc. Greater the angle poorer is the flowability. Dusts with fibrous or needle shaped particles have a slower feed rate than dusts with spherical particles.

- **Hardness**

Causes abrasion of shaping and dusting equipment

- **Surface density and sorption**

Adsorption and absorption depends upon the nature of the surface, size and shape. It affects caking and tendency to form lumps.

#### **Advantages**

- Ready to use, with no mixing



- Easy to apply
- Less phyto-toxicity
- Require simple equipment
- Used in areas where water is a limited source

#### **Disadvantages**

- Susceptible to drift
- Don not stick to surfaces like as sprays
- Easily washed off by rain or wind
- Residual life is short and repeated application is essential
- More inhalation hazards
- Dampness can cause clogging and lumping

#### **(ii) Wettable Powders (WP)**

Pesticide in a dry form with surfactant often mixed with or coated on, a fine solid carrier, for dispersion in water to form a suspension. Wettable powders contain 5 –95% active ingredient by weight, usually 50 % or more. The particles do not dissolve in water but are suspended. Wettable powders are one of the most widely used pesticide formulations. Eg. Carbaryl 50%WP and Thiodicarb 75%WP.

#### **Characteristics of an effective wettable powder**

- Quick wetting
- Complete dispersibility
- Suspension stability and should not cake
- Low foaming
- Rapid suspension and easy settling of solid particles.
- Good wettability and easy spreadability
- High retention on the sprayed plant surface

#### **Manufacture**

WP= a.i+ mixture of diluents + surface active agent + auxillary material + sticker- ground

Five steps involved in preparation of WP

- 1) Pre-blending
- 2) Pulverizing
- 3) Re-blending
- 4) Milling
- 5) Post blending

(The auxiliaries/adjuvants are in powder form step 2 & 3 can be avoided)

Solid technical material is first milled with the carrier as pulverizing aid to yield very fine particles of the size of about 1-5  $\mu$ . Then mixed with additives and carriers to get the product of desired strength.

Good wettable powders usually contain not less than 80 per cent of particles with a size below 3 $\mu$ .

They can be divided into three groups

- i) Preparations with a high content of the active ingredient (> 60%)
- ii) Preparations with a medium content (30 to 60%) and
- iii) Preparations with a low content (<30%).

The typical composition of wettable powders is

Components	Solid a.i.	Liquid or waxy a.i.
Active ingredient (s)	upto 90 %	upto 50 %
Wetting agent	1-5%	
Dispersing agent	3-10%	
Stabilizer, stickers, anti foam	0 – 5 %	
Colloidal silica	0-15%	Up to 40 %
Fillers	To make up final mass	

The ideal and universally accepted active ingredient in wettable powder formulation is in the range of 25-75%.

- In a high active ingredient content formulation, pure materials without oily impurities and a diluent with a low bulk density and relatively large sorptive capacity are used.
- Wettable powders without diluent can be prepared if the active ingredient has a high melting point and grinds well. With a poor quality diluent, the quantity of surface active agents has to be increased to avoid unstable suspensions.

High concentration wettable powders are produced by grinding a mixture of the active ingredients, diluent and the other ingredients in a colloidal mill. In the case of pesticides obtained by precipitation from aqueous solutions, all materials required for the preparation of the wettable powders are added to the precipitated and washed pesticide and then the mixture is dried in spray driers, thus avoiding the grinding. Ex. copper oxychloride, ziram and cuprous oxide.

#### **Advantages**

- Easy to store, transport and handle
- Easily measured and mixed
- Adhere well to the surfaces

- Possess excellent residual activity
- Do not harm treated plants, animals, and surfaces like emulsifiable concentrates
- Low risk of phytotoxicity
- Less absorption in skin and eye than ECs

#### **Disadvantages**

- Inhalation hazard to applicator while measuring and mixing the concentrated powder
- Require good and constant agitation in the spray tank otherwise it will quickly settle once the agitator is turned off
- Abrasive to many pumps and nozzles, causing them to wear out quickly
- Difficult to mix in very hard and alkaline water
- Often clog nozzles and screens
- Residues may be visible on treated surfaces

#### **(iii) Flowables (F)**

They are also called Suspension Concentrates consisting of insoluble active ingredient dispersed (normally at high concentration) in water.

#### **Dry flowable**

Dry flowables or water dispersible granules (WDG), containing granules which easily disperse in water to form a suspension. It is manufactured in the same way as wettable powders except that the powder is aggregated into granular particles. They are diluted with water and applied as a spray exactly as if they were a wettable powder. Dry flowables form a suspension in the spray tank; The formulation requires constant agitation to keep them suspended in water. The percentage of active ingredient is high, often as much as 90 percent by weight. WG is similar to WP, but are granule size particles except they are formulated into granular-sized particles. It contains 20-75% (a.i), 0-45% (diluents), 1-7% (dispersant), 0-2% (binder) and 0-2% (wetting agent). Eg. Flubendiamide 20WG, Thiamethoxam 25 WG.

#### **Advantages**

- Easily measured and mixed, free flowing
- Cause less inhalation hazard to the applicator during handling
- Transport and storage is economic and safe

#### **Disadvantages**

- Expensive, sensitive in the formulation processes

#### **Liquid flowable (Suspension concentrate-SC)**

A stable suspension of a.i in a fluid, which may contain other dissolved a.i intended for dilution with water before use. Eg. Fipronil 5 SC, Indoxacarb 14.5 SC. A liquid flowable or liquid formulation combines the characteristics of emulsifiable concentrates and wettable powders.

#### **Manufacture**

The finely ground active ingredients are mixed with a liquid, along with inert ingredients to form a suspension. The resulting liquid product is a flowable. The solid ranges from 5 to 60%. It is suitable for both soil and foliage application.

#### **Advantages**

- Do not require constant agitation due to the extremely small size of the suspended particles
- No inhalation hazard to the applicator
- Easy to handle and apply
- Seldom clog nozzles

#### **Disadvantages**

- Leave visible residues similar to those of wettable powders.
- Subject to spilling and splashing.
- Contain solid particles, so they contribute to abrasive wear of nozzles and pumps
- Settle in the containers and hence shaking before pouring is a pre requisite..

#### **Sprays - Emulsion Concentrates & Water Soluble Liquids**

##### **Sprays**

Liquid formulations are generally mixed with water, but in some instances labels may permit the use of crop oil, diesel fuel, kerosene, or some other light oil are also used as a carrier. They are preferred because of the efficiency and ease of application.

##### **Spray volume**

Depending upon the volume of spray required per hectare the application is categorized as

- **High volume:** More than 150 litres per ha, suitable for insecticides, fungicides and herbicides. Spraying can be done with knapsack sprayers, tractor mounted sprayers.
- **Low volume:** This is approximately 10 -150 litres per ha. This is suitable for insecticides. Spraying can be done with motorized knapsack sprayer, air craft, low rpm spinning disk appliances
- **Ultra low volume:** This uses approximately 1-5 litres per ha, suitable for insecticides. It can be done with high rpm spinning disc appliances, motorized knapsack sprayer fitted with spinning disc attachment and air craft.

In high volume spray droplet size > 300 microns and in low volume spray the droplet size of < 100 microns are lost by drift.

Liquids in pesticide formulation play a role of a solvent, diluent, carrier, impregnating agent or other dispersal aids.

Formulation solvents may be classified as

1. Composition
2. Nature of the chemical and
3. Structure or function

Solvents which are used to dissolve the a.i and other auxiliaries are the major carriers and diluents in liquid formulation. May be polar: water, alcohol etc and non-polar: paraffins, benzene etc. Eg. Major category: Ketones, alcohols, hydrocarbons, ethers, esters, halogenated hydrocarbons and solvent mixtures.

#### **(i) Emulsifiable concentrates (EC)**

A liquid, homogenous formulation to be applied as an emulsion after dilution in water.

Emulsifiable concentrates consist of an oil-soluble active ingredient dissolved in an appropriate oil-based solvent to which an emulsifying agent (emulsifier) is added. Emulsifiable concentrates are mixed with water and applied as a spray as they form an emulsion in the spray tank. Some agitation is typically required to maintain dispersion of the oil droplets. They are adaptable to many types of application equipments, including small portable sprayers, hydraulic sprayers, low-volume ground sprayers and mist blowers. The concentration of active ingredient ranges from 0.1 to 50 %. The size of the dispersed particle is  $> 2\mu\text{m}$ . Eg. Chlorpyrifos 20% EC, Quinalphos 25%EC.

#### **Solvent**

A liquid that dissolves pesticide to form a solution. Eg. Hydrocarbons, esters, petroleum products, creolin, coal tar oils.

#### **Characteristics of a good solvent**

- The pesticide should be highly soluble in it
- Should have no phyto toxicity
- Should be readily available
- Should have high flash point

#### **Emulsifier**

An emulsifying agent (emulsifier) is a non ionic / anionic surface agent in the formulated product which prevents the emulsion from separating by surrounding the oil droplets that contain the dissolved active ingredient. When two liquids of different specific gravity such as oil (immiscible pesticides) and water are mixed together, they tend to form different layers because they are immiscible. When an emulsifier is added, the immiscible liquid breaks into small droplets that float in water phase to give a homogenous emulsion. The emulsifiers reduce the interfacial surface tension between the two liquids. Most of the wetting and spreading agents function as emulsifiers. It is always better to avoid hard water because the electrolytes of hard water disturb the equilibrium between oil and water.

Eg. Calcium sulfonates, esters of polyethylene and polypropylene glycols, monoesters of sorbitol and mannitol, soaps, dry skimmed milk and naphthalenic acids.

#### **Characteristics of a good emulsifier**

- Completely dissolve in the solution of the pesticide
- No adverse effect on solubility
- Should not cause chemical decomposition of the toxicant

- Should be neutral or mildly acidic
- Should be free from impurities

### **Preparation of EC**

Prepared by taking individual constituents of the recipe in a dissolving/mixing tank. Stirring the contents at ambient temperature is good enough for mixing (heating may require to dissolve & mix the a.i.). The quality test to be done after thorough homogenization and filtered before packing. An emulsion is a mixture that occurs when one liquid is dispersed (as droplets) in another liquid. Emulsions usually have a “milky” appearance.

### **Advantages of EC**

- Easy to handle, transport, and store
- Little agitation required and will not settle out or separate when equipment is running
- Non-abrasive
- Do not plug screens or nozzles, leaves little visible residue on treated surfaces.

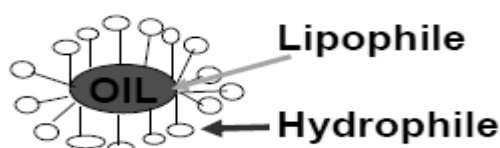
### **Disadvantages of EC**

- Emulsion may be undesirable if two or more formulated sprays are to be mixed.
- High concentration makes it easy to overdose or under dose through calibration errors
- Burn foliage at high doses (phytotoxic)
- Present dermal hazards
- Cause deterioration of rubber and plastic equipments
- Flammable (should be used and stored away from heat or open flame)
- May be corrosive
- Insoluble in water

### **Emulsion**

An emulsion is a mixture that occurs when one liquid is dispersed (as droplets) in another liquid. Each liquid will retain its original identity and some degree of agitation generally is required to keep the emulsion from separating. Emulsions usually have a “milky” appearance. The insecticide Demon EC is formulated as an emulsifiable concentrate. The active ingredient is dissolved in an oil-based solvent. When the product is mixed with water, an emulsion is formed.

**anionic/nonionic  
typically below CMC**



### **Types of emulsions**

- Oil in water (OW)** : Water is the external or continuous phase and oil is the internal or dispersion phase. This type of emulsion is commonly used.

- ii. **Water in oil (WO)** : Oil is the external phase and water is the internal phase
- iii. **Invert emulsion (IV)** : An invert emulsion contains a water-soluble pesticide dispersed in an oil carrier. Invert emulsions require a special kind of emulsifier that allows the pesticide to be mixed with a large volume of petroleum-based carrier, usually fuel oil. Invert emulsions aid in reducing drift. Because oil evaporates more slowly than water, invert emulsion droplets shrink less; therefore, more pesticide reaches the target. The oil helps to reduce runoff and improves rain resistance. It also serves as a sticker-spreader by improving surface coverage and absorption. Because droplets are relatively large and heavy, it is difficult to get thorough coverage on the undersides of foliage. It is used in areas where plant is sensitive to drift. The oil soluble herbicidal esters are in general formulated as Invert Emulsion Concentrates (IEC).

#### **Emulsion in water (EW)**

Emulsion in water results from the dispersion of a liquid or a low melting point active ingredient in a water continuous phase. The size of the dispersed particle range from 0.5 to 2 $\mu$ m. They are usually stabilized by a thickening agent in order to ensure long term stability. Eg. Cyfluthrin 5EW.

Emulsion in water (EW) offers the following advantages

- Reduced phytotoxicity
- Safer in transport and storage
- High flash point
- Less dermal toxicity
- Compatible with water based suspension concentrates

Disadvantages

1. Difficult to develop high quality stable formulation
2. High technical requirement for processing
3. Still packing and treatment problems

#### **Microemulsion (ME)**

It is a clear, thermodynamically stable mixture of (i) a hydrophobic liquid, a low melting solid or a solid in an organic solvent, a surfactant system and water. They are suited to active ingredients used at low application rates and for low active content formulations. But high surfactant content and solubilization of the a.i may give rise to enhanced biological activity. The droplet size < 0.05 micron size (50 nm). Eg. Neemazol 30 ME

#### **Suspoemulsion (SE)**

Mixture of suspension and oil in water emulsion with added surfactant to prevent flocculation and thickeners to prevent separation of the dispersed phase. A suspo emulsion is a formulation containing both solid and liquid (or low melting point solid + solvent) active ingredients dispersed in an aqueous phase. Different active ingredients with different physico – chemical characteristics can

be put together in the same water based formulation. Eg. Fenpropimorph 24.5+ Epiconazole 8.2 SE (not registered in India).

#### **(ii) Water soluble liquids (WSL)**

These are water soluble formulations in which the active ingredients form chemically stable solution in water.

#### **Soluble liquids (SL)**

A clear to opalescent liquid to be applied as a solution of the a.i after diluting in water. The liquid may contain water insoluble formulants. Soluble liquids are usually water-based products that contain a dissolved active ingredient (maybe a salt). This is one of the formulation types that actually contain dissolved molecules, not suspended particles. They mix easily in water and require minimal agitation after dilution, though some actives are dense enough to settle out over time. Toxicants are water miscible. They work like EC but without emulsifier. When diluted mixture is not milky. Eg. Monocrotophos 36 SL

#### **Granules, Aerosols and Fumigants**

##### **(i) Granules (G/GR)**

Solid formulation comprising particles of defined size  $> 80\ \mu\text{m}$  diameter, for application without further dilution, usually to soil. Granular formulation is the one in which the pesticide is impregnated in a suitable carrier and then converted to granules. The inert solid may be clay, sand, or plant materials. Granule-sized products will pass through a 4-mesh (number of wires per inch) sieve and be retained on an 80-mesh sieve. However, granules are available in several sizes as 10/20, 20/40, 30/60 etc., Granules are applied dry and usually are intended for soil applications. The amount of active ingredient is relatively low, usually ranging from 1 to 15%. Eg. Carbofuran 3G.

#### **Advantages**

- Ready to use; no mixing
- Drift hazard is low and particles settle quickly
- Reduce inhalation hazard
- Weight carries the formulation through foliage to target
- Simple application equipment, such as seeders or fertilizer spreaders
- May break down more slowly than WPs or ECs through a slow-release coating

#### **Disadvantages**

- Do not stick to foliage or other non level surfaces
- Need to be incorporated into soil or planting medium
- Need moisture to start pesticidal action
- Hazardous to non-target species, especially birds that feed on the granules

#### **Preparation of granule formulation**

Three types: 1. Absorbent or impregnated granule



2. Non-absorbent or coated granule

3. Compound granule

### **Techniques**

- Compaction and crushing
- Extrusion

### **(ii) Aerosols (AE)-a self contained sprayable product**

An aerosol is a system of particles of ultra microscopic size dispersed in a gas. These formulations contain one or more active ingredients and a solvent. Different methods are employed in the production of aerosols

- Burning various pesticide compositions that sublime to form smokes or clouds poisonous to insects. Vapourisation of pesticides with the aid of special heating equipment.
- Spraying solutions of pesticides in readily volatile solvents, which upon evaporation leave the pesticide in the air in the form of a fine dispersion. Solvent is atomized using propellant gas-insecticides suspended in air. Propellants: Butane or dimethyl ether or CO<sub>2</sub> or N.

### **• Ready-to-use Aerosols**

These aerosol formulations are usually small, self-contained units that release the pesticide when the nozzle valve is triggered. The pesticide is driven through a fine opening by an inert gas under pressure, creating fine droplets. These products are used in greenhouses, in small areas inside buildings, or in localized outdoor areas.

### **Advantages**

- Ready to use, easily stored, convenient way to buy small amount of a pesticide, retain potency over fairly long time

### **Disadvantages**

Practical for very limited uses, risk of inhalation injury, hazardous if punctured, overheated, or used near an open flame, difficult to confine to target site or pest.

### **Formulations for Smoke or Fog Generators**

These aerosol formulations are not under pressure. They are used in machines that break the liquid formulation into a fine mist or fog (aerosol) using a rapidly whirling disk or heated surface. These are used mainly to control insect pests in structures such as greenhouses and warehouses, and to control mosquitoes and biting flies outdoors.

### **Advantages**

- Easy way to fill entire space with pesticide

### **Disadvantages**

- Highly specialized use and equipment
- Difficult to confine to target site or pest
- May require respiratory protection to prevent risk of inhalation injury

### **(iii) Fumigants (F)**

Fumigants are substances sufficiently volatile to produce toxic concentration of vapour in closed space. It is expressed in wt/volume eg. mg/L or lbs/1000c.ft. The active ingredients are formulated, packaged and released as gases; others are liquids when packaged under high pressure and change to gases when they are released. Fumigants are used for storage pest control, in food and grain storage facilities and in regulatory pest control at ports of entry and at state and national borders. In agricultural pest control, fumigants are used in soil, greenhouses, granaries, and grain bins. Eg. Aluminium phosphide.

#### **Advantages**

- Toxic to a wide range of pests
- Can penetrate cracks, crevices, wood, and tightly packed areas such as soil or stored grains
- Single treatment usually kills most pests in treated area

#### **Disadvantages**

- The target site must be enclosed or covered to prevent the gas from escaping
- Nonspecific, highly toxic to humans and all other living organisms
- Causes dermal hazards. Substances absorbed through the skin included carbon disulphide, carbon tetrachloride, ethylene dichloride,  $\text{Cl}_2$ ,  $\text{I}_2$ , phenol, etc.
- Requires specialized application equipment
- Danger of inflammability.

#### **Draw backs of conventional formulations**

There are many problems associated with conventional formulations of pesticides.

- Wettable powder formulations are dusty and not easy to measure.
- Further, the dust clouds from WP are not only very fine but also have high concentration of pesticides endangering human health and contaminating the environment.
- The organic solvents used in EC formulations, enhance the percutaneous toxicity of the pesticide by altering the dermal penetration.
- Moreover these are inflammable and expensive.

Due to these disadvantages, the ecofriendly new generation formulations have been developed during the last decade. The most important of these are discussed here.

#### **Draw backs of conventional formulations**

##### **• Water-dispersible granules (WG)**

It is an improvement over wettable powder preparations. It looks like small spheres, flows like a liquid and be measured by volume. The product may be sometimes called as dry flowable (DF). Most of the sulfonylurea herbicides are available in this formulation. For safer use, these products are now available in water soluble polyvinyl alcohol bags in pre-measured quantity to avoid direct contact with

the workers.

- **Water emulsifiable gels (GL)**

It is an improved version of emulsifiable concentrate (EC). These gel formulations can be packaged in water soluble polyvinyl alcohol bags in pre-measured quantities to avoid exposure to pesticides.

- **Floating granules**

These formulations are characterized by the release of the active ingredient from the granules floating on the water surface and functioning as an efficient aquatic pest control measure.

- **Fine granules** (ordinary & FG)

Both these formulations are prepared with active material like systemic pesticides which may be absorbed and translocated through the plant tissue. The ordinary granules have particle size range of 105-297  $\mu\text{m}$  (150-48 mesh) whereas 90% of the fine granules lie in 62-210  $\mu\text{m}$  (250-65 mesh) range. These formulations are suitable for use in situation where-drift of the dust needs to be checked. These formulations are very efficient and environmentally safe, convenient to handle and less hazardous to workers.

- **Dust driftless (DL-dust)**

This formulation overcomes the drift problems associated with the conventional dusts. It has mean particle diameter of 20-30  $\mu\text{m}$  which differentiates it from the conventional dusts having mean diameter of only 10-12  $\mu\text{m}$ . It has good flowability which enables the coverage of lower side of the leaf also. It is environmentally safe, floats less during application and has good coverage of the target. In Japan, many organophosphate and carbamate insecticides are recently being formulated as DL-dust.

- **Controlled release formulations (CR)**

This formulation is a relatively new development aimed at providing controlled release (slow rate) of active ingredient (a.i) for specific types of biological actions. It involves a suitable natural and biodegradable polymer which acts as a rate controlling device, container or membrane, for the a.i. to be released at the desired rate as influenced by the moisture or soil microorganisms. There are two types of CR formulations viz., Chemical type-a chemical linkage exists between a.i. and polymer and (2) Physical type-where no chemical linkage exists. These can be further classified as:a) Micro and Macro capsules, b) Hollow fibres, c) Monolithic matrices, d) Laminated structures

- Microcapsules** [Encapsulated Suspension (CS)] are small particles of solid or liquid droplets of the a.i. enclosed in a thin polymeric wall material spherical in shape (5-50 microns) and normally dispersed in water for use. The capsules bigger in size are known as macrocapsules.
- Hollow fibres** - The hollow fibres comprise of fine capillary tubes sealed at one end which hold the liquid a.i. inside it by capillary action. The device is found suitable as insect attractant baits as well as insect mating disruption aids.
- Monolithic matrices** are made by incorporating a.i. into a polymeric or elastomeric matrix by extrusion, injection molding or casting. These are used for the preparation of CR larvicides, herbicides and

molluscicides.

- d. Laminated structures** consist mainly of three layers of laminated plastic material. The control layer is a reservoir for the a.i. and is sealed between two outer plastic layers to control its release. The pheromone is thus released by diffusion from the reservoir through the membrane. The advantages of these formulations include increased persistence of biological activity, reduced phytotoxicity, low mammalian toxicity with reduction in environment contamination. The highly toxic pesticides formulated as LS are mainly parathion, phorate and aldicarb.

- **Flowable (Suspension concentrates / SC)**

This involves dispersion of micronised technical grade solid pesticide in water. Hydrolytically stable, high melting point, friable crystal compounds having low solubility in water are formulated in this form. It has several advantages over the EC formulations and WDP such as non-dustiness, reduced operational hazards, minimum nozzle blockages, easier ULV application, non-inflammability, easy handling and transportation, low phytotoxicity and better biocidal activity. It is thus suitable for both soil and foliage application.

- **Briquette BR**

It is a solid block formulation and is made by mixing the a.i. with low density, inert granules and binding agents. It is convenient for the manual application of pesticides in aquatic environment where spray application is ineffective.

- **Smoke**

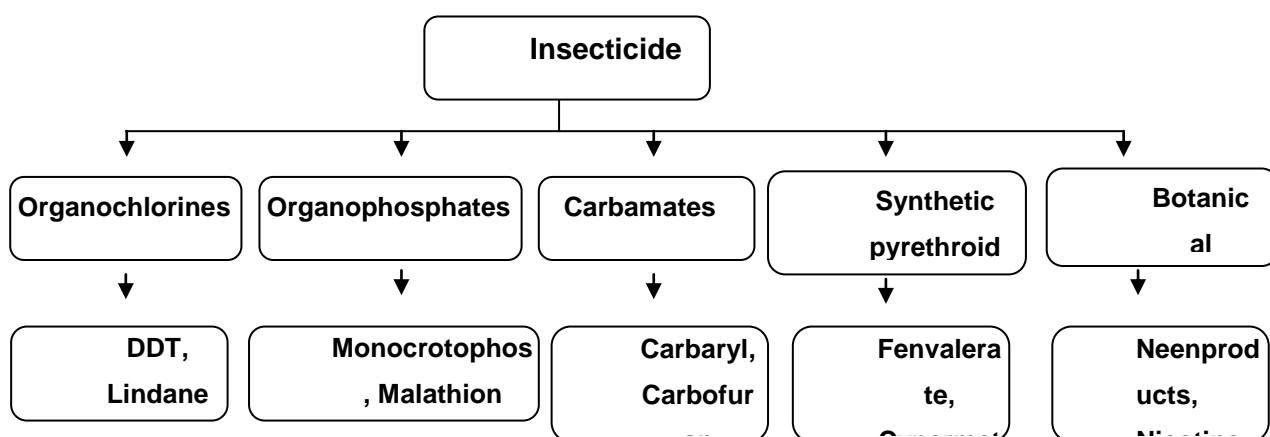
The pesticide is mixed with an oxidant and combustible material which generates large amount of hot gas. A special form of smoke generator is the mosquito coil.

## Lecture 11

### Insecticides classification -Characteristics, Mode of action and use of Organophosphates - Chlorpyrifos, Phorate, Dimethoate, Quinalphos & Profenophos

#### INSECTICIDE - CLASSIFICATION

Based on the chemical nature, the insecticides are classified as follows



Silent Spring is an environmental science book by Rachel Carson. The book was published on September 27, 1962, documenting the adverse environmental effects caused by the indiscriminate use of pesticides.

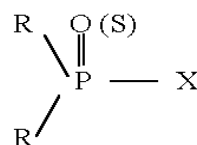
#### Organophosphates

Organophosphates are a group of chemicals that are most commonly used as insecticides. They are characterized by a Phosphorus molecule and are usually derivatives of phosphates ( $\text{PO}_4$ ). The main mechanism is blocking the enzyme acetylcholinesterase causing nervous and respiratory damages which results in the death of insects, but they are also hazardous to humans.

Schrader and his co-workers (1937) discovered the use of OP compounds. Insects also have the nervous system and acetylcholine produced in the system, which has to be removed by the enzyme choline esterase. He tried the compound TEPP (Tetra Ethyl Pyrophosphate), which he called BLADEN and was successful. Later on parathion was developed followed by Schradan and Demeton, the first systemic insecticides. As such today, more than 150 different organophosphorus compounds, have been synthesized. Of these more than 80 are used in agriculture (India 24 compounds registered).

Substances with a great variety of pesticidal properties like insecticides, acaricides, nematocides, herbicides including defoliants and plant growth regulators, fungicides and chemosterilant are found among the organophosphorus compounds. Also there are compounds with

a very short residual action such as TEPP and Mevinphos (Phosdrin) or with prolonged residual action such as diazinon and azinphos. There are also broad-spectrum insecticides like parathion and malathion and materials with very high specific action such as Schradan. Most of the compounds of this group are required only in small quantities for control of pests, pesticidal activity is very rapid and also less persistent. Hypothetical structure originally proposed by Schrader is,



Where, R and R - Short chain alkyl, alkoxy, alkyl thio or amide groups

X - labile leaving group

#### **Advantages of OP compounds over chlorinated compounds**

- Used as insecticides, acaricides, fungicides and herbicides
- Broad spectrum activity against number of insect pests
- Break down into nontoxic metabolites causing no environmental pollution
- Most of them have systemic properties which ensures their affectivity even at lower concentration
- High insect toxicity required in low quantity during application
- Very low persistence and don't accumulate in the ecosystem
- Low chronic toxicity

#### **Disadvantages**

- Some of the compounds have bad odours
- High mammalian toxicity
- Require special training for handling, storage and application

#### **Mode of action**

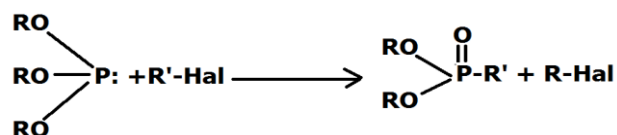
Organophosphorous compounds have higher anticholinesterase activity as they are structurally similar to acetylcholine. Acetylcholine esterase is an essential components of nervous systems of both insects and animals and plays an important role in the transmission of nerve impulses. The function of cholinesterases is to hydrolyse acetylcholine. Phosphatic compounds phosphorylate the vitally important enzymes esterases inhibiting normal functions in mammals and insects with the accumulation of acetylcholine which disrupts the normal life and finally leads to death. The inhibition of cholinesterases is irreversible whereas with carbamate the inhibition is reversible.

#### **Reactions involved in the preparation of OP compounds**

##### **i. Michaelis-Arbuzov reaction (Mi-German and Ar-Russia)**

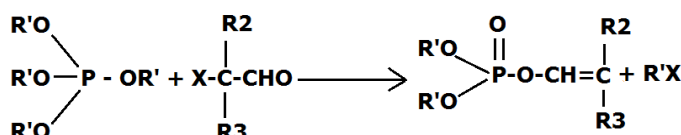
An interaction between an alkyl halides with and a trialkyl phosphite. The intermediate is a phosphonium salt which stabilizes by loss of alkyl halide and formation of

phosphonate. This reaction is used for the preparation of phosphonates, phosphinic acid esters and phosphine oxides.

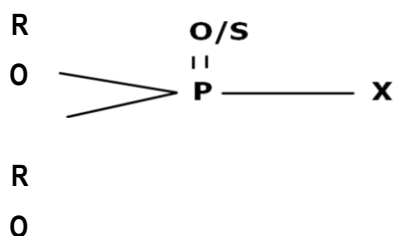


## ii. Perkow Reaction

In this trialkyl phosphite on reaction with a alpha halogenated carbonyl compounds yields vinyl phosphates. It is used for preparation of vinyl phosphates-dichlorvos, monocrotophos, phosphamidon etc.



General structure



R - Alkyl group (methyl/ethyl) and same in any one molecule

X - Complex aliphatic, homocyclic or heterocyclic group/ 'leaving group'

## Classification of Organophosphorus insecticides

Compounds of this group possessing insecticidal action can be classified as follows.

Derivatives of Phosphoric acid		Monocrotophos, Dicrotophos, Phosphamidon (Dichlorovos, Dimecron)
Thiophosphoric acid		Parathion, Demeton, Chlorpyrifos, Quinalphos
Dithiophosphoric acid		Malathion, Dimethoate, Phorate, Phosalone
Pyro Phosphoric acid		TEPP, Schradan, Triethyle, Pyrophosphate
Phosphonic acid and others		(EPN), Miscellaneous group

## Classification based on the way in which the P atom is found

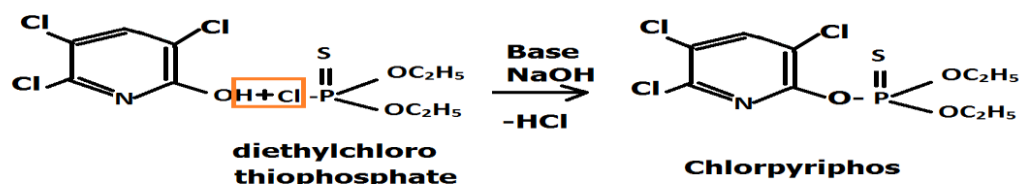
S.No.	Group		Members
1.	Phosphates	:	Phosphamidon, Monocrotophos
2.	Phosphonates	:	Trichlorphos

3.	Phosphorothionates	:	Parathion, Chlorpyrifos, Quinalphos
4.	Phosphorothiolates	:	Leptophos
5.	Phosphorodithionates	:	Malathion, Dimethoate, Phorate
6.	Phosphorodithiolates	:	Oxy demeton methyl
7.	Phosphoramidate	:	Crufamate
8.	Phosphoramidodithionate	:	Acephate

### a. Phosphorothionates

#### i. Chlorpyrifos (Dursban) O, O-diethyl O-(3,5,6-trichloro pyridyl-2) phosphorothionate.

It is synthesized by reacting the sodium salt of 3, 5, 6, trichloro-2- hydroxy pyridine with diethyl chlorothiophosphate in dimethyl formamide.



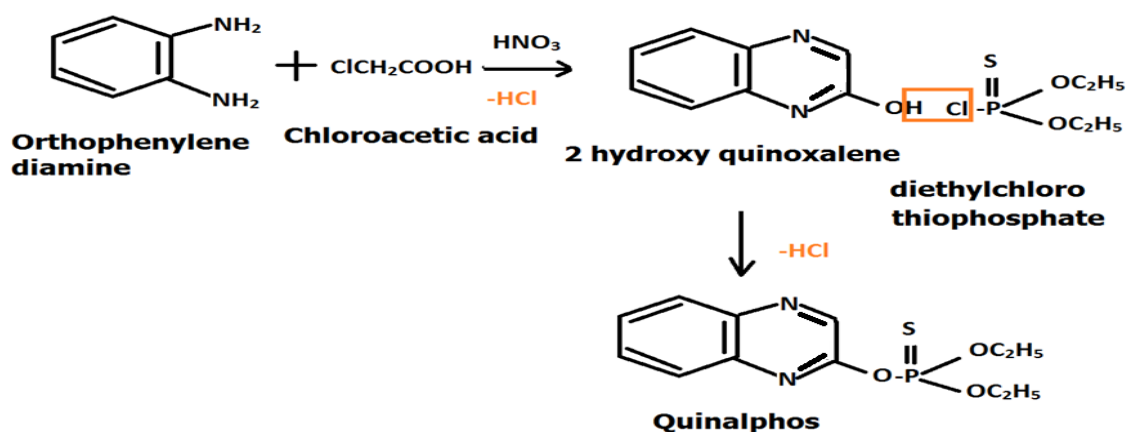
#### Characteristics

- Contact and respiratory action.
- Used for control of sucking and chewing pests.
- It is also used for control of termites (soil borne plant pests).
- Crystalline substance and m.p. is 41 to 43 °C.
- Highly soluble in organic solvents but insoluble in water.
- Stable except under strong acid and alkaline conditions.
- Moderately persistent and retains activity in soil for sometimes.
- Duration of action of the compound on different surfaces is 6 to 11 weeks, but on leaves, short action, due to its rapid hydrolysis under the influence of enzymes.
- The compound is active on grain plants for several weeks.

#### ii. Quinalphos (Ekalux)- 25% EC, 5% G and 1.5% D- O,O-diethyl-O-quinoxalin- 2yl-phosphorothioate

Prepared by the reaction between o-phenylenediamine with the chloroacetic acid followed by condensation of the product with O,O-diethyl phosphorochlorothioate





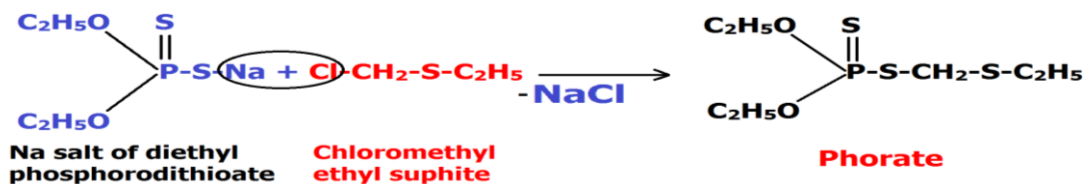
### Characteristics

- Heterocyclic moieties with nitrogen heterocycles which pyridine derivatives.
- Broad-spectrum contact and systemic insecticides, applied as spray to control pests in cereals, vegetables and many other crops.
- Quite safe as it decomposes in plant within a few days of application.
- Effective against sucking insects and lepidopterous larvae particularly of cotton and rice.
- Also an effective acaricide.
- Penetrates plant tissue by translaminar action
- LD50 for rat; oral 62-137 mg/kg.

### b. Phosphorodithionates

#### i. Phorate (Thimet-10G) O, O-diethyl-S-(ethyl thiomethyl) phosphorodithioate

It is prepared by reacting salts of diethyldithiophosphoric acid with chloromethyl ethylsulphide in acetone or other suitable solvents in the presence of  $\text{K}_2\text{CO}_3$ . The compound ranges from 70 to 80%.



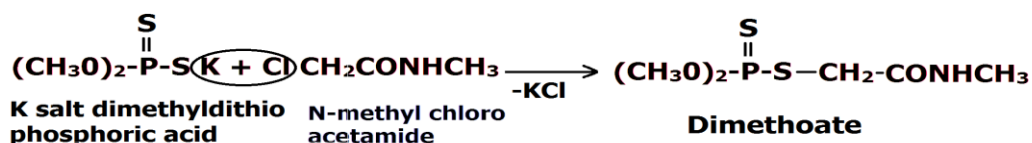
### Characteristics (seed and soil treatment pesticide)

- It is a clear liquid having boiling point 100 °C.
- Effective against sucking pest and is systemic in nature with good contact and vapour action.
- Systemic insecticide and acaricide with contact and stomach action, also some nematicidal activity
- Relatively unstable to hydrolysis (2hrs) and at 70 °C and pH 8.
- Relatively longer persistent in plant and soil because of the sulfoxide metabolite.
- Metabolites of phorate are highly toxic to animals as the parent compound.

- Does not persist for a longer period and gets metabolically oxidized yielding phosphorothioate and sulfone, which are readily hydrolysed.
- The final products of metabolism are particularly inactive biologically.

iii. Dimethoate (Rogor, 30% EC) - O, O-Dimethyl-S-(N-methyl carbanoyl methyl) dithiophosphate

Produced by reacting salts of dimethyl-dithiophosphoric acid with N-methylchloroacetamide, in aqueous medium in the presence of some organic solvents.

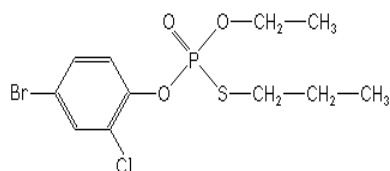


#### Characteristics

- Systemic and contact insecticide and acaricide.
- Used for the control of sucking pests and mites on ornamentals, vegetables, cotton and fruits.
- Phytotoxic to certain varieties of sorghum, chrysanthemum, etc.
- Pure dimethoate is a white crystalline substance with camphor-like odour having mp 51 to 52 °C.
- Technical material is a yellowish brown (amber) coloured oily liquid with sulphurous acid smell.
- On heating it gives isodimethoate which is more toxic.
- Technical product may contain several by-products like O,O,S-trimethyl phosphorothiolothionate and dimethoate acid methyl ester with oxygen analogue of dimethoate.
- These impurities increase the toxicity of dimethoate.
- On oxidation it is converted to O, O-dimethyl-S-(N-methyl carbanoylmethyl) thiophosphate.
- Depending on the dosage of dimethoate applied, it is usually broken down in plants in 15 to 20 days.
- On storage, dimethoate is relatively unstable and rapidly breaks down particularly at an elevated temperature.
- Impurities present in dimethoate catalyze its decomposition.
- Decomposes very quickly when it contains traces of organic bases or comes in contact with iron or salts of iron.
- Iron containers should not be used for storing dimethoate.

#### Profenofos (C<sub>11</sub>H<sub>15</sub>BrClO<sub>3</sub>PS)

The chemical of profenofos is O-4-bromo-2-chlorophenyl O-ethyl S-propyl phosphorothioate. It can be synthesized by reacting phosphorus oxychloride with sodium ethoxide and sodium 1-propanethiolate, followed by treatment with 4-bromo-2-chlorophenol.



### Characteristics

- Profenofos is a thiophosphate series organophosphate insecticide.
- It is a liquid with a pale yellow to amber color and a garlic-like odor.
- It is a contact and stomach poison exhibiting a broad spectrum of activity.
- It is non systemic insecticide and acaricide with translaminar action. Also has ovicidal effect.
- It is a wide-spectrum insecticide with easy biodegradation and a high bioactivity for antiloxic pests.
- It is used in cotton and vegetables against biting and sucking insects and against mites.
- Profenofos can be used against cotton mealybug, cabbage caterpillar, *Plutella xylostella* and asparagus caterpillars, as well as against wheat and cabbage aphids.
- The acute oral LD<sub>50</sub> for rats is 358 mg/kg.
- The profenofos 50% EC was marketed under the trade name of Curacron.
- It can be mixed with phoxim, cypermethrin, imidacloprid and deltamethrin. E.g. Profenofos 40% + cypermethrin 4% EC (Profex super, Kilcron plus).

Pesticide	Trade name	LD 50 rat (mg/kg)
Phosphamidon	Dimecron	15-27
Chlorpyrifos	Dursban	163
Quinalphos	Ekalux	70
Malathion	Cythion	1375
Phorate	Thimet	1.1-2.3
Dimethoate	Rogar	600
Profenophos	Curacron	358

### Banned OP in India

- Chlorfenvinphos, Ethyl parathion- pesticide banned for import, manufacture and sale
- Phosphamidon 85% SL-formulation banned for import, manufacture and sale
- Diazinon, fenitrothion, fenthion, methyl parathion-banned for agricultural use

## Lecture 12

### Characteristics, Mode of action and use of Carbamates (Carbaryl, Carbofuran, Carbosulfan & Aldicarb) and synthetic pyrethroids (Deltamethrin, Fenvalerate, Cypermethrin & Lambda cyclothrin)

A carbamate is an organic compound derived from esters of carbamic acid ( $\text{NH}_2\text{COOH}$ ). A carbamate group, carbamate ester (e.g., ethyl carbamate) and carbamic acids are functional groups that are inter-related structurally and often are interconverted chemically. Carbamic acid developed from alkaloid physostigmine, found in the Calabar bean (*Physostigma venenosum*), native of West Africa. It was isolated in 1864 and its structure was known by 1923. Physostigmine is the only known naturally occurring carbamate ester.

The carbamic acid does not occur in free form, since it decomposes into  $\text{CO}_2$  and ammonia. Carbamic acid can be stabilized by the formation of simple alkyl ester (ethyl carbamates). Several carbamates are systemic, transported in the xylem. It is possible to control pests on shoots and roots which are otherwise difficult to reach. Hence, they are used as soil insecticides and nematicides (aldicarb, carbofuran, oxamyl, etc.).

#### Classification of carbamates

The carbamates can be classified into following groups

- |  |  |
|--|--|
| 1. Phenyl carbamates (Aromatic)              | Eg. Carbaryl (Sevin), Carbofuran (Furadan), Aprocarb (Baygon, propoxur), Aminocarb (Metacil) |
| 2. N,N-dimethyl carbamates<br>(Heterocyclic) | Eg. Isolan, Pyrolan, Dimetilan, Primicarb  |
| 3. Oxime carbamates                          | Eg. Aldicarb (Temik), Oxamyl (Vydate), Methomyl (Lannate)                                    |

#### General Characteristics

- High insecticidal activity and reasonable biodegradation
- Easily detoxified
- Broad spectrum in nature
- Non accumulating in fat and milk
- Unstable in an alkaline medium
- Certain carbamates are susceptible to photodegradation and air oxidation
- The important reaction of carbamates is hydrolysis.

#### Mode of action

Carbamates have a similar mode of action that of OP as they also block the enzyme acetylcholinesterase (AChE). This process of enzyme inhibition is called carbamylation. The carbamylation process is relatively less stable, i.e., the enzyme is not blocked for so long. Because of its action as a reversible cholinesterase inhibitor its use is preferred over other insecticides, which

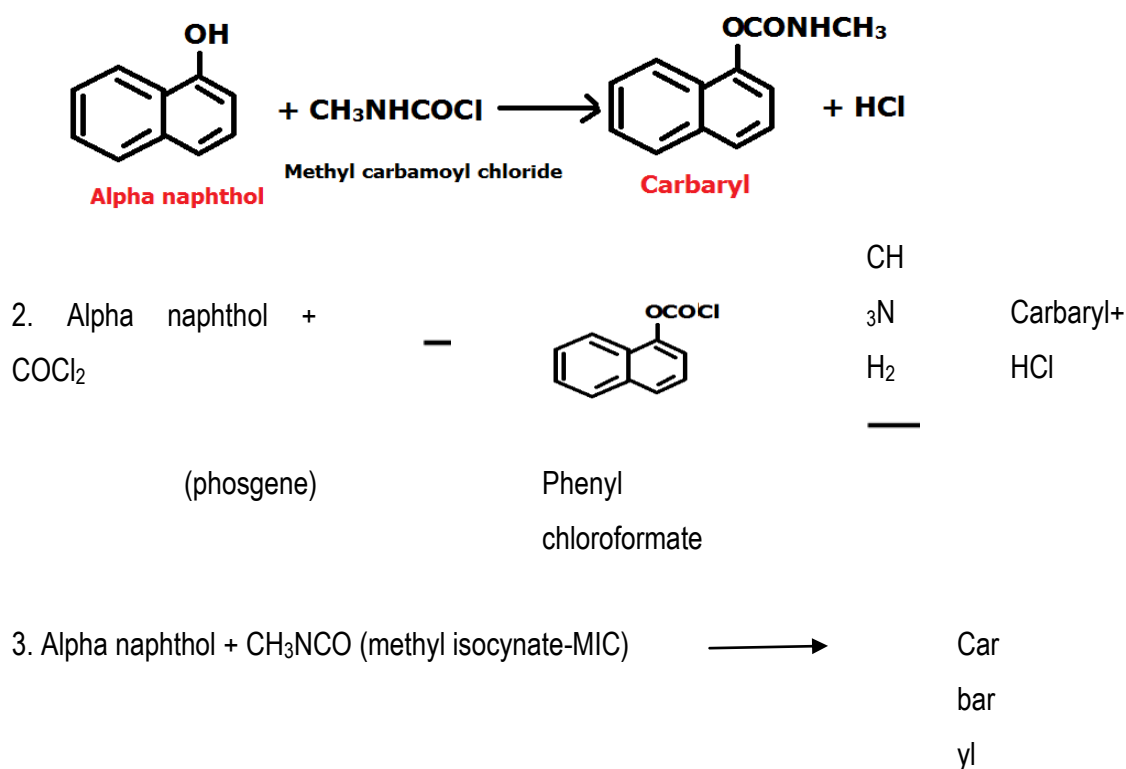
are irreversible cholinesterase inhibitors. Cholinesterase depression is common to all the carbamate pesticide both in blood and tissues. The reversibility of AChE inhibition confers advantage to carbamates over organophosphate.

### Phenyl carbamates

**Carbaryl** (Sevin): 1 naphthyl-N-methyl carbamate,  $C_{12}H_{11}NO_2$

Carbaryl, introduced by American union Carbide Company in 1956 was the first successful commercial carbamate. The carbaryl can prepared in three different way as follows

1. Prepared by treating alpha naphthol with methyl carbamoyl chloride or phosgene or methyl isocyanate

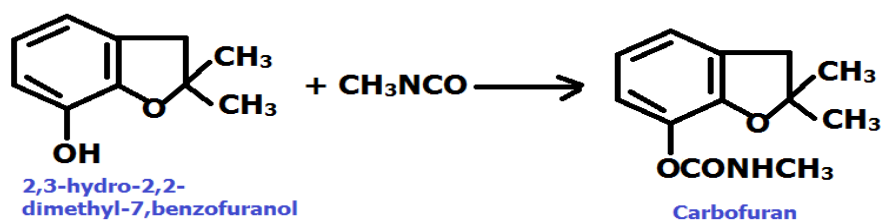


### Characteristics

- The rate of reaction is increased by removing the HCl that is formed with a stream of air or nitrogen (second method).
- Potent contact and respiratory poison and effective against chewing pests.
- White crystalline compound m.p 142 °C.
- Soluble in water less than 0.1 % and highly soluble in organic solvents.
- In alkaline conditions hydrolysed to alpha naphthol.
- It is not compatible with compounds of alkaline nature like Brodeaux Mixture.
- LD<sub>50</sub> rats, 250-350 mg/kg

**Carbofuran (Furadan)** 2,3-dihydro-2,2 –dimethyl-7-benzofuranyl N-methyl carbamate,  $C_{12}H_{15}NO_3$

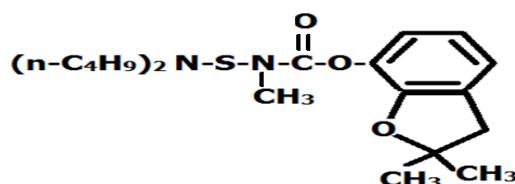
It is prepared by treating 2,3 dihydro-2,2 dimethyl-7 benzofuranol with methyl isocyanate.



### Characteristics

- White crystalline mp 153-154 °C.
- Broad spectrum systemic insecticide, nematocide and miticide (acaricide)
- It is stable in acid and neutral media but unstable in alkaline medium.
- It is compatible with non-alkaline pesticides and fertilizers.
- Non fumigating (nematicide action).
- Used for to control soil dwelling and foliar feeding insects.
- Carbofuran present in soil is degraded by hydrolysis depending on soil pH and clay content
- Major metabolites are 3-OH carbofuran and 3-keto carbofuran.
- LD<sub>50</sub>: rats, 5.3-8 mg/kg
- Liquid formulations of carbofuran are classified as Restricted Use Pesticides. They are active against soil nematodes.

### Carbosulfan (Marshal), C<sub>20</sub>H<sub>32</sub>N<sub>2</sub>O<sub>3</sub>S



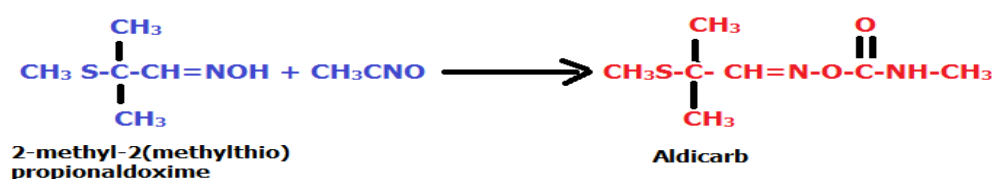
### Characteristics

- Carbosulfan, a sulphonylated derivative of carbofuran, acts as a contact and systemic insecticide.
- It is a Proinsecticide
- Procarbamates are a newer class of carbamates that contain an (often complex) substituent on the carbamyl nitrogen instead of the H or CH<sub>3</sub> present in simpler carbamates.
- Moreo  
ver, procarbamates often have lower acute mammalian toxicity than do their parent carbamates, primarily because they are only slowly converted to the active carbamate, allowing for alternative metabolism in mammals.
- It can  
be applied to the foliage or soil as a nematicide.

- It has a lower mammalian toxicity.
- The European Union banned use of carbosulfan in 2007.
- LD<sub>50</sub> 90 to 250 mg/kg.
- Carbo sulfan formulated as granules is used in vegetables. eg. brassicas, carrots and turnips.

**Aldicarb (Temik)** 2-Methyl-2-(methylthio) propanol O-Methylamino carbonyl oxime), C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S

Aldicarb is prepared by the reaction of 2-methyl-2(methylthion) propionaldoxime with methyl isocyanate.



### Characteristics

- Broad spectrum soil applied systemic pesticide
- Insecticide, acaricide, nematocide for soil use; only available as granules to reduce handling hazards.
- LD<sub>50</sub>: 0.93 mg/kg rat.
- Aldicarb is extremely toxic and is absorbed through skin.
- It is therefore marketed as a granular formulation.
- White crystalline substance m.p. 100°C. & sparingly soluble in water.
- It is effective for control of aphids, nematodes, flies beetles, leaf miners, thrips and white flies on a wide range of crops.
- Aldicarb is readily translocated in plants after soil application where it is metabolized to the sulfoxide and the sulphone which are also active (less).
- Aldicarb is effective where resistance to OP has developed, and is extremely important in potato production (control of soil-borne nematodes and some foliar pests)
- Its weakness is its high level of solubility, which restricts its use in certain areas where the water table is close to the surface.

### Synthetic Pyrethroids

(Deltamethrin, Fenvalerate, Cypermethrin and Lambda Cyhalothrin)

Pyrethrum is derived from the flowers of the plant *Chrysanthemum cinerariaefolium*. Refined pyrethrum is called pyrethrins, contains six insecticidally active components. The ketoalcoholic esters of chrysanthemic and pyrethroic acids are known as pyrethrins, cinerins and jasmolins. The synthesis of chrysanthemic acids and of cyclopentenolones opened up the possibility of obtaining synthetic pyrethroids (SP). Synthetic pyrethroids were developed to modify the structure of natural pyrethrins in order to increase photo-stability and to enhance insecticidal activity. There are two types that differ in chemical structure and symptoms of exposure.

The two types of synthetic pyrethroids are:

- Type I pyrethroids: It is non-cyano group of pyrethroids eg. Allethrin, tetramethrin, resmethrin, d-phenothrin, bioresmethrin and permethrin.
- Type II pyrethroids: It is  $\alpha$ -cyano group of pyrethroids eg. Cypermethrin, cyfluthrin, deltamethrin, fenvalerate and fluvalinate.

#### Development of synthetic pyrethroids

Generation	Examples
I generation (1949)	Allethrin
II generation (1960-73)	Resmethrin, bioresmethrin, bioallethrin
III generation (1970)	Fenpropathrin, Cypermethrin, Deltamethrin, fenvalerate
IV generation (1975-83)	Fluvalinate, cyfluthrin, flocythrinate

The first synthetic pyrethroid Allethrin appeared in the market in 1950. It was prepared by esterification of synthetic chrysanthemic acid with alcohol allethrolone. The activity of these compounds was further enhanced by introduction of (S)- $\alpha$ -cyano group to give cypermethrin. The replacement of chloro group by bromo group as in cypermethrin gives deltamethrin exhibited further improvement of properties such as quick knock down effect, low mammalian toxicity and high chemical stability. Similarly, 4-fluoro substituted cypermethrin called cyfluthrin was also prepared and found very active. Cyhalothrin in which one of the chlorine atoms in cypermethrin was replaced by  $\text{CF}_3$ , also exhibited enhanced activity. Later structural modifications yielded two more active compounds flumethrin and fenpropathrin having broad spectrum insecticidal and acaricidal activity.

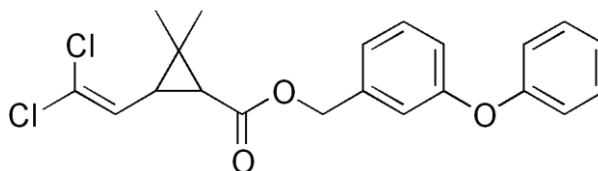
So far, it was believed that cyclopropane carboxylic acid moiety of chrysanthemic acid is indispensable for pyrethrin activity. Later phenylalkanoic acid can replace the cyclopropane carboxylic acid and yields highly active molecule like fenvalerate and flucythrinate.

- Phenoxy benzoyl or furyl methyl group light stability increase eg. Cypermethrin, deltamethrin

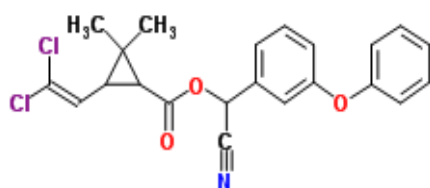


- **Cyano group** eg. Cypermethrin, fluvalinate, fenvalerate
- **Fluorine atom-effective** against mite eg. Fluvalinate,  $\lambda$ -cyhalothrin,  $\beta$ -cyfluthrin, bifenthrin

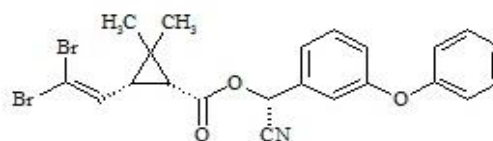
Permethrin



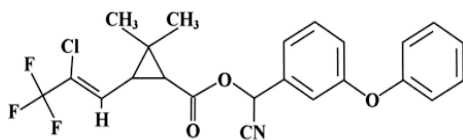
Cypermethrin



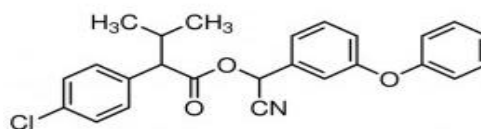
Deltamethrin



Cyhalothrin



Fenvalerate



### Characteristics of SP

- Broad spectrum activity
- Lack of persistence (instability in presence of light and air)
- Repellency (powerful insect repellent)
- Rapid action (knockdown effect;  $KD_{50}$ )
- Low mammalian toxicity-warm blooded animals
- Environmental safety
- Controls pests in stored foods and against household and industrial pests
- Insoluble in water and soluble in most organic solvents

### Mode of action

- Primary site of action is CNS symptomised by hyperactivity, lack of co-ordination, tremors and convulsions followed by paralysis and death.
- Control of sodium ion permeability through nerve membrane is vital to NS.

- Pyrethroids are neuro toxins affecting the kinetics of nerve membrane sodium channels.
- Act stereoselectivity on a small fraction of the first voltage dependent sodium ion channel in excitable nerve membrane on NS.
- Major effect is to delay the closing of the sodium ion channel agitation gate.

**Cypermethrin: Cyano-(3-phenoxyphenyl) methyl] 3-(2, 2-dichloroethenyl)-2, 2-dimethyl cyclopropane-1-carboxylate**

**Molecular formula:**  $C_{22}H_{19}Cl_2NO_3$

**Properties**

- It is a white, odourless, waxy solid
- The melting point of pure cypermethrin isomers is 81-83°C
- Exposure to sunlight, water and oxygen accelerates its decomposition.
- Easily degraded on soil and plants.

**Toxicity**

- Cypermethrin is highly toxic to fish, bees and aquatic insects.
- Excessive exposure can cause nausea, headache, muscle weakness, salivation, shortness of breath and seizures.
- In humans, cypermethrin is deactivated by enzymatic hydrolysis to several carboxylic acid metabolites, which are eliminated in the urine.
- Cypermethrin is classified as a possible human carcinogen.
- The LD<sub>50</sub> value is 303 - 4123 mg /kg for rats.

**Uses**

- It is a stomach and contact insecticide effective against broad range of pests
- The chemical is active against eggs and active growth stages particularly larvae and has antifeeding action.
- Used in large-scale commercial agricultural applications and in consumer products for domestic purposes.

**Deltamethrin ( $C_{22}H_{19}Br_2NO_3$ )**

Deltamethrin, {(S)-a-cyano-3-phenoxybenzyl (1R, 3R)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane carboxylate}, a pyrethroid ester insecticide, is used for the control of lepidopterous pests on various crops. It was prepared by replacement of chlorine atoms by bromine and the introduction of a cyano group from permethrin. This was discovered in 1974 is a potent insecticide known (0.0003 µg/insect) 50 times more active than Pyrethrin I.

## Properties

- This has reasonable photostability and very low mammalian toxicity.
- It is a colourless crystalline powder having melting point 98-101°C.
- It kills insects on contact and through ingestion by disrupting their nervous system and is effective against both sucking and chewing insects and has been widely used to control pests of various crops.
- It is stable to light, heat and air, but unstable in alkaline media, and non persistent, highly soluble in organic solvents but almost insoluble in water.
- It is an effective contact and stomach poison against a wide range of insects and recommended at a dosage varying from 12.5 to 15 g a.i./ha.
- It is also recommended for the control of mosquitoes and animal ectoparasites.
- Its acute oral LD<sub>50</sub> for rats is 135 mg/kg.
- It is toxic to fish and honey bees.
- The deltamethrin 2.8% EC was marketed in the trade name of Decis.

### **Lambda cyhalothrin** (C<sub>23</sub>H<sub>19</sub>ClF<sub>3</sub>NO<sub>3</sub>)

(RS)-α-cyano-3-phenoxybenzyl (±) cis, trans-(2VE)-2-chloro-3, 3,3- trifluoro prophenyl) -2, 2-dimethylcyclopropane-2-carboxylate).

## Properties

- Lambda-cyhalothrin is a mixture of isomers of cyhalothrin. It is a colourless solid melting point is 49.2 °C.
- It is a contact and stomach insecticide with quick knockdown and long residual action.
- It is effective against a wide range of pests of agriculture and public health importance.
- It is effective at very low doses (5-30 g a.i./ha) against major insect pests in many crops.
- It has a comparatively high mammalian toxicity (LD<sub>50</sub> Oral 60 mg/kg).
- At normal rates cyhalothrin shows low toxicity to birds with no accumulation in eggs or tissues and no effect on earthworms.
- The half life in soil is 3-12 weeks; in aerobic soils it undergoes extensive mineralization to CO<sub>2</sub>.
- In flooded soil degradation was slower and only hydrolysis products were detected.
- No phytotoxicity towards major crops and controls a wide spectrum of lepidopteran pests.
- This is valuable for the control of plant virus vectors.
- The lamda cyhalothrin 5% EC was marketed in the trade name of karate, warrior, whereas 2.5% EC was marketed in the name of kungfu, warrior plus.

### **Fenvalerate** (C<sub>25</sub>H<sub>22</sub>ClNO<sub>3</sub>)- (RS)-alpha-cyano-3-phenoxybenzyl (RS)-2-(4-chloro phenyl)-3-methyl butyrate

Fenvalerate is a mixture of four optical isomers which have different insecticidal activities. The 2-S *alpha*-S (or SS) configuration is the most insecticidally active isomer. Fenvalerate consists of

about 23% of this isomer. It is found in some emulsifiable concentrates, wettable powders, slow release formulations, insecticidal fogs and granules.

#### **Properties**

- Acts as contact and stomach poison
- Yellow-brown viscous liquid which may be partly crystallized at room temperature and has a specific odour.
- Not corrosive to metals.
- Insoluble in water (2µg/litre) and soluble in organic solvents.
- Stable to moderate heat and sunlight.
- Rapidly hydrolysed above pH 8 but relatively stable in acid media.
- Not stable in alcohols.

#### **Toxicity**

- Fenvalerate is an insecticide of moderate mammalian toxicity.
- Residue levels are minimized by low application rates.
- Most toxic to bees and fish.
- May irritate the skin and eyes on contact, & is also harmful if swallowed.
- LD<sub>50</sub> 451 mg/kg.

#### **Uses**

- Used to control insects in food, feed, and cotton products.
- Used for the control of flies and ticks in barns and stables.
- It does not affect plants, but is active for an extended period of time.
- It is a contact insecticide and LD<sub>50</sub> for rats is 450 mg /kg.

#### **Advantages of synthetic pyrethroids**

- Extremely high insecticidal activity at very low doses
- Biodegradable in nature
- Activity is pronounced against lepidopteran pests
- Effective against beetles, leaf miners and bugs
- Insecticidal activity is maintained for a longer period of time thereby controls overlapping generations of pests
- Strong antifeedant and repellent properties, after contact insects become moribund and stop feeding
- They have rainfastness (Not readily washed off by rain).
- The lipophilic character enables ready absorption on waxy layers of plant surface

- Due to low volatility movement in air is restricted
- Due to low polarity movement in soil and plant is restricted
- Compatible with organo phosphorus insecticide as an ultra-low volume spray.

#### **Disadvantages of synthetic pyrethroids**

- Non systemic and do not have translaminar action and hence not effective against sucking pests like aphids and mealy bugs
- Constant use increases incidence of mites in crops like cotton, tea, vegetables etc.,
- With large scale use, increased incidence of Alternaria disease in cotton mostly in sandy soil
- They are highly toxic to fish. Because of lipophilic nature, they are strongly absorbed by gills even at very low concentration in water
- Some of the synthetic pyrethroids do not have specific antidote.
- The synthetic pyrethroids are very expensive to prepare on a tonnage basis

## Lecture 13

**Characteristics, Mode of action and use of Botanicals (Nicotine and Neem), Insect Growth Regulators (Novaluron, Buprofezin and GABA inhibitors) and newer insecticides- Neonicotinoids (Imidachloprid, Thiachloprid, Acetamiprid and Thiomethoxam), Diamide (Flubendiamide and Chlorantraniliprole) and Others (Fipronil, Emamectin and Indoxacarb)**

### Botanicals

In the past, synthetic pesticides have played a major role in crop protection programmes and have immensely benefited mankind. Nevertheless, their indiscriminate use has resulted in the development of resistance by pests (insects, weeds, etc), resurgence and outbreak of new pests, toxicity to non-target organisms and hazardous effects on the environment endangering the sustainability of ecosystems. An interesting way of searching for biorational pesticides is screening naturally occurring compounds in plants. Plants, as long-lived stationary organisms, must resist attackers over their lifetime, so they produce and exude constituents of the secondary metabolism (PSMs), playing an important role in their defence mechanisms. The main groups of PSMs are (i) phenylpropanoids and phenolics, (ii) terpenoids and steroids, (iii) alkaloids and nitrogen compounds.

The development of botanicals used as pesticides resulted from two parallel methods: I) the observation of the traditional uses of plants and extracts for cattle and crop protection, followed by checking the efficiency of these practices and identification of the active molecules, II) the systematic screening of botanical families followed by biological tests in order to discover the active molecules.

Botanical insecticides are naturally occurring chemicals / insect toxins derived from plants. They are also called natural pesticides.

**a. Nicotine** ( $C_{10}H_{14}N_2$ ) 1-methyl-2, 3 (pyridyl pyrrolidine).

### Source

Nicotine is a simple alkaloid derived from tobacco, *Nictiana tabacum* and other Nicotiana species. Nicotine constitutes 2-8% of dried tobacco leaves. The tobacco contains 12 alkaloids- nictoine, nornictoine, and anabasine. The two isomers of nicotine are nornicotine ( $C_9H_{12}N_2$ ) and neonicotine or anabasine. *N.rustica* contain 5-14% nicotine. It is occurs in tobacco plants as a salt with citirc and maleic acid to extent of 1-8%. Insecticidal formulations generally contain nicotine in the form of 40% nicotine sulfate and are currently imported in small quantities from India.

Nornicotine is similar to nicotine except the methyl group attached to pyrrolidine ring which is replaced by H+ atom. It occurs in *N.Sylvester's*. It is a liquid alkaloid almost similar to nicotine.

Neonicotine occurs in seeds of *Anabasis aphylla*. It resembles nicotine

## Preparation

Nicotine is present in all stages and in all parts of the tobacco plant, the quantity ranging from traces in seedlings to maximum in mature leaves. It is extracted from the woody portions of the plant such as stems and leaf midribs unsuited for smoking or chewing tobacco. It is extracted with an organic solvent such as benzene, concentrated in vacuum and again extracted with dilute  $\text{H}_2\text{SO}_4$ . Nicotine is then liberated with alkali and extracted with petroleum ether, subsequently by distillation, pure nicotine is obtained.

Tobacco decoctions, useful for controlling aphids, thrips, etc is prepared by boiling 1 kg of tobacco waste in 10 litres of water for 30 minutes or keep it in cold water for a day. Then make up the infusion to 30 litres and add 90g of soap. Addition of soap improves wetting, spreading and killing properties

## Characteristics

- Pure nicotine is a colourless, odourless liquid, boiling at  $247.3^\circ\text{C}$  with a specific gravity of 1.0093.
- It is soluble in water only below  $60^\circ\text{C}$  and above  $210^\circ\text{C}$  it forms hydrates. Under room temperature, it is soluble in organic solvents.
- When exposed to air and light, it slowly darkens in colour and becomes more viscous.
- Oral  $\text{LD}_{50}$  value is 50 – 60 mg /kg; Dermal  $\text{LD}_{50}$  – 50 mg /kg

### Mode of action

Nicotine enters body through the spiracles in the trachea. The fumes of nicotine striking the walls of insects immediately dissolved, penetrate the vital tissues and bring paralysis of the nervous system of the insects. Nicotine-blocks synapses associated with nerves (motor). Nicotine penetrate into the synapses and is then converted to the nicotine ion containing +ve charge on the pyrrole ring. Non susceptible to enzymatic hydrolysis by AchE. This disruption results in rapid failure of body systems.

## Uses

It is used for the control of cardamom thrips. Dust formulation of nicotine sulphate releases nicotine in the presence of moisture. They are used to control pickleworms, aphids, leafhoppers, spider mites, harlequin bugs, cabbage worms.

### b. Neem

**Neem products** – Neem oil, Neem cake and Neem Seed Kernel extract (NSKE)

## Source

Neem products are derived from the neem tree, *Azadirachta indica*, which grows in arid tropical and subtropical regions on several continents. The one kg of neem seed constitutes about 25-31% neem seed kernel, which is giving 15-25% neem oil. The extracts of neem seed yield a large number of tetranortriterpenoids, one of principle active compound is azadirachtin (limonoid group), a bitter, complex chemical that is both a feeding deterrent and a growth regulator. Other

active components of neem are meliantriol, salannin, and many other minor components. Neem products include teas and dusts made from leaves and bark, extracts from whole fruits, seeds, or seed kernels, and an oil extracted from the seed kernel.

### **Neem oil**

#### **Preparation**

Neem oil is a vegetable oil pressed from the fruits and seeds of the neem through cold pressing or through a process incorporating temperature controls. It can also be obtained by solvent extraction of the neem seed, fruit, oil, cake or kernel.

To get 3% solution first mix 30 ml of neem oil with 5 ml of sticking agent teepol until white emulsion is formed. Then makeup to one litre using water and mix thoroughly for use of spray fluid.

#### **Characteristics**

- Neem oil is generally red as blood, and has a strong odour
- It is composed mainly of triglycerides and contains many triterpenoid compounds, which are responsible for the bitter taste.
- It is hydrophobic in nature, it has to be emulsified in water for application purposes
- It must be formulated with appropriate surfactants.
- The azadirachtin content of neem oil varies from 300 to > 2500 ppm.
- Neem oil also contains steroids like campesterol, beta-sitosterol and stigmasterol.

### **Neem seed kernel extracts (5 %)**

#### **Preparation**

For the preparation of 5% NSKE, take 50 g of powered seed kernel and soak it in a small quantity of water, overnight. Filter through double layer of muslin cloth and make up the volume to one litre. Add one ml of teepol per litre before spraying with high volume sprayer. The spray solution is mixed well and used. Freshly prepared NSKE is always used.

### **Neem cake**

Neem cake is used as organic manure. It is the by-product obtained in the process of cold pressing of Neem tree fruits and kernels, and the solvent extraction process of neem oil.

#### **Mode of action**

- Neem is a complex mixture of biologically active material.
- In insects, neem is most active as a feeding deterrent, also serves as a repellent, growth disruptor, oviposition (egg deposition) suppressant, sterilant, or toxin.
- As a repellent, neem prevents insects from initiating feeding.



- As a feeding deterrent, it causes insects to stop feeding either immediately after the first “taste”.
- As a growth disruptor, it disrupts normal development interfering with chitin synthesis.
- It is used against cut worms and army worms.
- The cake contains salannin, nimbin, azadirachtin and azadiradione as the major components.
- Of these, azadirachtin and meliantriol are used as locust antifeedants while salannin is used as an antifeedant for the housefly.

## Uses

- Oral LD<sub>50</sub> value is 13,000 mg /kg
- Neem oil repels a wide variety of pests including the mealy bug, beet armyworm, aphids, the cabbage worm, thrips, flies, leafminers, caterpillars and the Japanese beetle.
- It can be used as a household pesticide.
- Neem oil also controls black spot, powdery mildew, anthracnose and rust – fungal diseases
- Neem cake is effective in the management of insects and pests.
- The bitter principles of the oil and cake have been reported to have antifeedant, attractant, repellent, insecticide, nematicide, growth disruptor and antimicrobial activities.

**Neem oil and other neem products such as neem leaves and neem tea should not be consumed by pregnant women, women trying to conceive, or children.**

## **Insect Growth Regulators: Novaluron, Buprofezin and GABA inhibitors**

### **a. Insect Growth Regulators (IGRs)**

Insect Growth Regulators (IGRs) are chemical substances that disrupt insect growth and development, resulting eventually in death of insects. Currently there are five different types of IGRs namely, juvenoids, benzoylphenylureas, diacylhydrazines, triazines and thianidines. IGRs have very low mammalian toxicity, with oral LD<sub>50</sub> in rats ranging from 2000 to 5000 mg/kg.

Since the target sites of common insecticides on insects and mammals are known to be similar, it is desirable to develop insecticides whose primary target site does not exist in mammals for selective toxicity. IGRs may belong to this type of (selective) insecticides and can be grouped according to their mode of action, as follows: chitin synthesis inhibitors (i.e. of cuticle formation) and substances that interfere with the action of insect hormones (i.e. juvenile hormones, ecdysteroids). Juvenile hormones (JH) are more effective at the beginning stage of metamorphosis and embryogenesis in insects, such as freshly ecdysed last larval instars, freshly ecdysed pupal instars,

and deposited eggs. Thus embryogenesis is disrupted when young eggs are treated with JHs. Eg. Methoprene, Fenoxycarb and Pyriproxyfen etc.

#### **b. Chitin synthesis inhibitors**

The effects of these compound on insects varies but the effects can be grouped into two broad categories; inhibition of chitin synthesis or interference with the organization of exoskeletons. The first chitin synthesis inhibitor was discovered by scientists of Philips Duphar who were trying to discover some super herbicide based on Dichlobenil and diuron. It was found that 1-(2, 6-dichlorobenzoyl)-3- ) 3, 4-dichlorophenyl) possessed interesting insecticidal properties against several species of insects. Later on a number of benzoyl phenylureas (BPUs) namely diflubenzuron, teflubenzuron, triflumuron flufenoxuron, chlorfluazuron, novaluron etc. were developed which have been found effective as chitin synthesis inhibitors. The first chitin synthesis inhibitor introduced into the market as a novel insecticide was diflubenzuron under the trade name of Dimilin that was found effective against coleopteran, dipteran and lepidoptera.

Chitin synthesis inhibitors mainly act as a larvicide. The most likely working hypothesis is that central nervous system (CNS) act by interrupting the synthesis and or transport of specific proteins that are required for the assembly of chitin protein network to form laminated cuticle. In addition to chitin synthesis inhibiting activity, buprofezin is also found to inhibit prostaglandin biosynthesis, a sex hormone and thus more than the BPUs.

##### **1. Novaluron (Riman)**

Novaluron, ( $\pm$ ) -1-[3-chloro-4-(1,1,2-trifluoro-2-trifluoro-methoxyethoxy) phenyl]-3- (2,6-difluoro benzoyl) urea, is a chemical with pesticide properties, belonging to the class of insect growth regulators called BPUs developed by Makhteshim-Agan Industries Ltd,. Novaluron is an insecticide which inhibits chitin synthesis, affecting the moulting stages of insect development. It acts by ingestion and contact and causes abnormal endocuticular deposition and abortive moulting. It is used in agriculture/horticulture on a wide range of crops including cotton, soya, maize, pomefruit, citrus, potato and vegetables against a wide range of pests. In the United States, the compound has been used on food crops, including apples, potatoes, brassicas, ornamentals and cotton. It is effective against DBM on cabbage, tomato and chilli fruit borers, cotton bollworms and gram pod borer at 75-100 g a.i./ha. Patents and registrations have been approved or are ongoing in several other countries throughout Europe, Asia, Africa and South America, as well as Australia. The *US Environmental Protection Agency* and the *Canadian Pest Management Regulatory Agency* consider novaluron to pose low risk to the environment and non-target organisms, and value it an important option for integrated pest management that should decrease reliance on organophosphorus, carbamate and pyrethroid insecticides.

##### **2. Buprofezin (Applaud)**

Buprofezin, (Z)-2-*tert*-butylimino-3-isopropyl-5-phenyl- 1, 3, 5-thiadiazinan-4-one; is a thianidine insecticides. It is an insecticide with persistent larvicidal activity against sucking pests such as mealybugs, rice hoppers, scales and whiteflies in rice, potatoes, citrus, cotton and vegetables, through the inhibition of chitin biosynthesis and effects on the hormone levels of nymphs. Buprofezin is known to be a contact and stomach poison, but this toxicity is not translocated to the plant. Buprofezin 25 % SC is the insecticide used for the control of sucking pest of rice, cotton, chillies, mango and grapes particularly against plant hoppers, whiteflies, aphids, jassids, thrips, mites, hoppers, mealy bugs etc. Spray application of 0.0025 to 0.05% emulsions is effective against mango hoppers. Its oral LD<sub>50</sub> for rat is 2198 mg/kg and dermal for is > 5000 mg/kg.

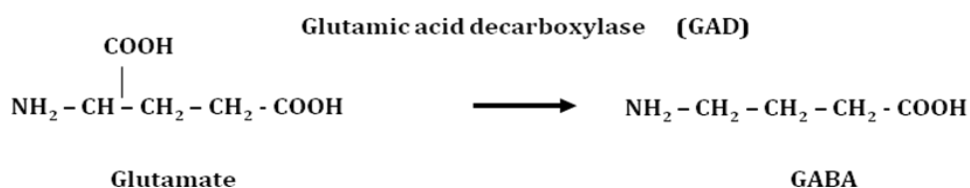
### Mode of action

Buprofezin has a novel mode of action - effective disease resistance management tool, controls organophosphate-resistant hard scales. It inhibits the molting of nymphs and larvae, leading to death, and also suppresses oviposition by adults such that exposed insects lay sterile eggs. It is specifically used to control of Homopteran pests. Low impact on beneficial insects - ideally suited for use in IPM programmes. Active on early instars (jassids) and crawlers (scale and mealybug) and spray applications must be carefully timed to target specific life stages. Usage should be based upon results of pest monitoring within orchards. It controls the pests primarily through contact activity - important to achieve good spray coverage.

### 3. Gamma Amino Butyric Acid (GABA) inhibitors

#### GABA synthesis

GABA is an amino acid neurotransmitter synthesized by decarboxylation of glutamate by the enzyme glutamic acid decarboxylase.



Synthetic organic insecticides are primarily nerve poisons acting on the cholinergic system (for organophosphorus compounds and methylcarbamates), the voltage-dependent sodium channel (for pyrethroids and DDT), and the GABA-gated chloride channel (for the cyclodienes and other polychlorocycloalkanes).

The insects GABA receptor chloride ionophore complex is found in the CNS and also at peripheral neuromuscular sites. GABA receptors belong to a superfamily of ligand gated ion channels as Cys-loop receptors that include nicotinic acetylcholine receptors and glutamate gated chloride channels. Cys-loop receptors are so named because all family subunits contain in their amino terminal two extracellular, adjacent cysteine residues. Each GABA receptor molecule consists of five subunits that form a central ion pore. Each subunit has a long N-terminal extracellular domain

contributes to the neurotransmitter (GABA) binding site and four transmembrane regions. GABA is an inhibitory neurotransmitter. The arrival of an action gated triggers GABA to be released from the presynaptic terminal. As a result, the chloride channel is opened and Cl ions flow into the postsynaptic neuron. This increased chloride permeability results in a hyperpolarization of the membrane (i.e more ions in the cell), exhibiting an inhibitory postsynaptic potential produced by Cl ions. The effect of this hyperpolarization is to maintain the membrane at its resting value so that is excitability is decreased. Insecticides including cyclodienes, lindane and phenylpyrazole (fipronil and ethiprole) bind to the chloride channel and block its activation by GABA. The absence of synaptic inhibition leads to hyperexcitation of the central nervous system (CNS), convulsions and finally death.

## Newer Insecticides

### i. Neonicotinoids

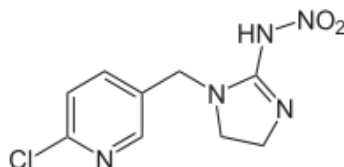
The neonicotinoids are among the most effective group of insecticides, especially for controlling sucking insects such as whiteflies, aphids and leafhoppers. The neonicotinoids represent a class of chemicals, nicotine mimics, in which the biochemical target is the nicotinic acetylcholine receptor (nAChR) of both the central and peripheral nervous system. Similar to the original nicotine, the neonicotinoids bind to these receptors, resulting in excitation and paralysis followed by insect death. The neonicotinoids have a broad spectrum insecticides, exhibiting systemic and translaminar properties and high residual activity. Recently, the use of some members of this class has been restricted in some countries due to strong evidence of a connection to honey-bee colony collapse disorder.

The neonicotinoid insecticides can be classified into two groups based on chemical structure as

1. Ring systems eg. Imidacloprid, thiacloprid and thiamethoxam
2. Non-cyclic compounds eg. Acetamiprid, clothianidin, nitenpyram and dinotefuran

#### a. Imidacloprid (C<sub>9</sub>H<sub>10</sub>ClN<sub>5</sub>O<sub>2</sub>)

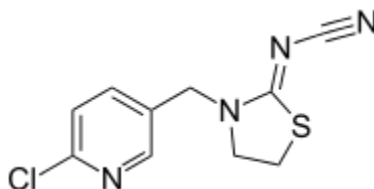
Imidacloprid is a chloronicotinyl nitroguanidine insecticide, with the IUPAC name 1-[(6-chloropyridin-3-yl) methyl]-N-nitro-4, 5-dihydroimidazol-2-amine. Imidacloprid is a systemic pesticide with physical/chemical properties that allow residues to move into treated plants and then throughout the plant via xylem transport and translaminar (between leaf surfaces) movement.



Imidacloprid was the first commercial neonicotinoid to successfully control agricultural pests. It is widely used as seed dressing and in soil applications, as it is considered to be a relatively polar material with good xylem mobility. Because of their systemic and translaminar properties the

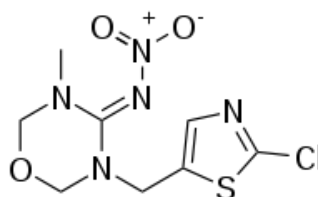
neonicotinoid insecticides are particularly effective in controlling sucking pests such as aphids, leafhoppers and whiteflies. It is systemic with particular efficacy against sucking insects and has a long residual activity. In India many formulations of imidacloprid are registered viz., 17.8% SL (Confidor), 70 % WG (Admire), 30.5% SC (Confidor super) as foliar spray and 70% WS (Gaucho), 48% FS as seed treatment. Imidacloprid 30.5 % SC is also used for protecting buildings from termite attack @ 0.075% a.i concentration. It has an oral LD<sub>50</sub> in rats of 450 mg/kg.

**b. Thiacloprid (C<sub>10</sub>H<sub>9</sub>ClN<sub>4</sub>S)**



The chemical of thiacloprid is (N-(3-(6-chloro-pyridin-3-ylmethyl)-thiazolidin-2-ylidene)-cyanamide) belongs to neonicotinoid group of insecticides. The technical material is a yellowish odorless crystal powder stable under higher temperature and unaffected by reducing agents. It has got half life of 2.4 - 27.4 days under field conditions. It acts as insecticide and molluscicide. It has a broad spectrum of activity against not only sucking insects but also chewing insects. It is a potent agonist of insect nicotinic acetylcholine receptors and disturbs synaptic signal transmissions. Formulated as 21.7% at 120 g a.i/ha effective against BPH, WBPH and GLH in rice. It's acute oral LD<sub>50</sub> for rat 444-836 mg/kg. It is marketed under the trade name of Calypso SC 480 (480 g/L), Alanto and Topstar.

**c. Thiamethoxam (C<sub>8</sub>H<sub>10</sub>ClN<sub>5</sub>O<sub>3</sub>S)**

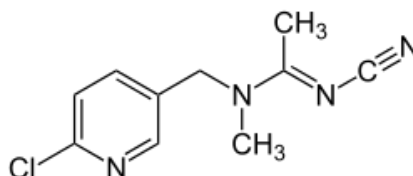


The chemical name of thiamethoxam is (EZ)-3-(2-chloro-1, 3-thiazol-5-ylmethyl)-5-methyl-1, 3, 5-oxadiazinan-4-ylidene (nitro) amine. It possesses contact and stomach activity. Its systemic properties has resulted in its use against foliar feeding insects via seed treatment, soil application, through irrigation systems, or applied to the trunks of trees. It is also registered for direct foliar application. Thiamethoxam is a broad-spectrum, systemic insecticide, which means it is absorbed quickly by plants and transported to all of its parts, including pollen, where it acts to deter insect feeding. An insect can absorb it in its stomach after feeding, or through direct contact, including through its tracheal system. The compound interferes with information transfer between nerve cells, making the insects become paralyzed.

Thiamethoxam is a broad spectrum systemic insecticide acting against stem borers, hoppers, jassids, whiteflies, aphids, mosquito bugs, psyllids and used in crops viz., rice, cotton, wheat, mustard, okra, mango, potato, tea and citrus etc. Formulated as 25% WG (foliar spray), 70%

WS and 30% FS (seed treatment) as Actara and Cruiser, respectively. Its oral LD<sub>50</sub> in rats is > 5000 mg/kg.

**d. Acetamiprid (C<sub>10</sub>H<sub>11</sub>ClN<sub>4</sub>)**



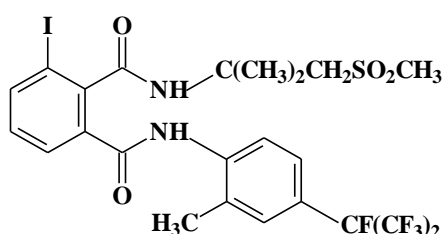
The IUPAC name of acetamiprid is (E)-N1-[(6-chloro-3-pyridyl) methyl]-N2-cyano-N1-methyl acetamidine. It is an odorless, highly soluble in water and is non-volatile. Based on its chemical properties it would not be expected to leach to groundwater. It is not persistence in soil systems but may be very persistent in aquatic systems under certain conditions. It has a moderate mammalian toxicity and it has a high potential for bioaccumulation. Acetamiprid is a recognised irritant. It is highly toxic to birds and earthworms and moderately toxic to most aquatic organisms. It is broad spectrum systemic insecticide used for control of pests of vegetables, fruit trees, tea etc. It found effective against sucking insect pests of cotton. Its oral LD<sub>50</sub> for rat >5000 mg/kg. It is formulated as Acetamiprid 20 % SP (Pride, Ennova).

**Mode of action of neonicotinoids**

The neonicotinoid insecticides act as agonists of the acetylcholine receptor. That is, they mimic the action of the neurotransmitter, acetylcholine (ACh). Although cholinesterase is not affected by these insecticides, the nerve is continually stimulated by the neonicotinoid itself, and the end result is similar to that caused by cholinesterase inhibitors-over stimulation of the nervous system leads to poisoning and death.

**ii. Diamide group insecticides** eg. Flubendiamide and chlorantraniliprole

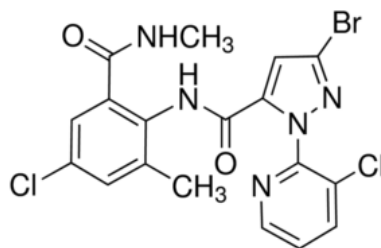
**a. Flubendiamide (C<sub>23</sub>H<sub>22</sub>F<sub>7</sub>IN<sub>2</sub>O<sub>4</sub>S)**



It is a novel insecticide belongs to a new chemical class named benzenedicarboxamide or phthalic acid diamide. Its unique chemical structure is characterized by a phthaloyl moiety, an aromatic amide moiety and an aliphatic amide moiety. It has stomach poison, excellent fast-acting and residual activity against a broad spectrum of lepidopterous insect pests, such as *Helicoverpa* spp., *Heliothis* spp., *Spodoptera* spp., *Plutella* spp., *Pseudoplusia* spp., *Trichoplusia* spp., and *Agrotis* spp., including resistant strains of them as well. It will be useful not only for insecticide resistance management (IRM) programs but also fit well into integrated pest management (IPM) programs. It is safe to non target organisms. Its oral acute oral LD<sub>50</sub> for

rat is > 2000 mg/kg, and for dermal for rat > 2000 mg/kg. It has been registered in India under different formulations such as 20 % WDG (Takumi) and 39.35% SC (Fame) which act on insect pests of rice (stem borer, leaf folder) and cotton (*H.armigera* and spotted bollworm).

**b. Chlorantraniliprole (Rynaxypyr™)-**  $C_{18}H_{14}BrCl_2N_5O_2$



The other new class of chemistry of this group is chlorantraniliprole to be specific it belongs to anthraanilic diamides. Chlorantraniliprole is being developed worldwide by DuPont in a broad range of crops to control a range of pests belonging to the Order Lepidoptera and some Coleoptera, Diptera and Isoptera species. It possesses a new mode of action (group 28 in the IRAC mode of action scheme), high biological activity, very low mammalian toxicity and selectivity to non-target arthropods. Upon exposure, the sensitive insect species rapidly stops feeding, becomes paralyzed, and ultimately die. This compound is primarily active on chewing pests by ingestion and by contact, showing good ovi-larvicidal and larvicidal activity. It has long lasting activity with new mode of action and safe to non target insects (parasitoids, predators and pollinators). It is also used to control insects which are found resistant to other insecticides and fits into IPM. In India registered in 2009 and available as 18.5% SC (Coragen) and 0.4 % GR (Ferterra). Its oral LD<sub>50</sub> in rats is > 5000 mg/kg.

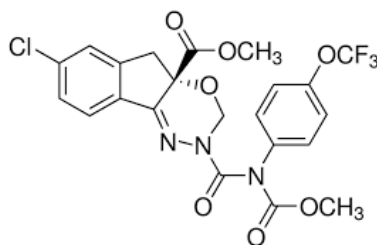
**Mode of action of diamide insecticides**

It is a novel activator of ryanodine-sensitive calcium release channels (ryanodine receptors, RyRs), which play a critical role in muscle function from internal stores into cytoplasm and because of depletion of calcium it causes paralysis and finally death.

**iii. Others**

**a. Indoxacarb** ( $C_{22}H_{17}ClF_3N_3O_7$ )

Many insects have developed resistance to conventional pesticide chemistries, such as organophosphates, carbamates, and pyrethroids. To combat these pesticide resistant pests new chemistries have been developed with novel modes of action unrelated to previous chemical classes to replace the old chemistries. The development of insecticidal pyrazoline moiety in the 1970s has led to the discovery of a pyrazoline type sodium channel blocker; indoxacarb is the first commercialized insecticide (Dupont) of the oxadiazine group.

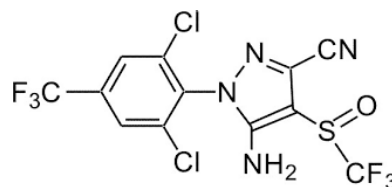


The chemical name of indoxacarb is (S)-methyl 7-chloro-2, 5-dihydro-2- [[[(methoxy carbonyl) [4(trifluoromethoxy) phenyl] amino] carbonyl] indeno [1, 2-e] [1, 3, 4] oxadiazine-4a (3H)-carboxylate. Indoxacarb affects insects from direct exposure when the pesticide is sprayed on the foliage and through ingestion of treated foliage or fruit. The technical material is a white powdered solid. Indoxacarb possesses both larvicidal and ovicidal activity. As a larvicide, it is active by ingestion and/or absorption into the insect. The importance of the entry route varies with the species affected and the crop situation. This insecticide has activity against lepidopteran pests as well as certain homopteran and coleopteran pests in vegetables, cotton, and other field and orchard crops. It is also effective against all stages of larvae of *Helicoverpa* spp. Its oral LD<sub>50</sub> in rats is 1732 mg/kg. Main advantage of indoxacarb is it can be used to control resistant *H.armigera* and DBM where they have developed resistance to all major insecticide compounds specially pyrethroids. Indoxacarb has several formulations including tablet, broadcast granule, water dispersible granule, and suspension concentrate. The formulation is 14.5 % SC and 15.8% EC. It is sold under the trade name of Avaunt and Avaunt EC.

#### Mode of action

It acts by inhibiting sodium ion entry into nerve cells resulting in paralysis and death of the target pest species. It is also a pro-insecticide that is bioactivated by esterase inside the insects following ingestion. The conversion of the pro-insecticide to the active compounds (S-enantiomers of the N-decarbomethoxylated metabolites), which are powerful sodium channel blockers is correlated with the appearance of neurotoxic symptoms eg. Several lepidopteran larvae can rapidly convert the pro-insecticide after ingestion.

#### b. Fipronil (C<sub>12</sub>H<sub>4</sub>Cl<sub>2</sub>F<sub>6</sub>N<sub>4</sub>OS)



This belongs to phenylpyrazoles, which comprise a new class of pesticides which exhibit insecticidal and acaricidal activities. Fipronil, (RS)-5-amino-1-[2, 6-dichloro-4-(trifluoromethyl) phenyl]-4- (trifluoromethyl sulfinyl) -1H-pyrazole-3-carbonitrile, is the first highly successful member of this class. It is active at the neuro inhibitory GABA gated chloride channels. Competitive bindings have demonstrated that this class of insecticides has greater affinity to the target site of insects than mammals, resulting in a high selectivity towards insects. Fipronil exhibits contact and stomach



poison activity against various insect pests such as soil insects (moderately systemic agent), foliar feeding pests such as the diamondback moth, *spodoptera* sp. and it has acaricidal activity. It is a highly effective and broad-spectrum insecticide against sucking, chewing pests and is widely used to control many species of soil and foliar insects on various crops such as rice, vegetables and fruits. It can be used to control insects resistant or tolerant to pyrethroid, organophosphates and carbamate insecticides. Its oral LD<sub>50</sub> in rats is 97 mg/kg. It is effective against stem borer, gall midge, DBM, thrips, shoot borers, root borers and can be used in crops viz., sugarcane, cruciferous crops, cotton and rice. In India the formulations registered are 5% SC, 80 WDG and 0.3 % GR under the trade name of Regent SC, Jump and Regent R, respectively. Fipronil is an excellent termite control product with no smell and prolonged years of activity on soil. Fipronil is low to moderately soluble in water, prefers lipophilic (organic) matrices such as lipids, oils, lignin, proteins, and organic solvents, and is stable at room temperatures. Fipronil forms a number of toxic metabolites in the environment such as fipronil-sulfone, fipronil desulfinyl and fipronil sulphide is the major.

#### **Mode of action**

Fipronil interferes with the  $\gamma$ -aminobutyric acid (GABA)-gated channels; fipronil disrupts normal nerve influx transmission (e.g., passage of chloride ions) by targeting the GABA-gated chloride channel and at sufficient doses, causes excessive neural excitation, severe paralysis and finally leads to insect death.

#### **c. Enamectin**

Enamectin is the 4"-deoxy-4"-methylamino derivative of abamectin, a 16-membered macrocyclic lactone produced by the fermentation of the soil actinomycete *Streptomyces avermitilis*. It is generally prepared as the salt with benzoic acid, emamectin benzoate, which is a white or faintly yellow powder. Enamectin is widely used in the US and Canada as an insecticide because of its chloride channel activation properties.

#### **Enamectin benzoate**

Enamectin benzoate (Proclaimm) is a novel macrocyclic lactone insecticide derived from the avermectin family. Enamectin obtained from abamectin via a five step synthesis, was discovered after screening several hundred avermectin derivatives in an in vivo screen using tobacco cutworm and southern armyworm. Later studies indicated that benzoate salt of emamectin had improved thermal stability and greater water solubility when compared with the original hydrochloride salt. As such, emamectin has broader spectrum insecticidal activity than abamectin B. It is a mixture of > 90% emamectin B1a benzoate and < 10% emamectin B1b benzoate. It is a stomach poison insecticide active against lepidopteron insect pests in vegetable, cotton, maize, peanuts, soybeans and strawberries. Its oral LD<sub>50</sub> in rats is 1516 mg/kg. It has registered uses in many countries on fruits, vegetables, cereals, tree nuts, oilseeds, herbs and tea. It is marketed as 5% SG under the trade name of Proclaim.

**Mode of action**

It acts by stimulating the release of  $\gamma$ -aminobutyric acid, an inhibitory neurotransmitter, thus causing insect paralysis within hours of ingestion, and subsequent insect death 2–4 days later. It is more effective when ingested, but it also somewhat effective on contact. Target pests are numerous. When sprayed to foliage, emamectin benzoate penetrates the leaf tissue and forms reservoir within treated leaves, which provides residual activity against pests that ingest the substance when feeding.

## Lecture 14

### Fungicides - Classification – Inorganics (Sulphur) and Organic fungicides (Chlorobenzene and Chlorothalnil) - Characteristics, mode of action and use

Fungicides are chemicals used to kill fungi or control fungi which cause plant diseases are called as fungicides. In India, Lawrence in 1904 used the Bordeaux mixture for the first time. Subsequently a number of synthetic fungicides were developed and have been widely used in India.

#### Requirements of an ideal fungicide

- Broad spectrum of activity (kill in single spray)
- Low toxicity (safe to mammals and beneficial to predators)
- Solubility (water soluble to give a cheap hydrophilic spray)
- Stability (stable during storage and application)
- Low fungi toxicity (not be toxic to plants)

#### Criteria for effective fungicide

- A fungicide itself or be converted into active fungitoxicant with in the host plant
- Have very low toxicity
- Capable of absorbed by roots, seeds or leaves of the plant and translocated within the plants

#### Classification of fungicides

The fungicides are classified into three major categories. They are

- I. Based on mode of action
- II. Based on use and
- III. Based on chemical structure/constitution

**I. Based on the mode of action**, the fungicides are classified as the fungicides are classified as fungi statics, protective, eradicant, curative and systemic fungicides.

**Fungistatics:** Chemicals which do not kill the fungi but inhibit the growth of the fungi.

**Protectants:** Prevent fungal infection by sporicidal activity. These arrest the germination of spores or kill the fungal hyphae as they penetrate the leaf or prevent their penetration. eg. COC, Zineb

**Eradicant:** are agents that control fungus even after the symptoms become visible and that kill both newly developed spores and the mycelium. eg Benomyl

**Systemic fungicide:** are chemicals taken up by the plant and translocated within the plant thus protecting from the fungal attack. eg. Vitavax, plantvax

**Curative fungicide:** Penetrate cuticle and kill young fungal mycelium growing in the epidermis and this prevents further development of fungal growth. Eg. Fongarid

## II. Based on use: 3 types

1. Seed treatment (seed protectant): used for seed or seedling dips for seed borne diseases.  
Eg. Captan
2. Seed dressings: used for dressing cuts and treatments of affected stems. Eg Imazalil
3. Foliage & flower protectants: used to avoid damage to leaves and flowers. Eg copper fungicide

## III. Based on chemical constitution/structure, the fungicides grouped into two major groups

### A. Inorganics

1. Sulphur fungicides
2. Copper fungicides and
3. Mercury fungicides

### B. Organics

Groups	Example
Diethylthiocarbamates	Zineb, Maneb,
Carboxamides	Carboxin, oxycarboxin
Acylalanine	Metalaxyl, furalaxyl
Benzimidazole derivatives	Carbendazim, benomyl
Heterocyclic fungicides	Captan, Folpet
Organomercurials	PMA, Cersan, Agallol
Organophosphorus	Edifenphos, Kitazin-P
Piperazine derivatives	Triforine
Quinoline derivatives	8 hydroxyquinoline
Antibiotics	Streptomycin
Quinines	Chloranil, Dichlone
Triazoles	Triadimefon
Azole compounds	Imazalil
Morpholine derivatives	Tridemorph

### Inorganic Fungicides

#### 1. Sulphur fungicides

It is one of the most important fungicides used for the control of various diseases, particularly powdery mildews in fruits, vegetables, flowers and tobacco. It act as contact and protectant fungicide. It is effective against apple scab and rust of field crops. The sulphur fungicides may be elemental sulphur, lime sulphur or calcium polysulphide and floatation sulphur.

#### **a. Elemental Sulphur**

- Occurs in both free state and also in combination
- Available in dust, wettable powder and colloidal forms.
- Efficiency increases with fineness of the particle size.
- Should pass through 200 – 300 mesh sieve.
- Wettable powders are made by grinding sulphur with protective colloidal materials such as caesin, bentonite clay, skimmed milk, flour or dextrin
- Sulphur dusting powders containing materials like gypsum, bentonite or talc in small amounts make sulphur flow freely and called as conditioned sulphur.

#### **Forms of Sulphur**

1. **Hydrophilic S** is prepared by passing  $\text{H}_2\text{S}$  through a saturated solution of  $\text{SO}_2$  in water or by reaction of  $\text{Na}_2\text{S}_2\text{O}_4$  and  $\text{H}_2\text{SO}_4$  or mineral acids.
2. **Hydrophobic** colloidal sulphur is prepared by acidifying lime-sulphur solution with mineral acids.

#### **b. Lime Sulphur or Calcium polysulphide**

- Prepared by boiling 1.8 parts of sulphur, 1 part of lime and 10 parts of water for one hour.
- The solution is filtered and diluted to specific gravity 1.003 for sprays.
- Clear orange coloured liquid – consist calcium polysulphides which break down on exposure to air to release elemental sulphur.
- Sucrose is added to lime sulphur to stabilise it and evaporated-this form is called dry lime sulphur.

#### **c. Floatation Sulphur**

- A by-product of the manufacture of fuel gas from coal
- Marketed as paste as well as wettable powders

##### **Mode of action**

- Acts as a hydrogen acceptor in the metabolic system
- Disturbs the normal hydrogenation and dehydrogenation reactions in the cells.
- Acts much like oxygen and forms  $\text{H}_2\text{S}$  instead of  $\text{H}_2\text{O}$  in the fermentation process thus causing a disturbance in the Kerb's cycle.
- Emit sufficient vapour to keep the growth of fungus spores

### **Substituted aromatics (substituted benzenes and phenols)**

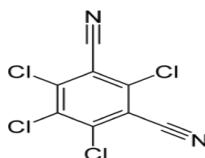
This group of fungicides contains several different subgroups, the chlorobenzene, phenols and the dicarboximide fungicides. Pentachloronitro benzene (PCNB) was introduced in the 1930s and is widely used as a soil fungicide for seed treatment and foliar application. Hexachlorobenzene (HCB) was introduced in 1945 to treat seeds and foliage. Chlorothalonil was introduced in 1964, it is a broad spectrum foliar or soil applied fungicide used on many crops. Dichloran is a popular and widely used fungicide for the protection of a variety of fruits and vegetables. The majority of phenols, especially those containing chlorine, are too phytotoxic to permit their use as agricultural fungicides. They are widely used as industrial fungicides. Cresols contribute to the fungicidal action of creosote which is used as a timber preservative. Pentachlorophenol, another chlorinated phenol and its esters are widely used as industrial biocides for the protection of such materials as wood and textiles.

### **Organic fungicides**

#### **Chlorobenzenes and related compounds**

The 2,6-dichloro-4-nitro aniline was marketed in 1959 by Boots Ltd. especially valuable for the control of Botrytis in tomatoes and against fungal organisms causing post harvest decay of fruits. Penta chloro nitro benzene (PCNB) called quintozone is a widely used soil fungicide for damping off diseases. Chloroneb is used to control soil borne fungi as seed dressings or by soil application.

#### **Chlorothalonil**



Chlorothalonil (2, 4, 5, 6-tetrachloro isophthalonitrile), is a colourless crystalline compound. The activity is caused by the high reactivity of the Cl atom with thiol enzymes of the fungi. It is chemically stable in both acid and alkaline media. It is an aromatic organic fungicide mainly used as a broad spectrum (multisite activity- excellent resistance management partner) and non-systemic fungicide. It is effective against all four fungi classes: Oomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes (Fungi Imperfecti). Chlorothalonil containing products are sold under the names Bravo and Kawach. It was first registered for use in the US in 1966. Its oral LD<sub>50</sub> for rats is 10,000 mg/kg. Chlorothalonil is of low toxicity to non-target terrestrial organisms.

#### **Mode of action**

Chlorothalonil reduces fungal intracellular glutathione (sulfhydryl group) molecules to alternate forms which cannot participate in essential enzymatic reactions, ultimately leading to cell death.

## Lecture 15

### Characteristics, mode of action and use of Systemic fungicides (Benomyl, Carbendazim, Metalaxyl, Quinones, Diclones, Dicarboximides –vincozolin)

A systemic fungicide is a compound taken up by a plant and then translocated within the plant for protecting it from pathogenic fungi. Systemic fungicides are the only fungicides that are absorbed into xylem and phloem and moves up and down in plants. Eg. phosphonates.

#### Criteria for effective systemic fungicide

- Must be fungicidal or converted into an active fungi toxicant within the host plant.
- Possess very low phytotoxicity
- Capable of being adsorbed by roots, seeds or leaves of the plant and translocated with in the plants

There are a number of systemic fungicides in the market, which may be divided into the following eight groups.

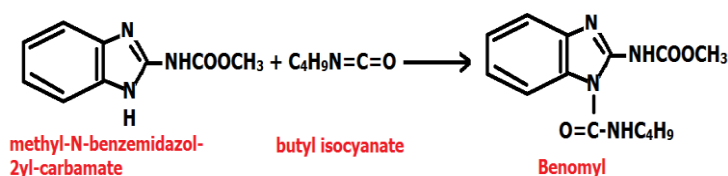
- |                  |                              |
|------------------|------------------------------|
| • Benzimidazoles | • Pyridines                  |
| • Thiophanates   | • Morpholines                |
| • Carboxamides   | • Azoles                     |
| • Pyrimidines    | • Organophosphorus compounds |

#### I. Benzimidazoles

These represent a new era in fungicide use when they were introduced in late 1960s. The most important group members are :

##### i. Benomyl (Benlate)- N-(1-butyl carbamoyl benzimidazole-2- yl) methyl carbamate

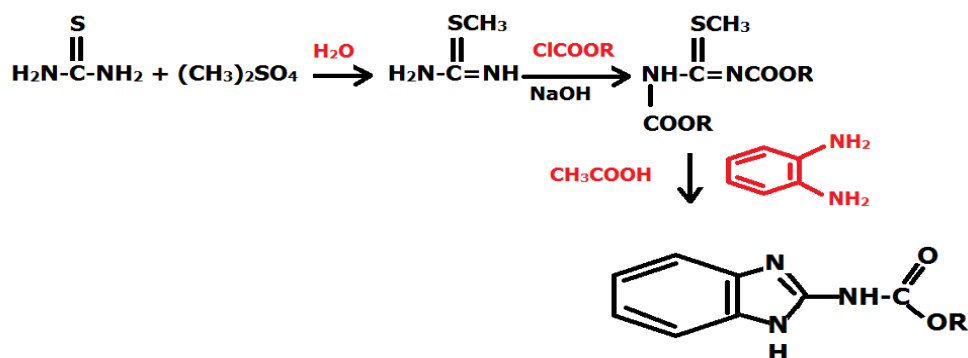
It is prepared by the reaction of methyl –N- benzimidazol-2yl-carbamte with butyl isocyanate.



- Protective and eradicative fungicide with systemic activity.
- Effective against a wide range of fungi affecting fruits, nuts and vegetables (grey mould, apple scab and powdery mildew)
- Foliage and soil fungicide and also very good seed protectant
- LD<sub>50</sub> > 9590 mg / kg body weight of rat
- In aqueous media, it is hydrolysed rapidly to methyl N-benzimidazol-2yl-carbamate (MBC)

##### ii. Carbendazim (methyl N-benzimidazol-2yl-carbamate, MBC) ,Trade name: Bavistin

It is prepared by methylation of thiourea with dimethylsulphate and subsequent N acylation with methyl ester of chloroformic acid. N,N' -bis (methoxycarbonyl)-S-methyl isothiurea is condensed with o-phenylene diamine in glacial acetic acid.

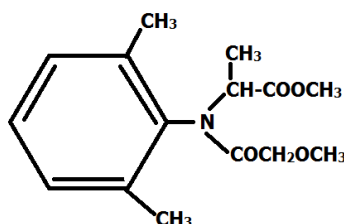


- It is light grey powder which decomposes slowly in alkaline solution.
- Carbendazim is a foliage fungicide with a broad spectrum of action
- It protects orchards, vineyards, vegetables, ornamental plants and field crops against many fungal diseases.
- Inactive against rust, LD<sub>50</sub> value for rat is 15000 mg/kg.
- Mode of action : inhibition of nuclear division due to their action on the microtubule assembly

## II. Phenylamides

First members of this group Metalaxyl and Furalaxyl were introduced by Ciba-Geigy in 1977 (Metalaxyl = Ridomil).

- i. **Metalaxyl** (methyl N-(2,6-dimethylphenyl)N-(2-methoxy acetyl)-DL-alaninate)



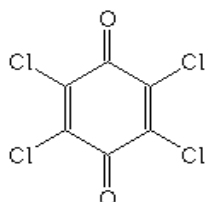
- Systemic fungicides and formulated as seed dressing
- Protective with systemic properties and are slightly toxic to fish
- Highly effective at low concentrations for foliar and soil application against diseases caused by both air and soil borne Oomycetes spp in agricultural and horticultural crops.
- LD<sub>50</sub> : 669 mg / kg body weight of rat
- Effective against downy mildew on vines, lettuce, maize and Pythium diseases

## III. Quinone fungicides

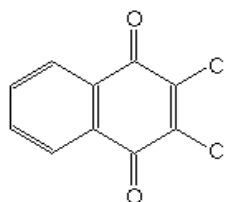
The first member of this group, chloranil (tetrachloro-*p*-benzoquinone), was first used as a fungicide in 1938. It is prepared by oxidative chlorination of phenol or by oxidative hydrolysis of pentachlorophenol. It has broad spectrum activity, inhibits electron transport, photophosphorylation



and CO<sub>2</sub> fixation. It was found to be useful as a seed protectant and foliage fungicide for downy mildew. The popular, related derivative known as dichlone (2, 3-dichloro-1,4-naphthoquinone), it was prepared by bubbling chlorine gas through a solution of 1,4 aminonaphthalene sulphonic acid in aqueous sulphuric acid. It can be used as foliage fungicide against powdery mildew of apple scab and gray mould. Dichlone is more stable in light has been used as a seed dressing agent and a foliage spray against powdery mildew. Chloranil and dichlone have been discontinued and are no longer available in the U.S.



Chloranil



Dichlone

### Toxicity

The quinone fungicides are low to moderate acute toxicity with oral LD<sub>50</sub> values (rat); chloranil 4000, dichlone 1,300 and dithianon 638 mg/kg. Under some conditions, these compounds may cause severe skin irritation in sensitive individuals.

### Mode of action

Quinones react with the sulfhydryl groups of enzymes such as amylase and oxycarboxylase. This reaction interferes with their activity and indirectly with other cellular processes such as oxidative phosphorylation.

### IV. Dicarboximide compounds

Dicarboximide (or dicarboxamide) fungicides are a family of agricultural fungicides that include vinclozoline, iprodione and procymidone. More recently a series of dicarboximide derivatives with excellent fungicidal action have been discovered in which the heterocyclic moiety is mostly pyrrolidine dione, oxazolidine dione or imidazolidine dione. All members contain the 3, 5 - dichlorophenyl moiety and the fungicidal activity depends on the presence of the two chlorine atoms in 3, 5 positions. This group of fungicides consists of vinclozoline, iprodione and procymidone have been extensively used for the control of *Botrytis* and *Scelrotinia* sp in cereals, fruits and vegetables but their use is restricted due to the development of resistance. Only procymidone acts systemically; however, vinclozoline and iprodione both exhibit protective and curative activities. The dicarboximides have low mammalian toxicities (LD<sub>50</sub> > 3500 mg/kg). This group of compounds is relatively nontoxic and is classified in toxicity categories III and IV.

These fungicides turn into 3, 5 - dichloroaniline in soil rapidly. Repeated use of dicarboximides over several years reduces their effectiveness. Resistances has developed against all dicarboximides in many plant species, including vines, strawberries and protected crops, and are recommended to be used in conjunction with other fungicides. First registered in 1981, vinclozoline is widely used but its

overall application has declined. As a pesticide, vinclozoline is regulated by the United States Environmental Protection Agency (U.S. EPA). In addition to these restrictions within the United States, as of 2006 the use of this pesticide was banned in several countries, including Denmark, Finland, Norway, and Sweden. It has gone through a series of tests and regulations in order to evaluate the risks and hazards to the environment and animals. Among the research, a main finding is that vinclozoline has been shown to be an endocrine disruptor with antiandrogenic effects.

Commercial products containing dicarboximide compounds

Compounds	Trade name
Vinclozoline	Curalan, Ronilan
Iprodione	Chipco, Rovral
Procymidone	Sumilex

### Mode of action

The two (vinclozoline and iprodione) members of dicarboximide group differ somewhat in their physical properties. Neither is truly systemic although both have limited eradicant activity. The precise biochemical mode of action of the dicarboximide is not well understood. There is some evidence for interference with membranes, cell walls and nuclear processes.

### Mode of action of fungicides

#### i. Non systemic (Sulfur, Copper and Mercury fungicides, Quinone derivatives)

- Sulphur acts as hydrogen acceptor in metabolic systems to form  $H_2S$ , and disrupts the normal hydrogenation and dehydrogenation reactions in the cell
- Cu ions precipitate or inactivate the proteins (enzymes of sulphydryl group) and thus kill the spores
- Mercury act either as vapour or in ionic form destroy the sulphydryl group of (-SH) enzymes. Organomercurials are more toxic than the inorganic mercuric ones due to enhanced lipid solubility facilitating diffusion through the spore membrane to the site of action.
- Binding of quinone nucleus to -SH and  $-NH_2$  groups in the cell leading to disturbance in the electronic transport systems.

#### ii. Systemic fungicides

Mode of action of systemic fungicides is associated with

1. Interference with electron transport chain influencing the energy budget of cell
2. Reduction in biosynthesis of new cell material required for growth and development of the organism, and
3. Disruption of cell structure and permeability of cell membrane. Examples are
  - Benomyl and its related compounds - interfere with mitosis in cell division in angiosperms and fungi.
  - Benzimidazoles, thiophanates, oxathins, phenylamides (metalaxyl derivatives) - influence DNA

synthesis and mitosis inhibitors.

- Triazole group of fungicides - interfere with the biosynthesis of fungal steroids and ergosterol which are important constituents of the cell wall.
- Pyrimidine derivatives - inhibit purine biosynthesis and several pyridoxal dependent enzymes.
- Morpholines - is still not well understood but inhibition of sterol biosynthesis.
- Organo phosphorus fungicides- inhibit permeation through cytoplasmic membrane of the substrates for chitin synthesis.
- Thiono compounds - inactive against fungi.

## Lecture 16

Herbicides - Classification of herbicides - Characteristics, Mode of action and use of 2, 4-D, Sulfonyl ureas - Metsulfuron, Pyrosulfuron, Imidazoline, Alachlor, Butachlor, Oxyfluorfen, Fulchloralin, Pendimethalin, Atrazine, Paraquat and Glyphosate. Bisperipac sodium

### Weed

A weed is any plant, wild or cultivated that is undesired in a particular place. Weeds are divided into broad leaved weeds (dicotyledonous plants) and grass weeds (monocotyledonous plants). Weeds compete with plants for water, light and food and the yield loss due to weeds is estimated as 9-10%.

### Herbicides

Herbicides are chemical substances used to kill or inhibit the growth of unwanted plants in cropped and non cropped areas. The normal field recommendations vary from few grams to 2 to 3 kilograms of active ingredient per hectare.

Although research into herbicides began in the early 20th century, the first major breakthrough was the result of research conducted in both the UK and the US during the Second World War into the potential use of herbicides in war. The first modern herbicide, 2,4-D, was first discovered and synthesized by W. G. Templeman at Imperial Chemical Industries. When 2,4-D was commercially

released in 1946, it triggered a worldwide revolution in agricultural output and became the first successful selective herbicide.

### **Classification**

Herbicides may be classified based on one or more common characteristics as follows

- A. According to selectivity: Selective and Non-selective
- B. Mode of action: Contact and Systemic
- C. Time of application: Pre plant application, Pre emergence and Post emergence
- D. Their chemical groups: Inorganic and Organic

#### **A. According to Selectivity of Herbicides**

- 1. **Selective herbicides:** Kill weeds alone selectively without affecting the crop Eg. Butachlor, Atrazine, 2,4-D, Pendimethalin, Fluchloralin
- 2. **Non-selective herbicides:** Kill both crop as well as weeds without any differentiation. These herbicides are used normally in noncropped fields and in wide spaced crops like cotton, sugarcane, banana etc. Eg. Paraquat, Diquat.

#### **B. According to mode of action**

- 1. **Contact** herbicides destroy only the plant tissue in contact with the chemical. Generally, these are the fastest acting herbicides. They are less effective on perennial plants, which are able to regrow from rhizomes, roots or tubers. Eg. PCP, Dinoseb, Paraquat, Cacodylic acid
- 2. **Systemic** herbicides are translocated through the plant, either from foliar application down to the roots, or from soil application up to the leaves. They are capable of controlling perennial plants and may be slower-acting, but ultimately more effective than contact herbicides. Eg. TCA, Dalapan, 2,4-D, 2,3,6, TBA Diuron, Linuron, Flumeturon, Siduron, Atrazine, Propazine, Prometone, Simazine

#### **C. Time of application**

Herbicides are applied during 3 different growth stages.

##### **1. Pre-sowing or Pre-planting Herbicides**

These herbicides are used to control the growth of weeds in the field before sowing of the crop plants. Eg. Paraquat is sprayed to kill weeds before taking up rice, planting especially under zero or minimum tillage. Fluchloralin is sprayed and incorporated in soil in groundnut under rainfed conditions. Similarly, in onion, bhendi and tomato field fluchloralin is sprayed as a pre-planting herbicide. After spraying the herbicides, the entire field is irrigated and seedlings are planted.

##### **2. Pre-Emergence Herbicides**

These herbicides are sprayed during third to fifth day after sowing before the weed seeds germinate. Most of the herbicides used are of pre-emergent type. Eg. Atrazine is sprayed third day after sowing in sorghum.

### 3. Post-Emergence Herbicides

These herbicides are used to control grown up weeds (may be 30-40 days after sowing).

Eg. 2,4-D sodium salt is sprayed 15 days after sowing in sorghum to control weeds.

#### D. Based on their chemical groups

1. **Inorganic herbicides** - These herbicides do not have carbon atoms in them. Eg. Sodium borate, copper sulphate
2. **Organic herbicides** - These herbicides have carbon atoms in them. Examples are follows

Chemical groups	Examples
Sulphonyl ureas	Metasulfuron-methyl, Sulpho sulfuron
Aliphatic	TCA, Dalapan
Amide	Alachlor, Butachlor, Propanil
Bipyridiums	Paraquat, Diquat
Dinitrianilines	Fluchloralin, Pendimethalin
Chloro phenoxy compound	2,4-D, 2,4,5-T
Triazines	Atrazine, Simazine
Ureas	Monouron, Diuron
Diphenyl ether	Nitrophen, Oxyflourfen
Phenoxy phenoxy alkanoic acid	Clodinofof, Fenoxa prop-ethyl
Thiocarbamate	Benthicarb
Organophosphorus	Glyphosate, Anilophos
Imidazolines	Imazethapyr, Imazaquin

#### Trade name of different herbicides

Chemical Name	Trade Name	Chemical Name	Trade Name
Atrazine	Atrato, Solaro	Metachlor	Dual
Alachlor	Lasso, Lazo	Nitrofen	Toke E-25
Butachlor	Machete, Delachlor	Oxyflourfen	Goal
Anilophos	Azalin	Paraquat	Gramaoxone
Diuron	Cormex	Propanil	Stamp F-34
Diquat	Reglone, Dextrone	Pendimethalin	Stomp
Fluchloralin	Basalin	Simazine	Tafasine
Glyphosate	Roundup	2, 4-D	Plantgard

#### Herbicide formulations

Herbicides are manufactured in four formulations as

1. **Soluble salt:** These herbicides are completely soluble in water eg. 2,4-D sodium salt.
2. **Wettable powder:** Wetting agent is added and it enables the herbicides to form stable suspension in water. Eg. Atrazine, Diuron.
3. **Emulsion concentrate:** These can be mixed with water and sprayed or they can be mixed with sand and applied. Eg. Fluchloralin, Pendimethalin.
4. **Granules:** Granular herbicides can be directly applied to the soil. They do not come in contact with the crop foliage and there is no drift in the field.

### **Mode of action of herbicides**

Affects physiological processes like cell division, tissue development and chlorophyll and plastid formation

#### **Cell division**

- Herbicides are called as mitotic poisons
- They may affect the processes at a particular stage such as between metaphase and anaphase and prevent cell wall formation resulting in multi nucleate cells.

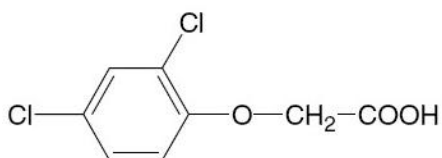
### ***Tissue development***

- Hormone type herbicides cause abnormal development and growth of cellular tissues such as xylem and phloem which interfere with the normal distribution of metabolites.
- Affects photosynthesis by blocking the normal pathway of electron transfer in light reaction. Some herbicides like Paraquat and Diquat act as electron acceptors and form free radicals. Such free radicals are oxidized to  $H_2O_2$  which when accumulated destroy the cells
- Affects respiration by inhibiting electron transfer, energy transfer and by acting as uncoupling agents
- Affects nitrogen metabolism by inhibiting RNAs and DNAs and by increasing the amino acid and protein contents
- Alters the enzyme activity by changing the molecular structure, by competing with the substrate for active sites, by forming complexes with enzymes or substrate and by competing with co-factor.

### **Phenoxyacetic Acid Derivatives**

#### **1. 2,4-D**

2,4-Dichlorophenoxyacetic acid (usually called 2,4-D) is one of the oldest and most widely available herbicides and defoliants in the world. It is a common systemic herbicide used in the control of broadleaf weeds. It is a member of phenoxy group of pesticides. 2,4-D is a synthetic auxin (plant hormone) and as such it is often used in laboratories for plant research and as a supplement in plant cell culture media.



### Manufacture

2,4-D is manufactured from chloroacetic acid and 2,4-dichlorophenol. Alternatively, it may be produced by the chlorination of phenoxyacetic acid. The production processes creates several contaminants including isomers, monochlorophenol, and other polychlorophenols and their acids.

### Properties

- It is a white to yellow powder
- Its solubility in water is 900 mg / L.
- Highly volatile
- Its LD<sub>50</sub> is 639 mg/kg.
- The great advantages are cheap manufacture and relatively low mammalian toxicity

### Mode of action

It works by causing uncontrolled cell division in vascular tissue. Abnormal increases in cell wall plasticity, biosynthesis of proteins and production of ethylene occur in plant tissues. The ester forms of 2,4-D penetrate foliage, whereas plant roots absorb the salt forms.

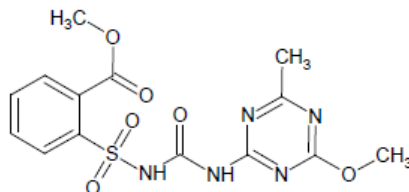
### Sulfonylureas

Introduced in 1982 by Dupont, this group has made a major impact on weed control technology. Sulfonyl urea herbicides are new group of selective herbicides and are used for the control of broad leaved weeds. These herbicides are applied at very low dosage of 10-40 g/ha. It possesses very low mammalian toxicity and very desirable environmental properties. They are remarkable active compounds, selectively controlling many dicotyledonous weeds. It has excellent herbicidal properties with both as pre and post emergence. Sulfonylureas are generally formulated as wettable powders or water dispersible granules and the compounds are readily absorbed by both the roots and foliage of plants. They are translocated by both the phloem and xylem. The important sulfonyl urea herbicides are listed in the table.

Herbicide	Trade name	Primary use	Dosage (g a.i./ha)
Bensulfuron-methyl	Londax	Rice	20-75
Chlorsulfuron	Glean	Small weeds	10-40
Chlorimuron-ethyl	Classic	Soybeans	8-13
Tribenuron-methyl	Express	Cereals	5-10
Metsulfuron-methyl	Ally, escort	Cereals	2-8
Pyrazosulfuron-ethyl	Agreen	Cereals	15-30

Nicosulfuron	Accent	Corn	35-70
Primisulfuron-methyl	Beacon	Corn	10-40
Ethametsulfuron-methyl	Muster	Canola	15-20

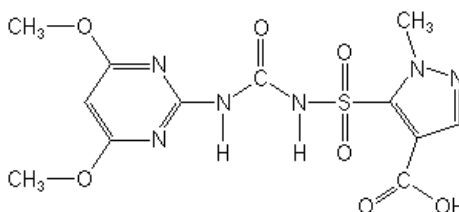
### **Metsulfuron-methyl**



Metsulfuron-methyl is an organic compound classified as a sulfonylurea herbicide, which kills broadleaf weeds and some annual grasses with the advantages of low rate of application. It is a systemic compound with foliar and soil activity, which inhibits cell division in shoots and roots. It has residual activity in soils, allowing it to be used infrequently but requiring up to 22 months before planting certain crops (sunflowers, flax, corn, or safflower). It has very low toxicity to mammals, birds, fish and insects but is a moderate eye irritant.

### **Pyrazosulfuron ethyl**

Ethyl 5-[(4,6-dimethoxypyrimidin-2-yl carbamoyl) sulfamoyl]-1-methyl pyrazole-4-carboxylate.



It is systemic herbicide, absorbed by roots and translocated to the meristems. Uses control of annual and perennial broadleaved weeds and sedges. It is used as pre or post emergence in wet sown and transplanted rice crops at extremely low use rates. It is formulated as GR, SC, WG and WP. Its oral LD<sub>50</sub> for rat and mice is > 5000 mg/kg.

### **Mode of action of sulfonylureas**

The high activity of the sulfonyl urea herbicides suggests that they act by a very specific mode of action. The sulfonylureas are potent inhibitors of plant growth, seed germination is generally affected but subsequent root and shoot growth is severely inhibited in sensitive seedlings. Death follows chlorosis and necrosis.

Genetic and biochemical studies indicated that sulfonylureas inhibit the action of enzymes acetolactate synthase (ALS) which catalyses the first stage in the biosynthesis of the essential aminoacids valine and isoleucine.

### **Imidazoline herbicides**

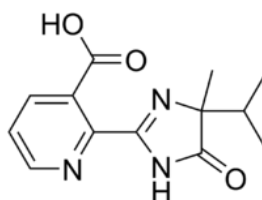
The imidazolines represent a new class of herbicide developed by the American Cyanamid Company in 1983 for control of mono and dicotyledonous weeds. The imidazolinones have a primary



role in weed control in many crops. Several of these compounds are popular, nonselective, broad spectrum and systemic herbicides. It has been found effective as pre and post emergence herbicides to control grasses and dicot weeds in soybeans and other leguminous crops. Imazaquin along with imazamethabenz-methyl, imazapyr, imazapic, imazethapyr and imazamox all comprise the unique class of synthetic compounds termed the imidazolinone herbicides. The chemical structures of these chemicals all closely resemble one another, with the compounds containing an identical imidazolinone ring structure with a carboxylic acid group attached to the backbone. They vary only in the attached ring structure. These six herbicides kill plants by inhibiting acetohydroxy acid synthase (AHAS). The imidazolinones were the second family introduced that have high specific activity: low (grams) active ingredient application rates per acre.

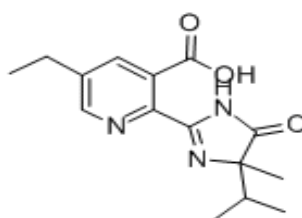
Imidazolinones are readily absorbed by roots and shoots. They translocate both apoplastically in the xylem and symplastically in the phloem. They readily move to the plant meristem where they exert their toxic action, growth stopping fairly quickly. In general, imidazolinone herbicides are more active against dicot species relative to monocot species.

#### **Imazapyr**



Imazapyr ((RS)-2-(4-Methyl-5-oxo-4-propan-2-yl-1H-imidazol-2-yl)pyridine-3-carboxylic acid), is a non-selective herbicide used for the control of a broad range of weeds including terrestrial annual and perennial grasses and broadleaved herbs, woody species and riparian and emergent aquatic species. Imazapyr is a systemic herbicide and is absorbed by the leaves and roots and moves rapidly through the plant. It accumulates in the meristem region (active growth region) of the plant. In plants, imazapyr disrupts protein synthesis and interferes with cell growth and DNA synthesis.

#### **Imazethapyr**

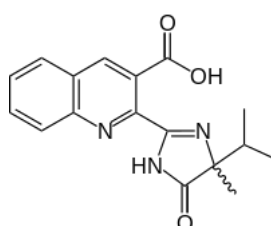


Imazethapyr has mixture of two isomeric derivatives. Its selectivity is not based on differences in uptake or translocation, nor is it based on differences in sensitivity of the acetolactate synthase (ALSase) target in plant species. It is based on metabolic detoxification differences between species. Imazethapyr was used as a selective post emergence herbicide effective against wild oats and some broad leaved weeds in barley, wheat and sunflower crops. It is highly effective

herbicide for difficult control grass and broad leaved weeds in soybean as well as other legumes including beans, alfalfa and peanuts. However, imazamethabenz was developed and found effective as selective systemic herbicide which is absorbed through roots and translocated to meristematic regions. It is used to kill lusters and deciduous trees.

Herbicides	Trade name
Imazapyr	Arsenal
Imazaquin	Image
Imazethapyr	Pursuit
Imazamthaben-methyl	Assert

### Imazaquin



Imazaquin is an imidazolinone herbicide that effectively controls a broad spectrum of weed species. It has the formula  $C_{17}H_{17}N_3O_3$ . Imazaquin is used for broad spectrum weed control (cocklebur, pigweed spp., Pennsylvania smartweed) in soybeans. It can be applied pre-emergence, pre-plant incorporated or post emergence. Soil applications require rainfall or irrigation to move the herbicides into the soil water for plant uptake.

Imazaquin is a non-volatile chemical leading to limited movement into soil that eventually breaks down within 4–6 months. The chemical breaks down microbially and is slowly reduced to carbon dioxide and metabolites. When present in soil, imazaquin is absorbed through the roots of plants where the chemical is either metabolized quickly with no effects or slowly metabolized or not metabolized at all which eventually will lead to the death of the plant. As for its breakdown in surface water, imazaquin has a hydrolytic half-life of 5.5 months at pH 9. At pH 3 and 5, it is stable to hydrolysis.

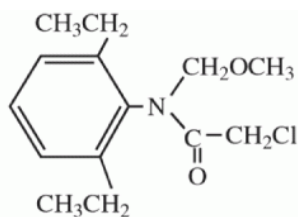
### Mode of action of Imidazoline herbicides

The imidazolines acts by inhibiting branched chain amino acid (valine, isoleucine, leucine) biosynthesis. Specifically, they inhibit the catalytic action of acetolactate synthase (ALSase), also known as acetohydroxyacid synthase (AHASase; the name preferred by American Cyanamid).

### Chloroacetanilide

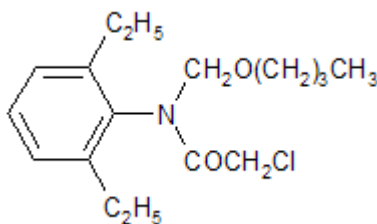
**1. Alachlor** (2-Chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetanilide), Lasso

It is a selective post emergence herbicide used against annual weed grass and broad leaved weeds with low mammalian toxicity. Mixes well with other herbicides and is found in mixed formulations with atrazine, glyphosate, trifluralin and imazaquin.



## 2. Butachlor (N-(Butoxymethyl)-2-chloro-N-(2, 6-diethylphenyl) acetanilide)

It is light yellow oil. It is used as a selective pre-emergent herbicide. It is extensively used in India in the form of granules in rice as post emergence herbicide. It is not persistent, degrades in ten weeks in the soil and is moderately toxic. The trade name is machete.

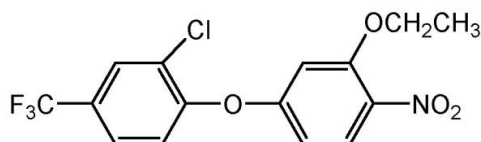


**Mode of action of Chloroacetanilide:** The biological mode of action of chloroacetanilide is inhibition of protein synthesis and GA production during germination.

## Diphenyl ether compounds

### 1. Oxyfluorfen (2-chloro -1-(3-ethoxy -4-nitrophenoxy)-4-(trifluoromethyl) benzene)

The trade name of oxyfluorfen is Goal. Oxyfluorfen is a diphenyl ether herbicide. It possesses low mammalian toxicity and applied as pre emergence herbicide against annual broad leaf weeds in soybean, cotton, tomato and green pepper.

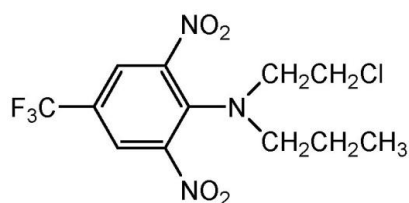


**Mode of action:** It interferes with the photosynthetic system of plants. They impair the noncyclic electron transport and photo-phosphorylation in chloroplast and mitochondria.

## Dinitroaniline compounds

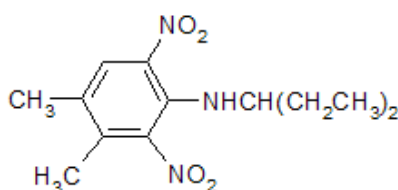
### 1. Fluchloralin (N-(2-chloroethyl)-2, 6-dinitro-N-propyl-4-(trifluoromethyl) aniline)

Fluchloralin is a dinitro aniline herbicide. It is a crystalline solid, orange yellow in colour. It is effective as volatile selective pre-planting herbicide. The trade name is basalin.



## 2. Pendimethalin (3, 4-Dimethyl-2, 6-dinitro-N-pentan-3-yl-aniline), Trade name: Stomp

Pendimethalin is a dinitro aniline herbicide. It is a crystalline solid, orange yellow in colour with fruity odour. Low mammalian toxicity and controls most annual grasses and any annual broad leaved weeds in cereals, vegetables, cotton as both pre and post emergence herbicide. Pendimethalin is available as emulsifiable concentrate, wettable powder or dispersible granule formulations.



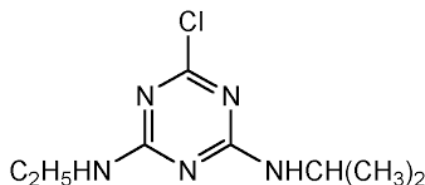
**Mode of action of Dinitroaniline:** Dinitroaniline compounds in general are growth inhibitors. The inhibition of mitosis in both mono and dicot plants affecting the synthesis of both RNA and DNA.

## Triazine compounds

These groups of herbicides are of great practical importance. Several triazine compounds have been synthesized by reacting cyanuric chloride with alkylamine.

### 1. Atrazine (2-Chloro-4-ethylamino-6-isopropylamino-2, 4, 6-triazine), Trade name: Atrataf

Atrazine is a triazine herbicide. It is colourless solid. It has high water solubility and it is a selective pre emergence herbicide for the control of broad leaved weeds in corn, sorghum, sugarcane and pine apple. Also a non selective herbicide in non cropped areas. Many varieties of maize and sugarcane detoxify Atrazine by hydrolysis in the plant tissues and hence it is very valuable for selective weed control in these crops.



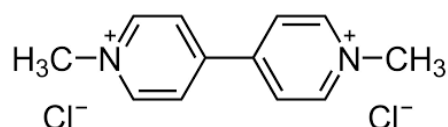
## Mode of action

Atrazine functions by binding to the plastoquinone-binding protein in photo system II, Plant death results from starvation and oxidative damage caused by breakdown in the electron transport process which is accelerated at high light intensity.

## Bipyridillium herbicide

### 1. Paraquat (1, 1'-Dimethyl-4, 4'-bipyridinium dichloride) Trade name: Gramoxone

Paraquat is a bipyridillium herbicide. It is an off-white coloured powder with high solubility in water. Paraquat is also found useful for pre-sowing and pre-emergence weed control in orchards and vineyards. It is more strongly adsorbed by soil than diquat. It is more toxic than diquat but both are non-toxic to bees and earthworms. Paraquat is also toxic to human beings and animals. Research has shown that it is linked to development of Parkinson's disease



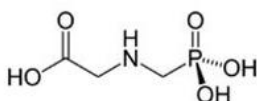
#### Mode of action

Paraquat acts by inhibiting photosynthesis. In light-exposed plants, it accepts electrons from photosystem I and transfers them to molecular oxygen. In this manner, destructive reactive oxygen species are produced. Paraquat increases the hydrogen peroxide levels which is the essential toxicant and kills the plant by lipid peroxidation-destroying cellular membranes

### Organophosphorus compounds

#### 1. Glyphosate (N-phosphonomethyl glycine), Trade name: Roundup

Glyphosate is the amino phosphonogenic analogue of the natural amino acid glycine. It is a white crystalline powder. It is a non selective, post emergence foliar spray herbicide, effective against monocot and dicot annual and perennial weeds. This is rapidly translocated from leaves to roots and is moderately toxic to mammals. Zero persistence in nature.



#### Mode of action

Glyphosate is known to inhibit the biosynthesis of aromatic acid acids.

#### Bispyribac-sodium

- It is a new post-emergence pyrimidinyl carboxy herbicide for the control of a wide range of weeds, in particular on *Echinochloa crusgalli*; the application done from the fourth unfolded leaf up to the tillering stage presents a good plant compatibility in direct-seed rice.
- This compound presents a good eco-toxicology profile; it is suitable for application on paddy rice.
- Bispyribac-sodium 10% SC (9.5% w/w) new generation broad spectrum post emergent herbicide containing Bispyribac-sodium as an active ingredient.
- It effectively controls most of weed species infesting rice crop, both in nurseries and main field

#### Mode of action

- It is to inhibit the enzyme acetolactate synthase (ALS), (also called acetohydroxy acid synthase or AHAS) inhibitor and
- The subsequent biosynthesis of essential amino acids, which in turn interferes with cell division and causes cessation of plant growth, leading to chlorosis, necrosis, and death of sensitive plants.

#### **Crops and target weeds**

- Nursery : 10-12 days of sowing for nursery rice. Weeds- *Echinochloa crusgalli*, *Echinochloa colonum*, *Ischaemum rugosum*
- Transplanted Rice : Within 10-14 days of transplanted rice when most of the weeds have already emerged and are of 3-4 leaf stage depending upon soil and climatic factors. Weeds- *Cyperus difformis*, *Cyperus iria*, *Fimbristylis milliacea*, *Eclipta alba*
- Direct seeded rice: Optimum time of application is within 15-25 days of the sowing. Weeds- *Ludwigia parviflora*, *Monochoria vaginalis*, *Alternanthera philoxeroides*, *Sphinochloa zeylanica*

## **Lecture 17**

### **Fate of pesticides in soil-Impact of pesticides on the environment, Highlights of Insecticide Act -1968 and Insecticide Rules -1971**

#### **Pesticide Residues**

The pesticide present on a surface where it was applied right after application is called deposit. Pesticide present in or on any substrate after a period of application or even without application is called residues. WHO defined as any specified substance in food, agricultural commodities, animal feed, soil or water resulting from the use of pesticides.

#### **Persistence and Maximum Residue Limit**

The time period for which a pesticide exists in its original chemical form over the application surface and effectively controls the target organism is known as persistence. Maximum Residue Limit (MRL) is defined as the maximum concentration of a pesticide residue (expressed as mg/kg) legally permitted in or on food commodities and animal feeds.

#### **Pesticides in Environment**

When pesticides are applied, many processes like adsorption, transfer, breakdown and degradation occur. Over 98% of sprayed insecticides and 95% of herbicides reach a destination

other than their target species, including non-target species, air, water, bottom sediments and food. The amount of pesticide that migrates from the intended application area is influenced by the pesticidal properties, soil properties and environmental factors. Some pesticides contribute to global warming and the depletion of the ozone layer.

Pesticide enters in the environment (soil, water or air) either through application, disposal or spill. Upon application, a number of environmental factors such as temperature, humidity, air current, light radiations, rainfall may remove the pesticide from substrate. Various degradation processes such as chemical reaction, microbial degradation or co-metabolism also dissipate pesticide from the substrate over a period of time.

### **Persistence of pesticides in plants and soil depends**

#### **I. Chemical factors**

- a. Structural stability: basic structure of pesticides is fundamental in influencing their persistence in plants and soil. Eg. Chlorinated pesticide-highly persistent while the OP and carbamate are not persistent.
- b. Volatilization: low to high vapour pressure
- c. Solubility: greatly influence the persistence of pesticide residue on plants
- d. Method of application and
- e. Formulations

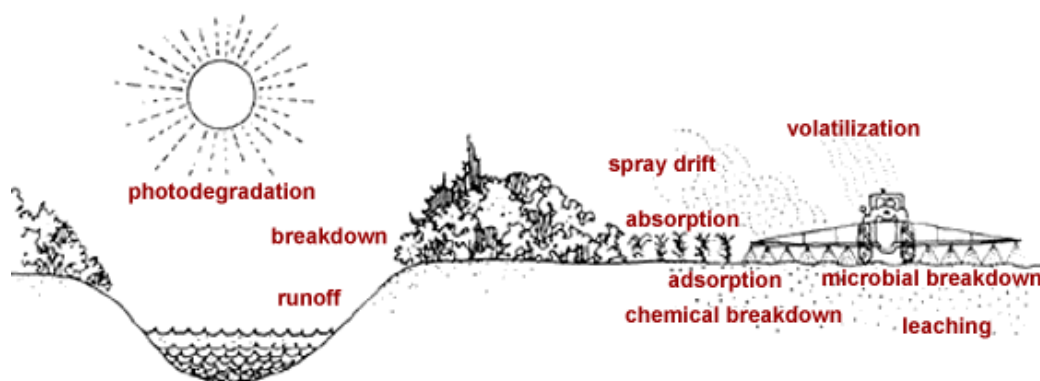
**II. Plant factors:** Plant species, leaf shape, leaf position, leaf surface and margins

**III. Soil factors:** Soil structure, b. clay content, organic matter content

**IV. Environmental factors:** Temperature, radiation and air movement

Major changes that may occur when a pesticide is applied are,

**The fate of pesticides in soil is represented below:**



#### **a. Adsorption**

In the soil pesticide can bind on to the soil particles, organic matter or clay minerals and become unavailable to plants. The presence of functional groups such as  $-OH$ ,  $-NH_2$ ,  $-NHR$ ,  $-CONH_2$  and  $-COOR$  encourages adsorption, especially on the humus. The amount adsorbed varies with the type of pesticide, soil, moisture, soil pH and soil texture. Pesticides are strongly adsorbed to soils that are high in clay or organic matter. They are not as strongly adsorbed to sandy soils. Most soil-bound pesticides are less susceptible to leaching and volatilization losses. They are also not easily taken up by plants.

## **b. Transfer**

Transfer includes processes that move the pesticide away from the target site as volatilization, spray drift, runoff, leaching, absorption and crop removal

### **i. Volatilization**

It is the process of solids or liquids converting into a gas, which can move away from the application site. This movement is called **vapour drift**. Vapour drift from some herbicides can damage nearby crops. Pesticides volatilize most readily from sandy and wet soils. Hot, dry, or windy weather and small spray drops increase volatilization. Incorporating the pesticide into the soil can help reduce volatilization. Soil fumigants such as methyl bromide, has high vapour pressure and is susceptible to volatilization.

### **ii. Spray Drift**

It is the airborne movement of spray droplets away from a treatment site during application. Spray drift is affected by spray droplet size (smaller the droplet, more is the drift) and distance between nozzle and target plant or ground (Drift increases with increased distance). Excessive drift reduces the pesticide applied to the target and can reduce the effectiveness of a treatment.

### **iii. Runoff**

Physical transport of pesticides over the ground surface by rainwater which does not penetrate the soil or carried with transported sediment. It is the movement of pesticides in water over a sloping surface. Pesticides may move with runoff as compounds dissolved in the water or attached to soil particles. The amount of pesticide runoff depends on the slope, vegetation, soil texture, soil moisture content, rainfall, pesticide solubility, pesticide formulation and application methods. The granular pesticide formulations are found in runoff water more than any other formulation. Pesticides with solubilities greater than 30 ppm are more likely to move with water.

### **iv. Leaching**

Movement of pesticides downward through the soil by rain or irrigation water is known as leaching. Conditions that encourage adsorption discourage leaching. Leaching increases when the



pesticide is water soluble; the soil is sandy; a rain-event occurring shortly after spraying and the pesticide is not strongly adsorbed to the soil. Generally herbicides are more prone to leaching than fungicides and insecticides.

#### **v. Plant Absorption**

It is the uptake of pesticides and other chemicals by plants. Most pesticides break down once they are absorbed. Pesticides may be broken down or remain inside the plant or animal and be released back into the environment when the animal dies or as the plant decays. Some degradation products are even more toxic than the original pesticide. Pesticide residues found in the edible plant parts are of critical concern to human beings.

#### **vi. Crop Removal**

Crop removal through harvest or grazing may remove pesticide residues.

### **c. Breakdown and Degradation**

#### **i. Microbial breakdown**

It is the breakdown of chemicals by microorganisms such as fungi and bacteria. Microbial breakdown tends to increase when temperatures are warm; soil pH is favourable; soil moisture and oxygen are adequate and soil fertility is good.

- Chlorinated hydrocarbons such as lindane and endosulphan are very slowly broken down in most soils.
- Organophosphate insecticides such as parathion are degraded, quite rapidly, by a variety of organisms.
- Most widely used herbicides, such as 2,4-D, the phenyl ureas, the aliphatic acids, and the carbamates, are readily attacked by host organisms. Exceptions are the triazines (e.g., Atrazine), which are degraded slowly, primarily by chemical action.
- Most organic fungicides are subject to slow microbial decomposition, causing residue problems.

#### **ii. Chemical breakdown**

It is the breakdown of pesticides by chemical reactions in the soil. The rate and type of chemical reactions that occur are influenced by the binding of pesticides to the soil, soil temperatures, pH levels (organophosphate insecticides, break down more rapidly in alkaline soils or in spray tank water with a high pH level) and moisture.

#### **iii. Photodegradation**

The breakdown of pesticides by light, particularly sunlight is called photodegradation (photolysis). Photodegradation can destroy pesticides on foliage, on the soil surface, and even in

the air. The intensity of light, properties of the application surface, the application method, and the properties of the pesticide affects rate of photodegradation.

- All pesticides are susceptible to photodegradation to some extent.
- Pesticides applied to foliage are more exposed to sunlight than pesticides that are incorporated into the soil.
- Pesticides may break down faster inside plastic-covered greenhouses than inside glass greenhouses, since glass filters out much of the ultraviolet light that degrades pesticides. Ex. DDT, diquat and the paraquat are subject to slow photodecomposition in the soil.

### **Persistence in soil**

- The persistence of pesticides in soil is a summation of all the reactions, movement and degradation affecting the residual toxicity of pesticides.
- Organophosphate insecticides remain in the soil only for a few days, 2,4-D for few weeks and other chlorinated hydrocarbons for 3 to 15 years.
- A pesticide with a half-life greater than 21 days may persist long enough to leach or move with surface runoff before it degrades.

### **Persistent Organic Pollutants**

- Persistent organic pollutants (POPs) are compounds that resist degradation and thus remain in the environment for many years.
- Some pesticides, including aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene, mirex, and toxaphene, are considered POPs.
- POPs have the ability to volatilize and travel great distances through the atmosphere to become deposited in remote regions.
- The chemicals also have the ability to bioaccumulate and biomagnify, and can bioconcentrate up to 70,000 times their original concentrations.
- Bioaccumulation is the process by which toxins enter the food web by building up in individual organisms, while biomagnification is the process by which toxins are passed from one trophic level to the next (and thereby increase in concentration) within a food web.
- POPs may continue to poison non-target organisms in the environment and increase the risk to human beings.

### **Pollution hazards of pesticides**

### i. Air pollution

- Pesticide drift occurs when pesticides suspended in the air as particles are carried by wind to other areas, potentially contaminating them.
- Ground spraying produces less pesticide drift than aerial spraying.
- Pesticides that are sprayed on to fields and used to fumigate soil can give off chemicals called volatile organic compounds, which can react with other chemicals and form a pollutant called tropospheric ozone.
- Pesticide use accounts for about 6 percent of total tropospheric ozone levels.

### ii. Water pollution

- There are four major routes through which pesticides reach the water: it may drift outside of the intended area when it is sprayed.
- It may percolate, or leach, through the soil, it may be carried to the water as runoff, or it may be spilled, for example accidentally or through neglect.
- Maximum limits of allowable concentrations for individual pesticides in public bodies of water are set by the Environmental Protection Agency (EPA) in US.

### Groundwater pollution

Groundwater may be contaminated if pesticides leach from treated fields, mixing sites, washing sites, or waste disposal areas. Groundwater contamination potential as influenced by water, pesticide and soil characteristics.

Characteristics	Low risk	High risk
<b>Pesticide</b>		
Water solubility	Low	High
Soil adsorption	High	Low
Persistence	Low	High
<b>Soil</b>		
Texture	Fine clay	Course sand
Organic matter	High	Low
Macropores	Few, small	Many, large
Depth to groundwater	Deep (100 ft or more)	Shallow (20 ft or less)

Water volume		
Rain/irrigation	Small volumes at frequent intervals	Large volumes at frequent intervals

### iii. Soil pollution

- Many pesticides are persistent soil contaminants, which adversely affect soil conservation.
- Use of pesticides decreases the general biodiversity in the soil.
- Due to less biological activity pesticides become more resistant to degradation.

### iv. Exposure through food

Edible portions of plants may get contaminated by the following means

- Foliar application of pesticides for pest control
- Translocation from pesticides used for seed treatment
- Drift from foliar application on adopting crops
- Translocation of pesticides from soil in food crops
- Contamination of fish, grown in water contaminated with pesticides

### Occupational exposure -respiration, oral and dermal

- During the process of manufacture of pesticides formulations packing and application of pesticides, a large number of workers get exposed to pesticides.
- Repots have suggested that intoxication and human infertilities from pesticides could occur most quickly in many workers when they totally neglect to follow the protective measures.

### v. Impact on crops

- Due to pesticides nitrogen fixation is hindered by plants.
- The insecticides DDT, methyl parathion, and especially pentachlorophenol interfere with legume-rhizobium chemical signaling.
- Reduction of these symbiotic chemical signaling results in reduced nitrogen fixation and thus reduced crop yields.

- Pesticides can kill bees resulting in pollinator decline and Colony Collapse Disorder, in which worker bees from a beehive abruptly disappear.
- Application of pesticides to crops that are in bloom can kill honeybees.
- Pesticides have some direct harmful effect on plant including poor root hair development, shoot yellowing and reduced plant growth.

#### **vi. Impact on birds and animals**

- Animals may be poisoned by pesticide residues that remain on food after spraying, when they enter sprayed fields.
- Pesticides can eliminate food sources of animals, causing the animals to starve.
- Birds can be harmed when they eat insects and worms that have consumed pesticides.
- They have had harmful effects on earthworms, which are in turn consumed by terrestrial vertebrates such as birds and small mammals.
- Some pesticides can bioaccumulate, affecting the food chain.
- By mistake, some granular pesticides are eaten by birds and other wildlife.

#### **vii. Impact on aquatic life**

- Application of herbicides to water bodies can kill fish when the dead plants rot and use up the water's oxygen, suffocating the fish.
- Some herbicides, such as copper sulfate, that are applied to water to kill plants are toxic to fish and other water animals.
- Insecticides are more toxic to aquatic life than herbicides and fungicides.
- A Canadian study showed that exposing tadpoles to endosulfan, kills them and causes growth abnormalities.
- Use of herbicide atrazine has shown sterility in male frogs.

#### **viii. Impact on human beings**

- Pesticides can enter the human body through inhalation of aerosols, dust and vapor that contain pesticides; through oral exposure by consuming food and water; and through dermal exposure by direct contact of pesticides with skin.
- Children are more susceptible and sensitive to pesticides.

- Exposure to pesticides can range from mild skin irritation to birth defects, tumors, genetic changes, blood and nerve disorders, endocrine disruption, and even coma or death.
- DDT and its breakdown product DDE, despite its ban, are known to disturb estrogenic activity and possibly lead to breast cancer.

### **Safe use of pesticides**

- Adopting Integrated Pest Management (Preventive, mechanical, cultural and biological methods)
- Preventing back siphoning and spilling of pesticides
- Considering weather and irrigation plans before pesticide application
- Reading the label directions on the pesticide container
- Disposing off excess chemical and pesticide containers in accordance with label directions
- Leaving buffer zones around sensitive areas
- Reducing off-target drift
- Maintenance and regular calibration of the appliances

### **Pesticides and the Law**

The hazard of pesticides can be prevented by regulation of marketing, evaluation of their properties, performance and hazards of the products through legislation to provide maximum protection to the society from the adverse effects.

### ***Need for Legislation***

- Prevention of misuse
- Protection of workers during preparation, transportation and application.
- Prevention of contamination of food stuffs.
- Maintenance of acceptable residues
- Protection of wild life and prevention of pollution.

### **Genesis of insecticide act**

In the plight of sustaining agricultural productivity, usage of plant protection chemicals is inevitable. Pesticides are toxic substances required to be used judiciously with great care to safeguard the users, animals and the environment. Hence Government of India passed a comprehensive legislation called the Insecticide Act in 1968.

### **Insecticide Act**

The objective of the act is to regulate the import, manufacture, sale, transport, distribution and use of insecticides with a view to prevent risk to human beings and animals. Insecticide act were brought into force with August 1st, 1971 with framing of the Insecticide Rules.

Due to legal reasons, the Act was called **Insecticide Act** and not the **Pesticide Act** and therefore under Section 93 (c) of the Act, the word insecticide means

- Any substance specified in the schedule
- Any other substance such as fungicides and the weedicides may be included after consultation with the Board and the Central Government
- Any preparation containing one or more of such substances

#### **Salient Features of the Insecticide Act**

- Compulsory registration of the product at the central level and licenses for manufacture, formulation and safe use at the state level
- The inter departmental / ministerial / organization coordination is achieved by a high level advisory board, the Central Insecticides Board with 24 members which has now been raised to 28 members drawn from various fields having expert knowledge in the subject
- Registration committee to attend the task of compulsory registration of all pesticides and their formulations
- Establishment of the enforcement machinery like the Insecticide Analysts at Central or State governments
- Establishment of the Central Insecticides Laboratory
- Power to inhibit the import, manufacture and to confiscate the stocks

#### **Functions of the Central Insecticides Board**

- To advise the Central Government on the manufacture of insecticides under the Industries Development Regulation Act, 1951
- To specify the use or classification of insecticides on the basis of their toxicity as well as their suitability for aerial application
- To advice on tolerance limits of insecticides residues and establishment of minimum intervals between the application of insecticides and harvest in respect of various commodities.
- To specify the shelf life of insecticides
- To carry out other functions such as re-supplemental, incidental and consequential.

#### **Central Insecticide Laboratory (CIL)**

Central Govt. establishes a CIL to carry out the functions of analysis of pesticides. Insecticides analysts are appointed by Central/ State Govt. The CIL is located at Faridabad, Haryana.

#### **Insecticide Inspectors**

An insecticide inspector is empowered

1. To enter and search premises for any offence under this act
2. To stop distribution, sale or use of insecticide in case of violation of this act
3. To take sample of insecticides and send them for analysis to the insecticide analyst

### **Registration committee**

The registration committee consists of a chairman and not more than 5 members including the Drug Controller of India and the Plant Protection Adviser to the Government of India. The main functions of the committee are

1. To register insecticides after scrutinizing their formulae and verify their claims made by the importers / manufacturers as regards their efficacy and safety to human beings and animals
2. To specify the precautions to be taken against poisoning through the use of handling insecticides
3. To carry out other incidental and consequential matters.

### **Registration procedure**

Any person who desires to import or manufacture any insecticide has to obtain a registration certificate from the registration committee.

### **Types of registration**

1. Provisional registration- first time in the country (2 year data)
2. Regular registration- complete data required
3. Repeat registration- subsequent registration

The entire registration procedure may be classified into four steps as enumerated below.

- (i) Inclusion of pesticides in the schedule of the act
- (ii) Provisional Registration under Section 9 (3B)
- (iii) Regular Registration under Section 9(3) of the Act
- (iv) Data requirement for repeat registration under Section 9(4) of the Act

#### **(i) Inclusion of pesticides in the schedule of the act**

Any pesticide which is to be imported or manufactured in India for use has to be first included in the schedule of the act by the Central Insecticides Board, for which he has to furnish the following particulars

- Chemical identity and physicochemical properties of the insecticide along with technical bulletin from the principal manufacturer
- Bio efficacy data on the product to prove that it is a potential insecticide



- The registration status of the product in other countries including the country of its origin
- The status of the insecticide as per Pesticide Manual, Pesticide Index or in any other standard pesticide bibliographical book
- Detailed information on mammalian toxicity
- Any supporting evidence to illustrate, if the need of the product has been substantiated by the Central / State Agricultural Research Organization / Agricultural University.

After an insecticide has been included in the schedule, any body can make an application for registration of the same for import or for manufacture.

**(ii) Provisional Registration under Section 9 (3B)**

This provisional registration under section 9(3B) is granted for a period of two years only for data generation under Indian conditions. Data requirement for consideration of provisional registration under Section 9 (3b) are

- Technical (Import)
- Formulation (Indigenous manufacturers)
- Packaging and labeling
- Efficacy
- Residues
- Toxicity (Both for technical and formulations)

**(iii) Regular Registration under Section 9(3) of the Act**

During the period of the provisional registration or after the expiry of provisional registration, the application is supposed to come for regular registration under Section 9(3) of the Act. Data requirement for regular registration under Section 9(3) of the act are

- Chemical specifications
- Packaging and labeling
- Bio efficacy and residues data
- Safety / Toxicity data requirement

**(iv) Data requirement for repeat registration under Section 9(4) of the Act**

Under Section 9(4) of the Insecticides Act, where in an insecticide has already been registered on the application of any person, any other person desiring to import or manufacture thereof shall make an application and on payment of a prescribed fee be allotted a registration number and grant a certificate of registration in respect of the same conditions in which the insecticide was originally registered. In this case, the applicant need not submit all the data on biological parameters, if he has already established the chemical equivalence with the earlier

registered product. However an outline of the following normal information have to be supplied to the Registration Committee for its satisfaction that the chemical applied is identical with that of the earlier registered one.

- Import of technical grade material
- Import of formulations
- Indigenous manufacture of technical grade material.

### **Compatibility of Pesticides with Fertilizers and other Agrochemicals**

Many of the pesticides cannot control all types of pests and diseases and hence it becomes necessary to use few of them together to control various pests and diseases. There is also considerable saving of labour, time and water especially in areas of water scarcity, if these could be mixed and applied in one single spray. Some pesticides are registered for use in combination with a liquid fertilizer. If pesticides may be combined safely and effectively, they are called *compatible*. If not, they are called *incompatible*. Incompatibility can be physical or chemical.

**Physical incompatibility** - means that the chemicals cannot physically be mixed together. Solid materials may become deposited at the bottom of the spray tank or the ingredients may become separated into two or more layers following agitation. In some cases, foaming or curdling may occur. The mixture may be unsuitable for spraying.

**Chemical incompatibility**- Even if some chemicals can be mixed together physically, there may be other kinds of incompatibility that may reduce effectiveness or cause injury to the plant as losing its pesticidal activity, becoming phytotoxic and adversely affecting the spraying equipments like clogging the nozzle or corroding the sprayer

### **Efficacy of pesticide combinations**

#### **1. Additive effects**

Occur when mixing two pesticides provide the same response as the combined effects of each material when applied alone. Such mixes save time, labour and equipment use.

#### **2. Synergistic effects**

Two pesticides provide a greater response than the added effects of each material when applied separately.

Eg. Addition of piperonyl butoxide with the pyrethrum insecticides

#### **3. Antagonism**

When two pesticides applied together produce less control than applied separately it is called antagonism. Antagonistic responses also may increase phytotoxicity to plants.

Eg. Herbicides Assert (Imazamethabenz-methyl) and Banvel (Dicamba)

#### 4. Enhancement

Enhancement occurs when a pesticide is mixed with an additive to provide a greater response than if you applied the pesticide alone. Ex. Mixing an adjuvant with a pesticide

##### **Compatibility of fertilizers**

##### **Compatibility**

- Urea + thiram, phosphamidon, dithane-M45, thiometon
- Urea + dichlorovos, parathion, carbaryl
- Neutral or acidic fertilizers with captan
- Ammonium phosphate + rogor
- Ammonium sulphate + FYM + phorate

##### **Incompatible**

- Urea + lime sulphur, Karathane
- NP fertilizers+ Rogor

since this combination is phytotoxic.

Compatibility, however, also depends on mixing containers, mode of mixing, emulsifier, wetting agents and other additives used. **Compatibility** is assessed by

- Jar test
- Germination percentage
- Yield of crops
- Phytotoxicity
- Percent of pests or diseases controlled

##### **Mixture of insecticides formulations registered in India**

1. Quinalphos 20%+ Cypermethrin 3 % EC (Viraat)
2. Chlorpyrifos 50% + Cypermethrin 5% EC (Nurelle D 505)
3. Profenophos 40% + Cypermethrin 4% EC (Polytrin-C)
4. Ethion 40% + Cypermethrin 5% EC
5. Triazophos 36%+ Deltamethrin 1%EC
6. Acephate 50 % Imidacloprid 1.8% SP (Lancer Gold)
7. Acetamiprid 7.7% + Indoxacarb 14.5% SC (Almighty)
8. Buprofezin 5.65% + Deltamethrin 0.72% EC (Dadeci)