SAC 324 crops and pesticide chemistry and nanotechnology

Unit 5

1.Nano fertilizers

Nano-fertilizers "Nano fertilizers are synthesized or modified form of traditional fertilizers, fertilizers bulk materials or extracted from different vegetative or reproductive parts of the plant by different chemical, physical, mechanical or biological methods with the help of nanotechnology used to improve soi

2. Nano herbicides

Nanoherbicides are formulated by exploiting the nanotechnological potential for effectual delivery of chemical or biological pesticides with the help of nanosized preparations or nanomaterials-based herbicide formulations

3.Nano Pesticides

Nanopesticides can be defined as the plant protection products which are developed using nanotechnology to enhance the efficacy and reduce the environmental load of pesticides.

4.Seed technology

seed technology as the methods through which the genetic and physical characteristics of seeds could be improved. It involves such activities as variety development, evaluation and release, seed production, processing, storage and certification.

5.Nano technology

Nanotechnology (or "*nanotech*") is manipulation of matter on an atomic, molecular, and supramolecular scale. ... *Nanotechnology* may be able to create many new materials and devices with a vast range of applications, such as in nanomedicine, nanoelectronics, biomaterials energy production, and consumer products.

6.Nano materials

Nanomaterials describe, in principle, materials of which a single unit small sized (in at least one dimension) between 1 to 100 nm (the usual definition of nanoscale) measured in kelvin. ... Materials with structure at the nanoscale often have unique optical, electronic, or mechanical properties

7. Nanobarcodes

Nanobarcode particles are manufactured via a semi-automated andhighly scalable process of electroplating of inert metals such as gold,
silver, etc. into templates defining particle diameter and thus resulting nanorods from the templates are released. These nanobarcodes are used
as identification tags for multiplexed analysis of gene expression. Nanotechnology assisted advancement in the field of biotechnology

has seen improvement in the plant resistance to environmental stresses such as drought, salinity and diseases. Nanotechnology-based gene
sequencing is capable of rapid and cost effective identification and utilization of plant gene trait resource

8. DNA nanocapsule

the capsule smuggles a short strand of foreign DNA into a living cell which, once released, hijacks cell machinery to express a specific protein (used for DNA vaccines)

Sputtering

Sputtering involves vaporizing materials from a solid surface by bombarding a target with high-velocity ions of an inert gas, which causes ejection of atoms and clusters

applications of the nanotechnologies	examples
1 Energy storage, production	CNT storage of Hand conversion
2 Agricultural productivity enhancement	Herbicide delivery
3 Water treatment & remediation	Nano-membranes
4 Disease diagnosis & screening	Lab-on-Chip
5 Drug delivery systems	Nano-capsules
6 Food processing & storage Coating/packaging	
7 Air pollution & remediation	Nano-catalysts
8 Construction Durability	
9 Health monitoring	Sensors
10 Vector & pest detection/control	Sensors and pesticides

Nanotechnology enables companies to manipulate the properties of the outer shell of a capsule in order to control the release of the substance to be delivered. 'Controlled release'strategies are highly prized in medicine since they can allow drugs to be absorbed more slowly, at a specific location in the body or at the say-so of an external trigger. With potential applications across the food chain (in pesticides, vaccines, veterinary medicine and nutritionally-enhanced food), these nano- and micro-formulations are being developed.

Slow release – the capsule releases its payload slowly over a longer period of time (*e.g.*, for slow delivery of a
substance in the body) (Garrard *et al.*, 2004)
Quick-release – the capsule shell breaks upon contact with a surface (*e.g.*, when pesticide hits a leaf)
Specific release – the shell is designed to break open when a molecular receptor binds to a specific chemical (*e.g.*, upon encountering a tumour or protein in the body)
Moisture release – the shell breaks down and releases contents in the presence of water (*e.g.*, in soil)
Heat-release – the shell releases ingredients only when the environment warms above a certain temperature
pH release – nanocapsule breaks up only in specific acid or alkaline environment (*e.g.*, in the stomach or inside a cell)

Ultrasound release – the capsule is ruptured by an external ultrasound frequency
Magnetic release – a magnetic particle in the capsule ruptures the shell when exposed to a magnetic field
DNA nanocapsule – the capsule smuggles a short strandof foreign DNA into a living cell which, once released, hijacks cell machinery to express a specific protein (used for DNA vaccines)

Top Down and Bottom up approaches

top-Down approaches refers to slicing or successive cutting of bulk material to get nano-sized particles.there are two types *attrition ,* milling

Top-down" starts from larger materials and structures and employs cutting or etching techniques to miniaturise the features until the required nano-structures are achieved. This can be compared to sculpting rock, where a large block is gradually chipped away until the required shape and detail is achieved

Bottom-up refers to methods where devices 'create themselves' by self-assembly. Chemical synthesis is a good example. Bottom-up should, broadly speaking, be able to produce devices in parallel and much cheaper than top-down methods, but getting control over the methods is difficult when things become larger and bulkier than what is normally made by chemical synthesis
Bottom-up" starts with basic building blocks such as small molecules or even atoms and assembles them into the required structure. This can be compared to a LEGO set, where a number of basic building blocks can be assembled in many different ways to produce structures of the required size and complexity.

Coprecipitation reactions involve the simultaneous occurrence of nucleation, growth, coarsening, and/or agglomeration processes.

Coprecipitation reactions exhibit the following characteristics:

(i) The products are generally insoluble species formed under conditions of high supersaturation. (ii) Nucleation is a key step, and a large number of small particles will be formed. (iii) Secondary processes, such as Ostwald ripening and aggregation, dramatically affect the size, morphology, and properties of the products. (iv) The supersaturation conditions necessary to induce precipitation are usually the result of a chemical reaction.

$xA^{y+}(aq) + yB^{x-}(aq) \qquad A_xB_y(s$

Typical coprecipitation synthetic methods: (i) metals formed from aqueous solutions, by reduction from nonaqueous solutions, electrochemical reduction, and decomposition of metallorganic precursors; (ii) oxides formed from aqueous and nonaqueous solutions; (iii) metal chalconides formed by reactions of molecular precursors; (iV) microwave/sonication-assisted coprecipitation.

The sol-gel process

is a wet-chemical technique that uses either a chemical solution (sol short for solution) or colloidal particles (sol for nanoscale particle) to produce an integrated network (gel).

Metal alkoxides and metal chlorides are typical precursors. They undergo hydrolysis and polycondensation reactions to form a colloid, a system composed of nanoparticles dispersed in a solvent. The sol evolves then towards the formation of an inorganic continuous network containing a liquid phase (gel).

Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

After a drying process, the liquid phase is removed from the gel. Then, a thermal treatment (calcination) may be performed in order to favor further polycondensation and enhance mechanical properties

Microemulsions

Microemulsions are clear, stable, isotropic liquid mixtures of oil, water and surfactant, frequently in combination with a cosurfactant.

The aqueous phase may contain salt(s) and/or other ingredients, and the "oil" may actually be a complex mixture of different hydrocarbons and olefins.

The two basic types of microe mulsions are direct (oil dispersed in water, o/w) and reversed (water dispersed in oil, w/o).

Microwave-Assisted Synthesis

Microwaves are a form of electromagnetic energy with frequencies in the range of 300 MHz to 300 GHz. The commonly used frequency is 2.45G Hz.

Interactions between materials and microwaves are based on two specific mechanisms: dipole interactions and ionic conduction. Both mechanisms require effective coupling between components of the target material and the rapidly oscillating electrical field of the microwaves.

Dipole interactions occur with polar molecules. The polar ends of a molecule tend to re-orientate themselves and oscillate in step with the oscillating electrical field of the microwaves. Heat is generated by molecular collision and friction. Generally, the more polar a molecule, the more effectively it will couple with the microwave field.

Microwave (MW) rapid heating has received considerable attention as a new promising method for the one-pot synthesis of metallic nanostructures in solutions.

In this concept, advantageous application of this method has been demonstrated by using some typical examples for the preparation of Ag, Au, Pt, and AuPd nanostructures. Not only spherical nanoparticles, but also single crystalline polygonal plates, sheets, rods, wires, tubes, and dendrites were prepared within a few minutes under MW heating. Morphologies and sizes of nanostructures could be controlled by changing various experimental parameters, such as the concentration of metallic salt and surfactant polymer, the chain length of the surfactant polymer, the solvent, and the reaction temperature. In general, nanostructures with smaller sizes, narrower size distributions, and a higher degree of crystallization were obtained under MW heating than those in conventional oil-bath heating

Sonochemical Synthesis

Ultrasound irradiation causes acoustic cavitation -- the formation, growth and implosive collapse of the bubbles in a liquid

The implosive collapse of the bubbles generates a localized hot spots of extremely high temperature (~5000K) and pressure (~20MPa).

The sonochemical method is advantageous as it is nonhazardous, rapid in reaction rate, and produces very small metal particles.

Biomimetic Synthesis

Nature is a school for material science and its associated discipline such as chemistry, biology, physics or engineering. Nature fascinates scientists and engineers with numerous examples of exceptionally building materials. These materials often show complex hierarchical organization from the nanometer to the macroscopic scale.

Learning from nature and imitating the growth and assembly processes found in nature enable new strategies for the design of nanoarchitectures. Biomimetic or bio-inspired processes generally occur under mild conditions such as room temperature, aqueous environment, and neutral pH, and thus are benign in comparison to traditional chemical reactions. Biologically inspired synthesis, hierarchical structuring, and stimuli-responsive materials chemistry may enable nanostructured materials systems with unprecedented functions .

Many exciting bioinspired materials concepts are currently under development, such as composite materials with nacre-like flaw tolerance, gecko-inspired reversible adhesives, and advanced photonic structures that mimic butterfly wings .

Gas-Phase Synthesis

Supe rsaturation achieved by vaporizing material into a background gas, then cooling the gas

Methods using solid precursors

- Inert Gas Condensation
- Pulsed Laser Ablation
- Spark Discharge Generation
- Ion Sputtering

Methods using liquid or vapor precursors

- Chemical Vapor Synthesis
- Spray Pyrolysis
- Laser Pyrolysis/ Photochemical Synthesis
- Thermal Plasma Synthesis
- Flame Synthesis
- Flame Spray Pyrolysis
- Low-Temperature Reactive Synthesis
-

Vapor-Phase Synthesis

- Same mechanism as liquid-phase reaction
- Elevated temperatures + vacuum (low concentration of growth)
- Vapor phase mixture rendered thermodynamically unstable relative to formation of desired solid material
- "supersaturated vapor"
- "chemical supersaturation"
- particles nucleate homogeneously if

- Degree of supersaturation is sufficient
- Reaction/ condensation kinetics permit
- Once nucleation occurs, remaining supersaturation is relieved by condensation, or reaction of vapor-phase molecules on resulting particles. This initiates particle growth phase.
- Rapid quenching after nucleation prevents particle growth by removing source of supersaturation, or slowing the kinetics.
- Coagulation rate proportional to square of number concentration (weak dependence on particle size)
- Nanoparticles in gas phase always agglomerate. Loosely agglomerated particles may be re-dispersed. Hard (partially sintered) agglomerates cannot be fully redispersed.
- size affections
- reaction and nucleation

1.Application of Nanotechnology in food systems

Over the past few decades, nanotechnology has increasingly been considered as to be attractive technology that has revolutionized the food sector. It is a technology on the nanometer scale and deals with the atoms, molecules, or the macromolecules with the size of approximately 1–100 nm to create and use materials that have novel properties. The created nanomaterials possess one or more external dimensions, or an internal structure, on the scale from 1 to 100 nm that allowed the observation and manipulation of matter at the nanoscale. It is observed that these materials have unique properties unlike their macroscale counterparts due to the high surface to volume ratio and other novel physiochemical properties like color, solubility, strength, diffusivity, toxicity, magnetic, optical, thermodynamic, etc. (Rai et al., 2009; Gupta et al., 2016). Nanotechnology has brought new industrial revolution and both developed and developing countries are interested in investing more in this technology (Qureshi et al., 2012). Therefore, nanotechnology offers a wide range of opportunities for the development and application of structures, materials, or system with new properties in various areas like agriculture, food, and medicine, etc.

The rising consumer concerns about food quality and health benefits are impelling the researchers to find the way that can enhance food quality while disturbing least the nutritional value of the product. The demand of nanoparticle-based materials has been increased in the food industry as many of them contain essential elements and also found to be non-toxic (Roselli et al., 2003). They have been also found to be stable at high temperature and pressures (Sawai, 2003). Nanotechnology offers complete food solutions from food manufacturing, processing to packaging. Nanomaterials bring about a great difference not only in the food quality and safety but also in health benefits that food delivers. Many organizations, researchers, and industries are coming up with novel techniques, methods, and products that have a direct application of nanotechnology in food science (Dasgupta et al., 2015).

The applications of nanotechnology in food sector can be summarized in two main groups that are food nanostructured ingredients and food nanosensing. Food nanostructured ingredients encompass a wide area from food processing to food packaging. In food processing, theses nanostructures can be used as food additives, carriers for smart delivery of nutrients, anti-caking agents, antimicrobial agents, fillers for improving mechanical strength and durability of the packaging material, etc. whereas food nanosensing can be applied to achieve better food quality and safety evaluation (Ezhilarasi et al., 2013). In this review, we have summarized the role of nanotechnology in food science and food microbiology and also discussed some negative facts associated with this technology.

Nanotechnology in Food Processing

The nanostructured food ingredients are being developed with the claims that they offer improved taste, texture, and consistency (Cientifica Report, 2006). Nanotechnology increasing the shelf-life of different kinds of food materials and also help brought down the extent of wastage of food due to microbial infestation (Pradhan et al., 2015). Nowadays nanocarriers are being utilized as delivery systems to carry food additives in food products without disturbing their basic morphology. Particle size may directly affect the delivery of any bioactive compound to various sites within the body as it was noticed that in some cell lines, only submicron nanoparticles can be absorbed efficiently but not the larger size micro-particles (Ezhilarasi et al., 2013). An ideal delivery system is supposed to have following properties: (i) able to deliver the active compound precisely at the target place (ii) ensure availability at a target time and specific rate, and (iii) efficient to maintain active compounds at suitable levels for long periods of time (in storage condition). Nanotechnology being applied in the formation of encapsulation, emulsions, biopolymer matrices, simple solutions, and association colloids offers efficient delivery systems with all the above-mentioned qualities. Nano polymers are trying to replace conventional materials in food packaging. Nanosensors can be used to prove the presence of contaminants, mycotoxins, and microorganisms in food (Bratovčić, 2015).

Nanoparticles have better properties for encapsulation and release efficiency than traditional encapsulation systems. Nanoencapsulations mask odors or tastes, control interactions of active ingredients with the food matrix, control the release of the active agents, ensure availability at a target time and specific rate, and protect them from moisture, heat (Ubbink and Kruger, 2006), chemical, or biological degradation during processing, storage, and utilization, and also exhibit compatibility with other compounds in the system (Weiss et al., 2006). Moreover, these delivery systems possess the ability to penetrate deeply into tissues due to their smaller size and thus allow efficient delivery of active compounds to target sites in the body (Lamprecht et al., 2004). Various synthetic and natural polymer-based encapsulating delivery systems have been elaborated for the improved bioavailability and preservation of the active food components (Table 1). Further, the importance of nanotechnology in food processing can be evaluated by considering its role in the improvement of food products in terms of (i) food texture, (ii) food appearance, (iii) food taste, (iv) nutritional value of the food, and (v) food shelf-life. It is a matter of fact that surprisingly nanotechnology not only touches all the above-mentioned aspects but has also brought about significant alterations in food products providing them novel qualities.

Texture, Taste, and Appearance of Food

Nanotechnology provides a range of options to improve the food quality and also helps in enhancing food taste. Nanoencapsulation techniques have been used broadly to improve the flavor release and retention and to deliver culinary balance (Nakagawa, 2014). Zhang et al. (2014) used the nanoencapsulation for the highly reactive and unstable plant pigment anthocyanins which have various biological activities. Through, encapsulating cyanidin-3-O-glucoside (C3G) molecules within the inner cavity of apo recombinant soybean seed H-2 subunit ferritin (rH-2) improved the thermal stability and photostability. This design and fabrication of multifunctional nanocarriers for bioactive molecule protection and delivery. Rutin is a common dietary flavonoid with great important pharmacological activities but due to poor solubility, its application in the food industry is limited. The ferritin nanocages encapsulation enhanced the solubility, thermal and UV radiation stability of ferritin trapped rutin as compared to free rutin (Yang et al., 2015). The use of nanoemulsions to deliver lipid-soluble bioactive compounds is much popular since they can be produced using natural food ingredients using easy production methods, and may be designed to enhance water-dispersion and bioavailability (Ozturk et al., 2015).

As compared to larger particles which generally release encapsulated compounds more slowly and over longer time periods, nanoparticles provide promising means of improving the bioavailability of nutraceutical compounds due to their subcellular size leading to a higher drug bioavailability. Many metallic oxides such as titanium dioxide and silicon dioxide (SiO2) have conventionally been used as color or flow agents in food items (Ottaway, 2010). SiO2 nanomaterials are also one of the most used food nanomaterials as carriers of fragrances or flavors in food products (Dekkers et al., 2011).

Nutritional Value

A majority of bioactive compounds such as lipids, proteins, carbohydrates, and vitamins are sensitive to high acidic environment and enzyme activity of the stomach and duodenum. Encapsulation of these bioactive compounds not only enables them to resist such adverse conditions but also allows them to assimilate readily in food products, which is quite hard to achieve in non-capsulated form due to low water-solubility of these bioactive compounds. Nanoparticles-based tiny edible capsules with the aim to improve delivery of medicines, vitamins or fragile micronutrients in the daily foods are being created to provide significant health benefits (Yan and Gilbert, 2004; Koo et al., 2005). The nanocomposite, nano-emulsification, and nanostructuration are the different techniques which have been applied to encapsulate the substances in miniature forms to more effectively deliver nutrients like protein and antioxidants for precisely targeted nutritional and health benefits. Polymeric nanoparticles are found to be suitable for the encapsulation of bioactive compounds (e.g., flavonoids and vitamins) to protect and transport bioactive compounds to target functions (Langer and Peppas, 2003).

Preservation or Shelf-Life

In functional foods where bioactive component often gets degraded and eventually led to inactivation due to the hostile environment, nanoencapsulation of these bioactive components extends the shelf-life of food products by slowing down the degradation processes or prevents degradation until the product is delivered at the target site. Moreover, the edible nano-coatings on various food materials could provide a barrier to moisture and gas exchange and deliver colors, flavors, antioxidants, enzymes, and anti-browning agents and could also increase the shelf-life of manufactured foods, even after the packaging is opened (Renton, 2006; Weiss et al., 2006). Encapsulating functional components within the droplets often enables a slowdown of chemical degradation processes by engineering the properties of the interfacial layer surrounding them. For example, curcumin the most active and least stable bioactive component of turmeric (Curcuma longa) showed reduced antioxidant activity and found to be stable to pasteurization and at different ionic strength upon encapsulation (Sari et al., 2015).

Nanotechnology in Food Packaging

A desirable packaging material must have gas and moisture permeability combined with strength and biodegradability (Couch et al., 2016). Nano-based "smart" and "active" food packagings confer several advantages over conventional packaging methods from providing better packaging material with improved mechanical strength, barrier properties, antimicrobial films to nanosensing for pathogen detection and alerting consumers to the safety status of food (Mihindukulasuriya and Lim, 2014).

Application of nanocomposites as an active material for packaging and material coating can also be used to improve food packaging (Pinto et al., 2013). Many researchers were interested in studying the antimicrobial properties of organic compounds like essential oils, organic acids, and bacteriocins (Gálvez et al., 2007; Schirmer et al., 2009) and their use in polymeric matrices as antimicrobial packaging. However, these compounds do not fit into the many food processing steps which require high temperatures and pressures as they are highly sensitive to these physical conditions. Using inorganic nanoparticles, a strong antibacterial activity can be achieved in low concentrations and more stability in extreme conditions. Therefore, in recent years, it has been a great interest of using these nanoparticles in antimicrobial food packaging. An antimicrobial packaging is actually a form of active packaging which contacts with the food product or the headspace inside to inhibit or retard the microbial growth that may be present on food surfaces (Soares et al., 2009). Many nanoparticles such as silver, copper, chitosan, and metal oxide nanoparticles like titanium oxide or zinc oxide have been reported to have antibacterial property (Bradley et al., 2011; Tan et al., 2013).

The application of nanoparticles is not limited to antimicrobial food packaging but nanocomposite and nanolaminates have been actively used in food packaging to provide a barrier from extreme thermal and mechanical shock extending food shelf-life. In this way, the incorporation of nanoparticles into packaging materials offers quality food with longer shelf-life. The purpose of creating polymer composites is to have more mechanical and thermostable packing materials. Many inorganic or organic fillers are being used in order to achieve improved polymer composites. The incorporation of nanoparticles in polymers has allowed developing more resist packaging material with cost effectiveness (Sorrentino et al., 2007). Use of inert nanoscale fillers such as clay and silicate nanoplatelets, silica ($SiO2$) nanoparticles, chitin or chitosan into the polymer matrix renders it lighter, stronger, fire resistance, and better thermal properties (Duncan, 2011; Othman, 2014). Antimicrobial nanocomposite films which are prepared by impregnating the fillers (having at least one dimension in the nanometric range or nanoparticles) into the polymers offer two-way benefit because of their structural integrity and barrier properties (Rhim and Ng, 2007).

Nanosensors for Pathogen Detection

Nanomaterials for use in the construction of biosensors offers the high level of sensitivity and other novel attributes. In food microbiology, nanosensors or nanobiosensors are used for the detection of pathogens in processing plants or in food material, quantification of available food constituents, alerting consumers and distributors on the safety status of food (Cheng et al., 2006; Helmke and Minerick, 2006). The nanosensor works as an indicator that responds to changes in environmental conditions such as humidity or temperature in storage rooms, microbial contamination, or products degradation (Bouwmeester et al., 2009). Various nanostructures like thin films, nanorods, nanoparticles and nanofibers have been examined to their possible applications in biosensors (Jianrong et al., 2004). Thin film-based optical immunosensors for detection of microbial substances or cells have led to the rapid and highly sensitive detection systems. In these immunosensors, specific antibodies, antigens, or protein molecules are immobilized on thin nano-films or sensor chips which emit signals on detection of target molecules (Subramanian, 2006). A dimethylsiloxane microfluidic immunosensor integrated with specific antibody immobilized on an alumina nanoporous membrane was developed for rapid detection of foodborne pathogens Escherichia coli O157:H7 and Staphylococcus aureus with electrochemical impedance spectrum (Tan et al., 2011). Nanotechnology can also assist in the detection of pesticides (Liu et al., 2008), pathogens (Inbaraj and Chen, 2015), and toxins (Palchetti and Mascini, 2008) serving in the food quality tracking–tracing–monitoring chain. Biosensors based on carbon nanotubes also gained much attention due to their rapid detection, simplicity and cost effectiveness and have also been successfully applied for the detection of microorganisms, toxins, and other degraded products in food and beverages (Nachay, 2007). Toxin antibodies attached to these nanotubes causes a detectable change in conductivity when bound to waterborne toxins and therefore are used to detect waterborne toxins (Wang et al., 2009). Further, the use of electronic tongue or nose which is consists of the array of nanosensors monitor the food condition by giving signals on aroma or gases released by food items (Garcia et al., 2006). The quartz crystal microbalance (QCM)-based electric nose can detect the interaction between various odorants and chemicals that have been coated on the crystal surface of the QCM. Many studies on small molecule detection have used quartz crystal surfaces that have been modified with different functional groups or biological molecules, such as amines, enzymes, lipids, and various polymers (Kanazawa and Cho, 2009).

CVD

Chemical vapor deposition (CVD) is a widely used method for depositing thin films of a large variety of materials.

Growing thin layer of advanced materials on the surface of the substrate.

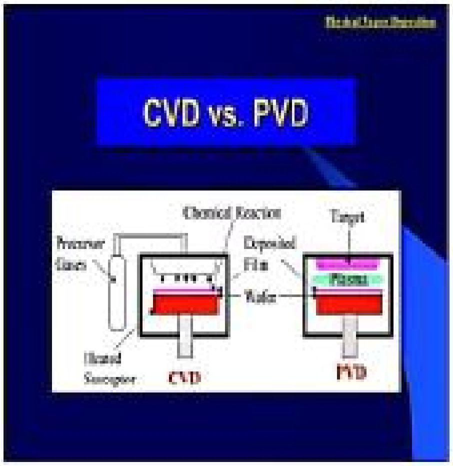
The process is often used in the semiconductor industry to produce thin films.

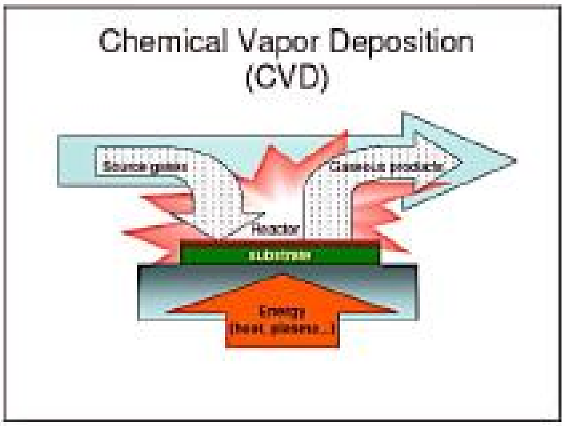
The CVD process is also used to produce synthetic diamonds

In a typical CVD process, reactant gases (precursor) at room temperature enter the reaction chamber.

The gas mixture is heated as it approaches the deposition surface

The reactant gases undergo homogeneous chemical reactions in the vapor phase before striking the surface forming the deposited material.





Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber

Versatile – can deposit any element or compound
High Purity – typically 99.99-99.999%
High Density – nearly 100%
Economical in production, since many parts can be coated at the same time
Coats powders
Able to penetrate porous bodies, blind holes etc
(not a line-of-sight process) – (multidirectional deposition)
Coats internal passages with high length-to-diameter ratios

PVD

Physical Vapor Deposition

Physical methods produce the atoms that deposit on the substrate

- Evaporation
- Sputtering

Sometimes called vacuum deposition because the process is usually done in an evacuated chamber

- PVD is used for metals.
- Dielectrics can be deposited using specialized equipment

Rely on thermal energy supplied to the crucible or boat to evaporate atoms

Evaporated atoms travel through the evacuated space between the source and the sample and stick to the sample

- Few, if any, chemical reactions occur due to low pressure
- Can force a reaction by flowing a gas near the crucible

Surface reactions usually occur very rapidly and there is very little rearrangement of the surface atoms after sticking

- Thickness uniformity and shadowing by surface topography, and step coverage are issues

~ 63% of molecules undergo a collision in a distance less than l and ~0.6% travel more than 5 l.

where d_o is the diameter of the evaporatant and n is the concentration of gas molecules in the chamber

$$\lambda = \frac{1}{\sqrt{2}\pi d_o^2 n}$$

$$PV = nRT \text{ (Ideal Gas Law)}$$

$$\lambda = \frac{0.05}{P(\text{in torr})}$$

At sufficiently low pressure and reasonable distances between source and wafer, evaporant travel in straight line to the wafer

Step coverage is close to zero

If the source is small, we can treat it as a point source

If the source emission is isotropic, it is easy to compute the distribution of atoms at the surface of the wafer

- Nonuniformity of evaporatant can occur when angular emission of evaporant is narrower than the ideal source
  - Crucible geometry
  - Melt depth to melt area ratio
  - Density of gas atoms over the surface of the melt
- Other deposition techniques include
  - Sputter deposition (DC, RF, and reactive)
  - Bias sputtering
  - Magnetron sputtering
  - Collimated and ionized sputter deposition
  - Hot sputter deposition
- Sputter deposition is done in a vacuum chamber (~10mTorr) as follows:
  - Plasma is generated by applying an RF signal producing energetic ions.

- Target is bombarded by these ions (usually Ar^+).
- Ions knock the atoms from the target.
- Sputtered atoms are transported to the substrate where deposition occurs.

Advantages

Wide variety of materials can be deposited because material is put into the vapor phase by a mechanical rather than a chemical or thermal process (including alloys and insulators).

Excellent step coverage of the sharp topologies because of a higher chamber pressure, causing large number of scattering events as target material travels towards wafers.

Film stress can be controlled to some degree by the chamber pressure and RF power.

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Disadvantages

High capital expenses are required

Rates of deposition of some materials (such as SiO_2) are relatively low

Some materials such as organic solids are easily degraded by ionic bombardment

Greater probability to introduce impurities in the substrate because the former operates under a higher pressure

Characterization of nanoparticles

Two of the main parameters studied in the characterization of NPs are size and shape. We can also measure size distribution, degree of aggregation, surface charge and surface area, and to some extent evaluate the surface chemistry.5 Size, size distribution and organic ligands present on the surface of the particles may affect other properties and possible applications of the NPs. In addition, the crystal structure of the NPs and their chemical composition are thoroughly investigated as a first step after nanoparticle synthesis. Until now, there were no standardized protocols for this aim. Credible and robust measurement methods for NPs will greatly affect the uptake of these materials in commercial applications and allow the industry to comply with regulation. Nevertheless, there are important challenges in the analysis of nanomaterials because of the interdisciplinary nature of the field, the absence of suitable reference materials for the calibration of analytical tools, the difficulties linked to the sample preparation for analysis and the interpretation of the data. In addition, there are unmet challenges in the characterization of NPs such as the measurement of their concentration in situ and on-line, especially in a scaled-up production, as well as their analysis in complex matrices. Waste and effluent from mass production will also need to be monitored.6 With the scale-up of nanoparticle manufacture, more reliable quantification technique.will be required. For this reason, it is crucial to characterize the nanomaterials prepared in several ways to the maximum extent. We do not only focus on the characterization of the nanoparticle core, but also on the surface ligands that influence the physical properties

Characterization Techniques of	**Nano materials**
XRD (group: X-ray based techniques)	Crystal structure, composition, crystalline grain size
XAS (EXAFS, XANES)	X-ray absorption coefficient (element-specific) – chemical state of species, interatomic distances, Debye–Waller factors, also for non-crystalline NPs
SAXS	Particle size, size distribution, growth kinetics
XPS	Electronic structure, elemental composition, oxidation states, ligand binding (surface-sensitive)
FTIR (group: further techniques for structure/composition/main properties)	Surface composition, ligand binding
NMR (all types)	Ligand density and arrangement, electronic core structure, atomic composition, influence of ligands on NP shape, NP size
BET	Surface area
TGA	Mass and composition of stabilizers
LEIS	Thickness and chemical composition of self-assembled

	monolayers of NPs
UV-Vis	Optical properties, size, concentration, agglomeration state, hints on NP shape
PL spectroscopy	Optical properties – relation to structure features such as defects, size, composition
DLS	Hydrodynamic size, detection of agglomerates
NTA	NP size and size distribution
DCS	NP size and size distribution
ICP-MS	Elemental composition, size, size distribution, NP concentration
SIMS, ToF-SIMS, MALDI	Chemical information (surface-sensitive) on functional group, molecular orientation and conformation, surface topography, MALDI for NP size
RMM-MEMS, ζ-potential, pH, EPM, GPC, DSC, *etc.*	*Please check the relevant parts of the manuscript*
SQUID-nanoSQUID (group: magnetic nanomaterials)	Magnetization saturation, magnetization remanence, blocking temperature
VSM	Similar to SQUID through M–H plots and ZFC-FC curves
Mössbauer	Oxidation state, symmetry, surface spins, magnetic ordering of Fe atoms, magnetic anisotropy energy, thermal unblocking, distinguish between iron oxides
FMR	NP size, size distribution, shape, crystallographic imperfection, surface composition, *M* values, magnetic anisotropic constant, demagnetization field
XMCD	Site symmetry and magnetic moments of transition metal ions in ferro- and ferri-magnetic materials, element specific
Magnetic susceptibility, magnetophoretic mobility	*Please check the relevant parts of the manuscript*
Superparamagnetic relaxometry	Core properties, hydrodynamic size distribution, detect and localize superparamagnetic NPs
TEM (group: microscopy techniques)	NP size, size monodispersity, shape, aggregation state, detect and localize/quantify NPs in matrices, study growth kinetics
HRTEM	All information by conventional TEM but also on the crystal structure of single particles. Distinguish monocrystalline, polycrystalline and amorphous NPs. Study defects

Characterization Techniques of	**Nano materials**
Liquid TEM	Depict NP growth in real time, study growth mechanism, single particle motion, superlattice formation
Cryo-TEM	Study complex growth mechanisms, aggregation pathways, good for molecular biology and colloid chemistry to avoid the presence of artefacts or destroyed samples
Electron diffraction	Crystal structure, lattice parameters, study order–disorder transformation, long-range order parameters
STEM	Combined with HAADF, EDX for morphology study, crystal structure, elemental composition. Study the atomic structure of hetero-interfaces
Aberration-corrected (STEM, TEM)	Atomic structure of NP clusters, especially bimetallic ones, as a function of composition, alloy homogeneity, phase segregation
EELS (EELS-STEM)	Type and quantity of atoms present, chemical state of atoms, collective interactions of atoms with neighbors, bulk plasmon resonance
Electron tomography	Realistic 3D particle visualization, snapshots, video, quantitative information down to the atomic scale
SEM-HRSEM, T-SEM-EDX	Morphology, dispersion of NPs in cells and other matrices/supports, precision in lateral dimensions of NPs, quick examination–elemental composition
EBSD	Structure, crystal orientation and phase of materials in SEM. Examine microstructures, reveal texture, defects, grain morphology, deformation
AFM	NP size and shape in 3D mode, evaluate degree of covering of a surface with NP morphology, dispersion of NPs in cells and other matrices/supports, precision in lateral dimensions of NPs, quick examination–elemental composition
MFM	Standard AFM imaging together with the information of magnetic moments of single NPs. Study magnetic NPs in the interior of cells. Discriminate from non-magnetic NPs

Characterization techniques used during nano particles synthesis

- UV-vis: Offers information on the size, structure, stabilization and aggregation of NPs NPs shape and size determination
- TEM: Examines the shape, size (10−10 m), morphology and allographic structure of NPs

- HTEM: Examines the arrangement of the atoms and their local microstructures, viz. lattice fringe, glide plane, lattice vacancies and defects,screw axes and surface atomic arrangement of crystalline NPs
- SEM: Examines the morphology by direct visualization
- AFM: Examines the size and form, i.e. length, width and height, and other physical properties, viz. morphology and surface texture
- DLS: Displays the particle size distribution Surface charge FTIR: Describes NPs to understand their functional groups and determine
- the emission, absorption, photoconductivity or Raman scattering of a solid,liquid or gas
- XPS: Examines the mechanism of reaction that occurs on the surface of magnetic NPs and the characteristics of bonding of different elementsinvolved, in addition to confirming the structure and speciation of elements present in the chemical composition of the magnetic NPs
- TGA: Approves the formation of coatings, viz. surfactants or polymers, to estimate the binding efficiency on the surface of magnetic NPs
- Zeta potential: Determines the stability and surface charge of colloidal NPs as well as the nature of materials encapsulated inside the NPs or coated on their surface
- Crystallinity XRD: Identifies and quantifies the various crystalline forms or elemental compositions of NPs Magnetic properties
- Vibrating sample magnetometry: Estimates the magnetization of magnetic NPs
- Superconducting quantum interference device magnetometry: Examines the magnetic properties of magnetic NPs
- Other techniques Chromatography and related techniques: Separate NPs on the basis of their affinity towards the mobile phase
- EDX: Identifies the elemental composition of NPs
- Field flow flotation: Separates different NPs based on their magnetic susceptibility
- Filtration and centrifugation technique: Fractionates the preparative size of NPs
- Laser-induced breakdown detection: Examines the concentration and size of colloids
- Mass spectrometry: Examines the fluorescent labelled NPs
- Small angle X-ray scattering: Performs the structural characterization of solid and fluid materials in the nanometre range
- X-ray fluorescence spectroscopy: Recognizes and examines the concentrations of elements present in solid, powdered or liquid samples
- Hyperspectral imaging: Identifies the type of NPs, studies the fate and transformation of these particles in water samples and characterizes the unique surface chemistry and functional groups added to the NM

Biosynthesis of nanoparticles

The common method of synthesizing metallic nanoparticles is wet-chemical procedures.

A typical procedure involves growing nanoparticles in a liquid medium containing reducing agents (eg, sodium borohydride or potassium bi tartrate or methoxy polyethylene glycol or hydrazine), a stabilizing agent such as sodium dodecyl benzyl sulfate or polyvinyl pyrrolidone to prevent the agglomeration of metallic nanoparticles, which are added to the reaction mixture.

Generally, the chemical methods are low-cost for high volume; however, their drawbacks include contamination from precursor chemicals, use of toxic solvents, and generation of hazardous by-products. Need to use high temperature, pressure and energy

The situation is pressing to develop high-yield, low cost, nontoxic, and environmentally benign procedures for synthesis of metallic NPs.

Therefore, the biological approach for synthesis of nanoparticles becomes significant. A vast array of biological resources available in nature including plants and plant products, algae, fungi, yeast, bacteria, and viruses could be employed for synthesis of NPs

Both unicellular and multicellular organisms have been known to produce intracellular or extracellular inorganic materials.

Nanoparticles obtained from biogenic routes are free from toxic contamination of by-products , otherwise which are normally attached to the nanoparticles during physiochemical synthesis, which in turn limits the biomedical applications

Rapid and eco-friendly production methodologies and the cost-effective and nanoparticles through biological routes are biocompatible in nature

Nanoparticles through biogenic route does not require stabilizing agents because plant and microorganism constituents themselves act as capping and stabilizing agents

The surfaces of biological nanoparticles progressively and selectively adsorb bio molecules when they contact complex biological fluids, forming a corona that provide additional efficacy

Abundant metabolites with pharmacological activity that are hypothesized to attach to the synthesized nanoparticles during the synthesis , providing additional benefit by enhancing the efficacies of the nanoparticles

Reduce the number of required steps, including the attachment of some functional groups to the nanoparticle surface to make them biologically active, where an additional step required in physiochemical synthesis and the time required for biosynthesizing nanoparticles is shorter than that for physiochemical approaches

Microorganisms have the ability to accumulate and detoxify heavy metals due to various reductase enzymes, which are able to reduce metal salts to metal nanoparticles with a narrow size distribution and, therefore, less polydispersity.

The antioxidant or reducing properties in biological resources are responsible for the reduction of metal compounds to their respective nanoparticles

Nanoparticles are biosynthesized when the microorganisms absorb target ions from their environment and then turn converts metal ions into the element metal through enzymes generated by the cell activities.

The route of synthesizing of nanomaterials using microorganisms are classified into intracellular and extracellular synthesis according to the location where synthesized

The intracellular method consists of transporting ions into the microbial cell to form nanoparticles in the presence of enzymes, where as the extracellular synthesis of nanoparticles involves trapping the metal ions on the surface of the cells and reducing ions in the presence of enzymes

Compared with bacteria, fungi have higher tolerances to metals, due to high wall-binding capability of metal salts with fungal biomass for the high-yield production of nanoparticles

Synthesis of nanoparticles using bacteria depends on enzymes, for instance, the nitrate reductase enzyme was found to be responsible for silver nanoparticle synthesis in B. licheniformis

Three possible mechanisms have been proposed to explain the mycosynthesis of metal nanoparticles: nitrate reductase action; electron shuttle quinones; or both. Fungal enzymes, such as the reductase enzymes from Penicillium species and Fusarium oxysporum, nitrate reductase, and /□-NADPH-dependent reductases, were found to have a significant role in nanoparticle synthesis

Nanoparticles are formed on the inner surface of the fungal / actinomycetes cell and not in solution.

Trapping of ions on the surface of fungal/ actinomycetes cell.

Ions are reduced by enzyme (reductases) present in the cell wall or in the cytoplasmic membrane.

The cell wall of the microorganisms play a major role in the intracellular synthesis of nanoparticles. The cell wall being negatively charged interacts electrostatically with the positively charged metal ions. The enzymes present within the cell wall bioreduce the metal ions to nanoparticles, and finally the smaller sized nanoparticles get diffused of through the cell wall.

The mechanism of trapping, bioreduction and synthesis are reported in Verticillium sp. The fungal cell surface when it comes in contact with metal ions interacts electrostatically and traps the ions. The enzymes present in the cell wall bioreduce the metal ions. Finally, aggregation of particles and synthesis of nanoparticles take place.

In Lactobacillus sp., there is an electrostatic interaction between the bacterial cell and metal clusters , lead to the formation of nanoclusters, where smaller sized nanoclusters get diffused to the formation of nanoclusters
Microorganisms are capable of secreting some polymeric materials like polysaccharides which forms complex with metal ions and bind extracellularly.
After culturing the microorganisms for 1–2 days in a rotating shaker under optimum conditions (including pH, temperature, medium components, etc.), the culture is centrifuged to remove the biomass.
The obtained supernatant is used to synthesize nanoparticles by adding a filter-sterilized metal salt solution
The nanoparticle synthesis is monitored by observing a change in the color of the culture medium; for instance, for silver nanoparticles, the color changes to deep brown, whereas, for gold nanoparticles, it changes from ruby red to a deep purple color.
After incubation, the reaction mixture can be centrifuged at different speeds to remove any medium components or large particles.
Finally, the nanoparticles are centrifuged at high speed or with a density gradient, washed thoroughly in water/solvent (ethanol/methanol) and collected in the form of a bottom pellet

The synthesis of nanoparticles using bacteria and actinomycetes usually involves the intracellular synthesis method, in which the bacterial cell filtrate is treated with metal salt solution and kept in a shaker in dark at ambient temperature and pressure conditions

For the extracellular synthesis of nanoparticles using bacteria, the bacterial culture is centrifuged at 8,000 rpm and the supernatant is challenged with metal salt solution

In case of fungi , nanoparticles are intracellularly synthesized by treating the fungal mycelium with metal salt solution and further incubation for 24 h. Dried mycelium of fungi is also used for synthesis of Nanoparticles, where the fungal mycelium is harvested by centrifugation and subsequently freeze dried, and this freeze-dried mycelium is immersed in metal salt solution and kept on a shaker Collection of fresh and healthy leaves of Tulsi (O. sanctum), which are washed thoroughly with double-distilled water, and cut into small pieces.

Transferring of cut pieces of leaves into three different 250-mL beakers containing 100 mL distilled water and boiled for 10 min. After cooling, the aqueous leaf extract are filtered through ordinary filter paper, the filtrates are collected in 100-mL volumetric flasks, and 10% broth solutions stored in a refrigerator for further use.

O. sanctum leaf extracts of 5 ml are transferred into 100-mL conical flasks containing 45 mL of 10−3 M silver nitrate solution to reach final volume of 50 mL.

Keep the solution under direct sunlight; gradual colour change appeared which is an indication of silver nanoparticle formation and confirmed by UV-vis spectrophotometric measurements

Many chemical methods are available for synthesis of nanoparticles, which use toxic chemicals so the need of the hour is to use environmentally benign, greener and ecofriendly routes. Researchers arelooking forward for various biological entities like bacteria, fungi, higher plants, actinomycetes and viruses for nanoparticles synthesis asthey can also reduce the salts to corresponding nanoparticles. Different
biological sources have been used for the synthesis of nanoparticles andare being used in agriculture

Nanobiosensors

Nanobiosensors can be productively used in sensing a broad array of agriculture like in fertilizers, herbicide, pesticide, insecticide, moisture and soil pH. Controlled use of biosensors can assist in sustainable agriculture for increasing crop productivity. Precision farming, with the aid of smart sensors, could enhance productivity as this technology ensures better fertilization management, reduced input cost and environment safety. Nanosensors based smart delivery systems could help in the efficient use of natural resources like water, nutrients and agrochemicals by precision farming [133]. The presence of plant viruses, the level of soil nutrients and crop pathogens can be detected by nanosensors [134,135]. A nanobiosensor based on atomic force microscopy tip functionalized with the acetolactate synthase enzyme was detected for herbicide metsulfuronmethyl (an acetolactate synthase inhibitor) through the acquisition of force curves [136]. Bionanosensors also makes it possible for rapid detection of bacteria and viruses with precise quantification and thereby increasing the food safety for the customer [137]. A highly sensitive organophosphorus pesticide biosensor constructed with the help of surface functionalized carbon nanotubes tailored with amino groups to control the efficient immobilization of acetylcholinesterase onto the surface of glassy carbon electrode and these have been successfully used for the direct analysis of vegetable samples [138].
An acetyl cholinesterase biosensor based on assembly of multiwall carbon nanotubes onto liposome bioreactors was developed for detection of organophosphates pesticides [139]. A highly sensitive acetylcholinesterase biosensor modified with hollow gold nanospheres with the detection limits 0.06 μg/dm3 for chlorpyrifos and 0.08 μg/dm3 for carbofuran

Zn-Se quantum dot immobilized acetylcholinesterase has been used for detection of organophosphate pesticides using graphene-chitosan nanocomposite modified electrode.
Organophosphate pesticides have been detected with this biosensor using methyl parathion as a model enzyme inhibitor, with a detection limit of 0.2 nmol/dm3 [141]. For determination of pesticides methylparathion and chlorpyrifos; an electrochemical biosensor based on

acetylcholinesterase immobilized on polyaniline precipitated on vertically assembled carbon nanotubes and wrapped with ssDNA was

prepared. The pesticides were determined via inhibition of enzyme reaction acetylcholinesterase-acetylcholine that caused small changes of local pH in the surrounding of an electrode surface and the detection limit of the biosensor for both the pesticides was found to be

1 & 903;10–12 mol/dm3 [142]. Electrochemically functionalized single walled carbon nanotubes (SWCNTs) based nanosensors with metal/metal oxide nanoparticles or nanotubes for gases viz. ammonia, nitrogen oxides, hydrogen sulfide,sulfur dioxide and volatile organics have potential application in monitoring agricultural pollutants and assessment of impacts on living

matter or health and in increase of crop productivity [143]. Screeningof organophosphorus agents with gold nanoparticles and fluorescence spectroscopy has been reported with high sensitivity (1.0 µmol/dm3)

Unit - 3 - 4

Lecture: 19 Out lines of organic chemistry –Theory of vitalism –Classification of organic compounds based on their chemical nature/structure with examples .

AGRICULTURAL CHEMICALS

Agricultural chemicals are the chemical substances that are used in the field of agriculture, particularly in crop production practices. Fertilizers, pesticides, growth regulators, amendments *etc.*, belong to this class.

Consumption of agricultural chemicals increasing steadily. In India, consumption of pesticides was 15,000 tonnes in 1965. By 1997 it reached 2,05,000 tonnes.

Zone wise - south zone accounts for more than 40 per cent of India's total consumption due to cash crops like cotton, tobacco, sugarcane , chillies etc .,

Among the agrochemicals, insecticides find widest use (80%), others are fungicides(10 %) , herbicides (7%) , rodenticides (1.6 %) , others (1.4 %).

In A.P Guntur district ranks first in consumption of agricultural chemicals .In A.P. pesticides use is more on cash crops.

There are two main classes of chemical compounds i.e., organic and inorganic .The compounds, which are of mineral origin, are known as inorganic and those of plant and animal origin are called organic.

ORGANIC CHEMISTRY

It was assumed that the organic compounds could be produced only living matter, for living matter was thought to possess "Vital force". This theory is known as theory of vitalism or Vital force, which is proposed by the scientist namely **Berzelius.** As long as this concept prevailed no effort was made to produce organic compounds in the laboratory and the vital force or vitalism theory long went unchallenged.

In 1828, the German chemist, **Friedrich Wohler** heated ammonium cyanate derived from inorganic substances and obtained the organic compound urea. Hence, the theory of vitalism was disproved by **Friedrich Wohler**.

The urea formed in this way proved to be identical in all respects with urea isolated from urine.

$$KOCN + NH_4Cl \rightarrow NH_4OCN + KCl$$

$$NH_4OCN \rightarrow H_2N\,CO\,NH_2 \quad \text{(urea)}$$

It had become evident that most of the compounds formed by living cells (plants and animals) contained carbon. Hence, the emphasis was shifted from origin to composition and organic compounds came to be considered as those containing carbon.

Organic chemistry is the study of the compounds of carbon. Since, all organic compounds could be considered as derived from hydrocarbons, a more exact definition would be organic chemistry is the study of hydrocarbons and their derivatives.

Lecture:20 Differences between organic and inorganic compounds .Functional groups .Isomerism and stereoisomerism

Differences between organic and inorganic compounds

S. No.	Organic compounds	Inorganic compounds
1	These are formed from few elements like C, H, O, N, P, S and halogens.	Formed from any of more than 100 elements known
2	These are of living origin	These are of mineral origin
3	Exhibit covalent bonding	Exhibit ionic bonding
4	Exhibit isomerism	Isomerism is not possible
5	Have low melting and boiling points	Have high melting and boiling points.
6	Highly combustible	Non- combustible
7	Highly volatile	Non-volatile
8	Low solubility in water, Highly soluble in organic solvents	Highly soluble in water but less soluble in organic solvents.
9	These are non conductors of electricity	Solutions are good conductors of electricity
10	Reactions are slow require catalysts	Reactions are rapid, in general donot require catalysts.

Functional groups:

An atom or a group of atoms that determines the properties and reactivity of an organic compound is called functional groups .

Some common functional groups are as follows

1	Alcoholic	-OH
2	Aldehyde	$-\overset{\overset{O}{\vert}}{C}-H$
3	Carbonyl (Ketone)	$-\underset{\vert}{C}=O$
4	Ester	$-\overset{\overset{O}{\vert}}{C}-O$
5	Ether	- O -
6	Carboxyl	$-\overset{\overset{O}{\vert}}{C}-OH$
7	Thioether	=S
8	Amine	$-NH_2$
9	Amide	$-CONH_2$
10	Imine	=N- H
11	Oxime	=C=N-O
12	Nitriles	$-C\equiv N$
13	Thiol or mercapton	- SH
14	Nitro	=N-

Homologous series *(Homos* = the same ; *legein* = to speak i.e, to have similar properties): If a number of organic compounds with the same functional groups are arranged in an ascending order of their molecular weights and in a systematic way , the resulting series (of the compounds) is called a Homologous series , in which the adjacent members differ by a CH_2 group. The individual members are called homologs.

Example :

CH_3 OH
C_2H_5 OH
C_3H_7 OH
C_4H_9 OH

Each member differs from adjacent member by CH_2 group

General characteristics:

1. All the compounds in the series contain the same elements and the functional groups
2. All the compounds can be represented by general formula
3. The molecular formula of each homolog differs one above and one below by CH_2 unit
4. All the compounds in the series can be prepared by similar methods
5. All the compounds in the series have similar chemical properties
6. There is a gradual variation in physical properties in increasing molecular weight, decrease in reactions.

CHEMICAL BONDS

Atoms of an element try to attain a stable configuration similar to that of the nearest zero group element. This tendency is responsible for the formation of chemical bond. A bond is kind of force or attraction that tends to keep two atoms or ions or radicals or molecules together.

The principal bonds that join atoms or ions or ion radicals are

1. **Ionic bond**: Formed by the loss or gains of electrons between two participating atoms. It is a very strong bond. So, melting and boiling points are very high. Because of charged ions, they are water-soluble and solutions conduct electricity i.e., electrolyzed.
2. **Covalent bond:** Formed by the sharing of electrons between two atoms, so that the electron pair is used by each in full comparatively weaker bond.
3. **Hydrogen bond:** Is formed between molecules in which hydrogen atom is attached to an atom of an element with large electro- negativity and very small size. Because of hydrogen bond the molecules associate themselves and hence possess higher boiling and melting point.

   The hydrogen bond formed between two molecules is called intermolecular hydrogen bond. Hydrogen bond is formed between different groups of the same molecule is called intra molecular hydrogen bond.
4. **Coordinate covalent bond:** This is a special type of covalent bond in which shared pair of electrons is contributed by one of the two bonded atoms. This was proposed by **Sidgwick .**

In ammonia molecule, nitrogen atom has a lone pair of electrons in its valence shell. Hydrogen ion (H^+) can take two electrons to get stability .A coordinate bond is formed between NH_3 and H^+ to form NH_4^+ (ammonium ion) in which the loan pair of electrons of N is shared by both N and H^+ .

The atom that contributes the loan pair for bonding is called donar and the one which shares is called acceptor .In the above example, N is the donar and H^+ is the acceptor. The coordinate bond is represented by putting an arrow (→) between the symbols of the two atoms directing from the donar towards acceptor.

ISOMERISM

Two (or) more compounds consist of equal number of like atoms. These compounds have the same molecular formula but differ from each other in physical or chemical properties and are called isomers and the phenomenon is called isomerism(**Greek Iso**= equal; **meros** = parts).This is due to different modes of combination or arrangement of atoms within the molecule.

There are two main types of isomerism

I. **Structural isomerism and**

II. **Space or stereoisomerism**

I. **Structural isomerism is divided in to 5 types. They are**

1. **Chain isomerism**
2. **Position isomerism**
3. **Functional isomerism**
4. **Metamerism**
5. **Tautomerism**

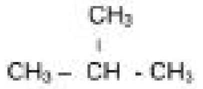
II. **Space or stereoisomerism is of two types viz.,**

1. **Geometrical isomerism or Cis-trans isomerism**
2. **Optical isomerism**

I. **Structural isomerism:** This is due to difference in the arrangement of atoms within the molecules with out any reference to space. They are compounds that have the same molecular formula but different structural formulae.

1. **Chain isomerism:** Compounds have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other .

   Eg. $CH_3 - CH_2 - CH_2 - CH_3$ n -butane



$$CH_3 - \overset{\overset{CH_3}{|}}{CH} - CH_3$$

isobutane

2. **Position isomerism**: Compounds have same molecular formula but differ in the position of a functional group on the carbon .

Eg.

$CH_2 = CH - CH_2 - CH_3$ 1 butene

$CH_3 - CH = CH - CH_3$ 2 butene

3. **Functional isomerism:** Have the same molecular formula but different functional groups .

Eg.

$CH_3 - CH_2 - OH$ Ethyl alcohol

$CH_3 - O - CH_3$ Dimethyl ether

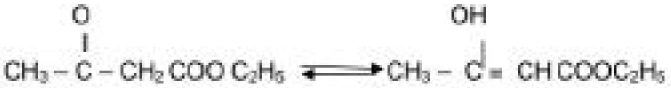
4. **Metamerism:** Is due to the unequal distribution of carbon atoms on either side of the functional group.

   Eg.

   $CH_3 - CH_2 - O - CH_2 - CH_3$ Diethyl ether

   $CH_3 - O - CH_2 - CH_2 - CH_3$ Methyl propyl ether

5. **Tautomerism:** It is a special type of functional isomerism in which the isomers are in dynamic equilibrium with each other .For example ethyl aceto acetate is an equilibrium mixture of 93 per cent of keto form and 6 per cent of enol form.



$$CH_3 - \overset{\overset{O}{|}}{C} - CH_2COO\,C_2H_5 \rightleftharpoons CH_3 - \overset{\overset{OH}{|}}{C} = CH\,COOC_2H_5$$

Ketoform Enol form

II. **Stereoisomerism:** When isomerism is caused by the different arrangement of atoms or groups in space, the phenomenon is called stereoisomerism. Compounds have the same structural formula but differ in configuration.

1. **Geometrical isomerism: It** results from a restriction in rotation about double bonds or about single bonds in cyclic compounds.

Cis- isomer: is one in which two similar groups on the same side of the double bond .This is less stable

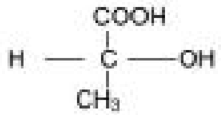
Trans- isomer: Is one in which two similar groups are on the opposite side of the double bond. This is more stable

2. **Optical isomerism:** The compounds have the ability to rotate plane polarized light in opposite directions i.e., the optically active compound can exist in two isomeric form .Optical isomers have at least one asymmetric carbon atom .The isomer which rotates the light towards right is called dextro-rotatory and towards left is called leavo- rotatory .

   Example: 1. .D- Glucose , L –Glucose

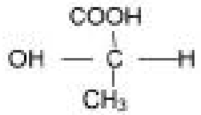
   Example: 2.

   D(-) Lactic acid



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

L(+)Lactic acid



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

* is the asymmetric carbon atom (Chiral centre)

The two are mirror image isomers of each other. i.e., enantiomers.

CLASSIFICATION OF ORGANIC COMPOUNDS

Organic compounds are divided into two groups.

1) **Aliphatic compounds**
2) **Aromatic compounds**

1) Aliphatic compounds: These are open chained structures. The term is used to denote compounds that don't have the special stability of aromatic compounds. All non-cyclic organic compounds are aliphatic.

Cyclic aliphatic compounds are said to be alicyclic.

Eg. A) Alkanes (Paraffins) saturated hydrocarbons

B) Alkenes (Olefines ,Olefins) unsaturated double bonds

C) Alkynes unsaturated having one or more triple bonds

Alkanes, alkenes that have one double bond and alkynes that have one triple bond can form homologous series

2) Aromatic compounds: These are closed chain structures. Compounds that contain a benzene ring in their molecule or that have chemical properties similar to benzene. These are divided into two groups.

A) Homocyclic
B) Heterocyclic

A) Homocyclic: All the atoms in the ring are the same type.

Eg. Benzene (C_6H_6); Cyclohexane ($C_6 H_{12}$)

In the above compounds in the ring, all are carbon atoms only.

B) **Heterocyclic:** If different atoms are present in the ring .

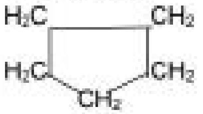
In the ring C and N atoms are present

The aromatic rings are again divided into

I. Five (5) membered ring structure
II. Six(6) membered ring structure

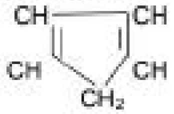
I. Five (5) membered ring structure

1. Saturated



Cyclopentane

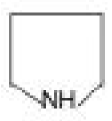
2.Unsaturated



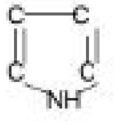
Cyclopentadiene

Saturated N containing

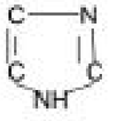
unsaturated N containing



Pyrrolidine



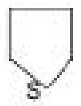
Pyrrole



Imidazole

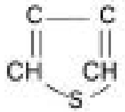
Pyrazole

Saturated S containing



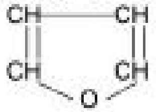
Thiophane

Unsaturated S containing



Thiophene

Unsaturated O containing



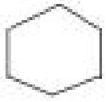
Furan

Furan is present in insecticides like carbofuran

Pyrrole is present in chlorophyll, alkaloids ,riboflavin etc.,

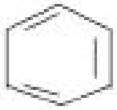
II. Six(6) membered ring structure

1. Saturated



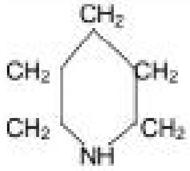
Cyclohexane

2. Unsaturated



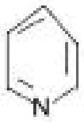
Benzene

Saturated N containing

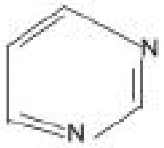


Piperdine

Unsaturated N containing

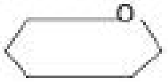


Pyridine



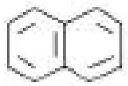
Pyrimidine

Unsaturated O containing

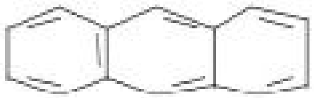


Pyran

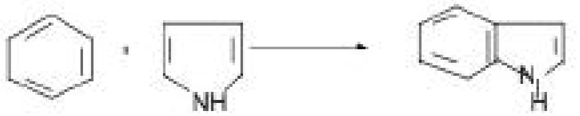
1) When two benzene rings fused to form Naphthalene



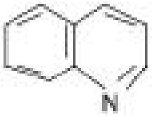
2)**When three benzene rings are fused to form Anthracene**



1) When benzene ring is fused with pyrrole, then it is called indole .It is present in IAA , Jasmine flowers etc



2) When benzene is fused with pyridine, it gives quinoline

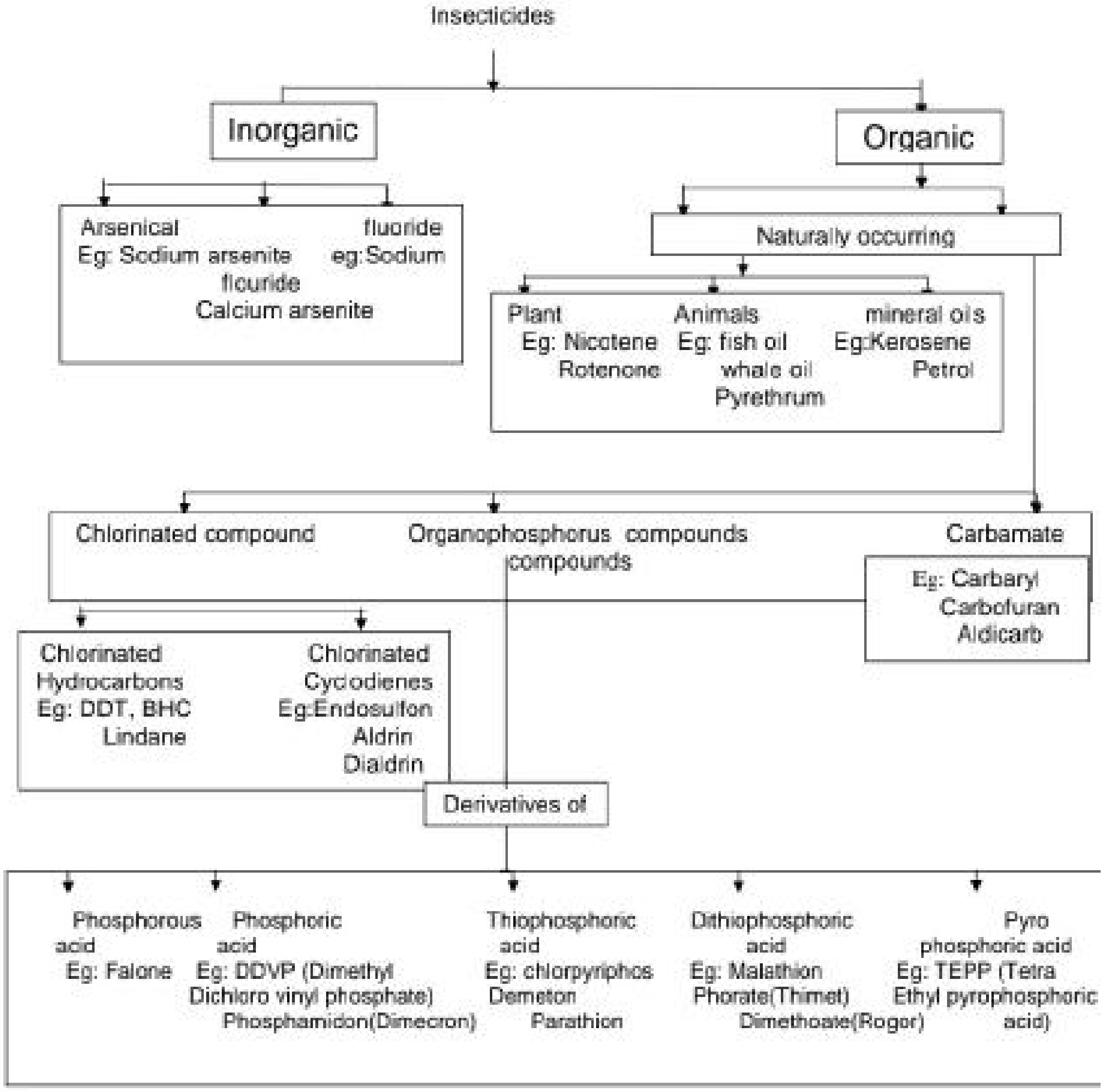


Lecture : 21 Diverse types of agrochemicals –Classification based on their use with examples. Classification of insecticides based on their chemical nature with examples. Botanical insecticides –Brief mention about vegetable oils (Fixed oils) and essential oils.

Classification of agricultural chemicals based on the purpose:

1. Insecticides : Eg.Malathion , phorate
2. Fungicides : Eg.Zineb, captan
3. Herbicides : Eg.Paraquat, Butachlor
4. Acaricides : To kill mites and ticks , Eg.Dicofol and sulphur
5. Nematicides : Eg. Nemegon, carbofuran, Aldicarb
6. Zococides : To kill the rodents and other small creatures. Eg. Aluminum phosphide, warfarin, zinc phosphide, Celphos tablets
7. Bactericides : To control bacteria Eg.Oxime , Streptomycin
8. Algicides : To destruct algae and other aquatic vegetation Eg. Phygon, Diculose
9. Molluscicides : To control molluscs including gastropods or slugs Eg.Metaldehyde
10. Antibiotics : Eg. Cycloheximide, Phycoactin and Aphomide
11. Antiseptics : Eg. Zinc oxide
12. Sex attractants : Eg. Gyplure, Helilure
13. Chemosterilant : Eg. TEPA, Aphomide, Azaridine
14. Insect attractants : Methyl Eugenol
15. Insect repellants : Citronella oil , Naphthalene
16. Fumigants : Methyl Bromide
17. Plant growth regulators : IAA, Kinetin , Gibberellic acid
18. Fertilizers : Urea , SSP, K_2SO_4
19. Amendments : Lime , Sulphur, Gypsum
20. Soil sterilants : Borax
21. Nitrification inhibitors : Eg. N-Serve and A M
22. Chitin inhibitors : Eg.Diflubenzuron
23. Defoliants : To remove leaves from plants Eg. Gramoxone
24. Desiccants : : To remove moisture from plants Eg.Penta Chloro Phenol

Classification of insecticides based on chemical nature:



BOTANICAL INSECTICIDES

Plant materials are important sources of insecticides .The toxicant may be present in any part of the plant and these toxic materials are collected and dried and powdered and that powder is used as insecticide. The toxicant also extracted from the powder using some solvent and chemical compound thus obtained used as insecticide.

Plant products which are used as insecticides may be classified as

1. **Primary toxicants** such as nicotine , rotenone
2. **Essential oils**(structure resembles to menthane)such as Pine oil,citronella oil
3. **Fixed oils** like Cotton seed oil and Neem oil
4. **Miscellaneous oils** such as walnut shell flour , plant gurr

Advantages of botanical insecticides

1. Relatively cheaper
2. Don't pollute the environment
3. Don't leave any residue
4. Availability is relatively easier
5. Don't harm the beneficial organisms.

Disadvantages or difficulties involved in the use of botanical insecticides:

1. It takes fairly long time (**2-5 years)** to establish a plant in a new environment. Some times the plant can't be introduced at all.
2. Availability of botanical insecticides is confined to a particular season , making import compulsory in off season .
3. Botanical insecticides decompose very fast and don't have long self life.
4. Testing of biological materials as botanical insecticides is very difficult and time consuming process and so far, a fraction of flora and fauna has been tested.

Lecture: 22 &23 Natural pyrethrum –Discovery –Sources –Chemistry-Extraction and properties .Neem and its products –Extraction –Mode of action of neem based products .Advantages and Disadvantages of natural botanical insecticides .Brief note on synthetic pyrethroids

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PYRETHRUM

The original home of pyrethrum is said to be East or Middle East. In the 19th century it was introduced to U.S.A., Japan, U.K., Africa and South America. At the beginning of 20th century, Dalmatia and adjoining countries became leading producers. In 1941, Japan became the leading producer. However, at present, the principal producer of pyrethrum is KENYA. Other countries producing pyrethrum are Congo, Uganda, Tanzania, Ethiopia, Equador and Brazil .

In INDIA also pyrethrum is grown to a small extent in the

1. Hilly belts of Assam
2. Himalyan mountain range of J & K
3. Nilgiri areas of Tamil Nadu

Pyrethrum has been used for the control of harmful insects for many countries.

SOURCE:

Pyrethrum is found to occur in the flowers of some plants belonging to family compositae / Asteraceae. Important sources are

1. ***Chrysanthemum cinerariefolium***
2. ***C . coccineum***
3. ***C.roseum***
4. ***C.marshalli***
5. ***C.tamrutene***

Extraction of Pyrethrum:

Pyrethrum is present in the Achenes of flower heads. The content is maximum when the flowers are in full bloom stage. At this stage, the flowers are harvested by hand picking .They are then dried at 54.4 ^{0}C and compressed. In the industries the dried and compressed flowers are ground to a fine powder. The powder / dust can be used as an insecticide.

The toxicant can be extracted by extracting with an organic solvent like Isopropanol, acetone or odor less kerosene. The solvent is repeatedly percolated through the powder and the weak extract is evaporated in a vacuum still to get concentrated extract .The concentrated extract together with an emulsifier is sold in the market for the use.

Also, the concentrated extract can be mixed uniformly with an inert carrier like benonite clay, charcoal powder, diatomaceous earth and the mixture can be used as a ready to use low power dust.

The extracted powder containing traces of pyrethrum is some times used as carrier in the dust preparation .To increase the pyrethrum activity compounds like DDT and Rotenone etc., are added.

CHEMISTRY AND STRUCTURE OF PYRETHRUM

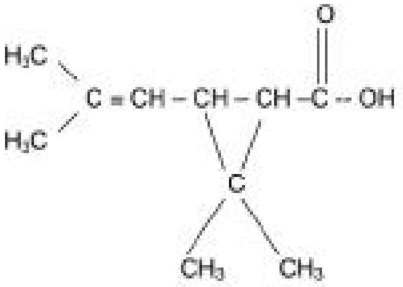
Elucidation of the chemical nature and structure of natural pyrethrum was by no means an easy task. Three groups of scientists worked together for decade for unfolding mystery of chemistry of pyrethrum .They are

1. **Staudinger and Ruzicka**
2. **La Forge and Barthel**
3. **Godin , Beevor and Snarey**

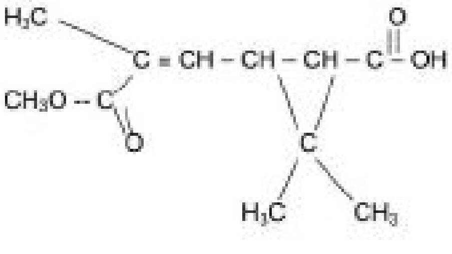
Natural pyrethrum is composed of **six (6) esters**. An ester product formed by reaction of an acid with an alcohol. The six esters are formed by reacting to two carboxylic acids and three alcohols in different combinations

The two carboxylic acids are

1. **Chrysanthemum Monocarboxylic Acid (CMA)** or Cyclopropane monocarboxylic acid or Chrysanthemic acid

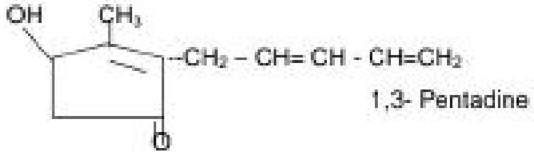


2. **Chrysanthemum Dicarboxylic Acid (CDA) or** Cyclopropane dicarboxylic acid or Pyrethric acid

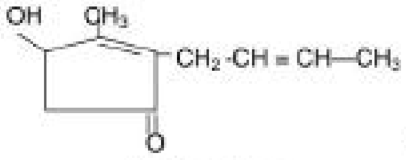


The alcohols are

1. Pyrethrolone :

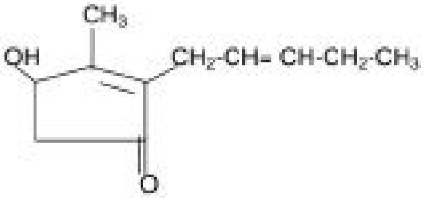


2. Cinerolone:



2- Butene

3. Jasmalone:



3-Pentene

Alcohols contains

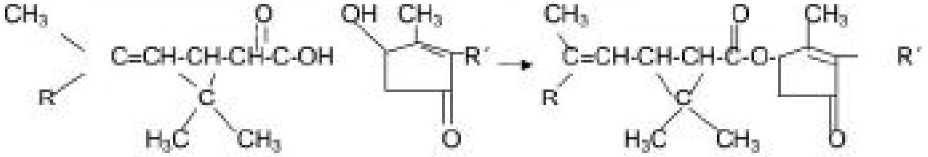
2. Cyclopentane ring
3. A keto group
4. A methyl group
5. A hydroxyl group
6. An aliphatic side chain

An ester is formed by the reaction between an organic acid and an alcohol

General structure of pyrethrum esters:

S.No.	Ester	R	R1
1	Pyrethrin -I	CH_3	$-CH_2.CH{=}CH\ .CH{=}\ CH_2$ (1,3 pentadiene)
2	Pyrethrin-II	$COOCH_3$	---------------do---------------------------
3	Cinerin -I	CH_3	$-CH_2.CH{=}CH\ .CH_3$ (2 butene)
4	Cinerin -II	$COOCH_3$	$-CH_2.CH{=}CH\ .CH_3$ (2 butene)
5	Jasmolin -I	CH_3	$-CH_2.CH{=}CH.\ CH_2.CH_3$ (3 pentene)
6	Jasmolin-II	$COOCH_3$	-------------- do------------

General formula of acid + alcohol → Pyrethrum



Another way of representing esters of pyrethrum is

S.No.	Ester	Acid	Alcohol
1	Pyrethrin -I	Chrysanthemic acid	Pyrethrolone
2	Pyrethrin -II	Pyrethric acid	---do------
3	Cinerin -I	Chrysanthemic acid	Cinerolone
4	Cinerin-II	Pyrethric acid	Cinerolone
5	Jasmolin -I	Chrysanthemic acid	Jasmolone
6	Jasmolin-II	Pyrethric acid	Jasmolone

Properties of pyrethrum:

1. It is an amber coloured viscous liquid
2. Insoluble in water but soluble in organic solvents
3. It is non-volatile, hence non-fumigant action.
4. Being an ester, it is easily decomposed by acid, alkali or even by moisture on long standing to produce primary constituents.
5. On prolonged storage, pyrethrum looses its insecticidal action due to degradation by oxidation .Hence; antioxidants like hydroquinolene are added to increase the life.
6. An exposure to sunlight, it is degraded to nontoxic products in no time i.e., highly photodegradable. This is what restricts the use of natural pyrethrum in out door agriculture.

Insecticidal action:

- Pyrethrins are more toxic than cinerins and Jasmolins .Cinerins are however, better knock down agents
- The toxicity of pyrethrum can be increased by the addition of non –toxic substances called synergistics such as piperonyl butoxide, sesamin , sesamex etc.,
- Pyrethrum affects the Central Nervous System of insects.
- It is relatively safe for mammals .LD50 value for rats is **570** mg/Kg body weight (oral) and 1880 mg /Kg body weight(dermal)

NEEM

Neem, ***Azadirachta inidaca*** **A.Juss** is grown throughout India, since time immemorial , it is a very useful plant and utilized in diverse ways .

The interest of entomologists towards the use of neem in pest management arose with the discovery of **Pradhan et al (1963) who reported** the extraordinary **anti feeding** property of neem seed kernel against desert locust. Now there is a global attention for the use of neem for pest control.

Although, all parts of the neem tree are biologically active but the highest activity could be seen in seed kernel. Havie et al (1967) were first to report the isolation of **teriterpenoid alcohol** (Meliantriol) from the fruits of Dharek *(Melia azedarach)* and neem which inhibits the feeding of desert locusts.

Butterworth and Morgan (1968) isolated **tetranotriterpinoid, azadirachtin** from neem seed kernel, which is stronger inhibitor than Meliantriol.This is also present in the leaves of neem and also in fruits of neem

Henderson et al (1964) isolated **salanin** from neem and was found poor feeding deterrent

Kraus et al (1980) isolated

a) Diacetyl vilasinin }
b) 3 – desacetyl salanin } From Neem Seed
c) Nimbandiol }
d) Salannin }

Thus , Neem owes its toxic attributes due to the presence of **azadirachtin , Melantriol, Salannin , Nimbandiol , Diacetyl vilasinin etc.,** Among which azadirachtin is more potent .

Neem seed contains 0.2 to 0.3 % azadirachtin .Neem has diverse affect on insects such as

1. Feeding deterrent
2. Growth disruptor
3. Repellant
4. ovispositional deterrent
5. Insecticidal etc.,

In few insects hatchability and reproduction are impaired .Pest resurgence has not been in neem treated plots. Insects cannot develop resistance to neem compounds as they contain a number of bioactive principles.

Azadirachtin, causes disorders in metmorphosis. In some insects when neem seed extract mixed with food caused growth inhibition, mal formation, mortality and reduced fecundity . Neem seed extraction at 12 percent concentration has been found as potential anti feedant for brown plant hopper.

Neem has systemic activity , non phytotoxic remain active in plants up to 25 days .Neem products are highly degradable (photo) residual action of neem can be increased by the addition of adsorbents . It has no adverse effect on the environment and have no toxic residue in the harvested agro - commodities.

Neem products : Nimbecidine , Neemgaurd, Neemplus , Neemrich, Cropgaurd, Neemostar, Azadit-20, Radon, Jawan, ,Neem mark, Navagaurd, ,Margosol, nemidin

SYNTHETIC PYRETHROIDS

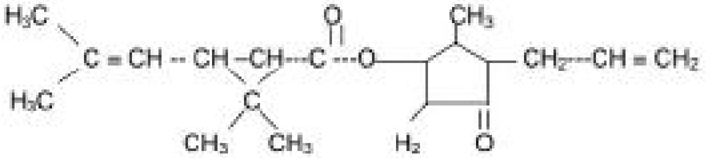
These are 4th generation insecticides .The unstable nature of pyrethrum, coupled with the establishment of structure of pyrethrum. Many workers stimulated their research on synthetic pyrethroids. Synthetic pyrethroids are more stable than many of the organic phosphorus compounds and carbamate insecticides .These are insecticidally more active than others.

1. Synthetic pyrethroids are viscous, lypophilic liquids, insoluble in water,
2. Biodegradable,
3. Have low mammalian toxicity,
4. Don't leave any residues in biological systems and cause less contamination to the environment.
5. Cause less contamination to the environment.

1. ALLETHRIN / DIVINYL PYRETHRIN –I (DVP-I)

It was introduced with trade name **pynamin** .It is also called as divinyl pyrethrum –I . This was the first synthetic pyrethroid.This was first reported by **LAFORGE&SCHECHTER** . It is a pale yellow oil sparingly soluble in water, soluble in organic solvents .It has a more stable side chain than pryethrins. It is more persistent and contact insecticide effective against houseflies, mosquitoes, but less effective against household pests.

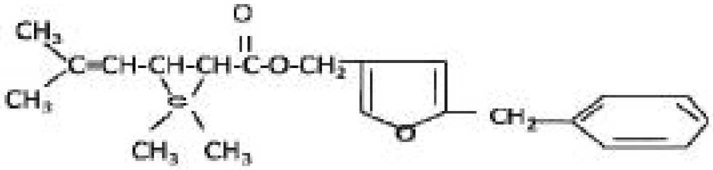
It is an allyl analog of pyretrhrin –I.



2-methyl-4-oxo-3(2-propenyl)-2 cyclopentane-1-cis trans -3(2,2-dimethy vinyl-2,2-dimethyl cyclopropane-1-carboxylate.

2.BIORESMETHRIN

- First synthesized at Rothemsted Experimental station (1966)
- CMA+5 Benzyl furyl 3 methanol



More toxic(50 times) than to natural pyrethrum(house flies)

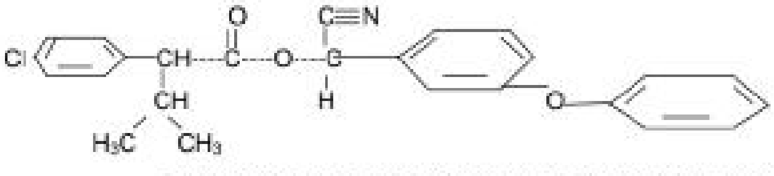
LD_{50} = 7070 mg - 8000mg / kg body weight

4. FENVALERATE /SUMICIDIN/ FEN FEN/ FENVOL

Synthesized by Sumitomo chemical company of Japan

Properties:

1. It is a viscous yellow liquid , less soluble in water .More soluble in organic solvents
2. It is thermally stable, more stable in acid medium than in alkaline medium.
3. It is a contact and stomach poison.
4. It is effective against cotton boll worm, lepidopteron larvae and used in public health management and animal husbandry.
5. It is a cyanide containing synthetic pyrethroids



α-cyano-3-phenylbenzyl-s-isopropyl-p-chlorophenyl acetate

5. PERMETHRIN

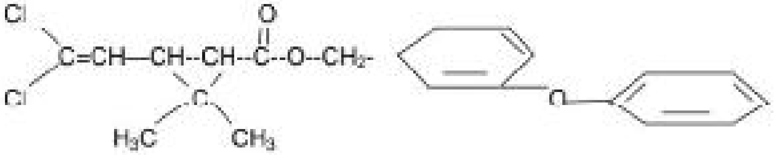
Trade names AMBUSH, TALCORD, KALFIL

This was first reported by **MICHEAL ELLIOTT**.

Properties:

It is a yellowish brown liquid, highly viscous, insoluble in water, highly soluble in organic solvents.

- Stable to heat , more stable in acid than in alkaline medium .
- It is a contact insecticide
- It has good residual activity
- It has low mammalian toxicity
- It is very effective against lepidopetrous lavare and used in live-stock management .



α-3 phenoxy benzyl (±) cis trans -3(2,2-dichlorovinyl-2,2-dimethyl-cyclopropane-1-carboxylate)

Synthetic pyrethroid containing two chlorine atoms is Permethrin, one chlorine atom is Fenvalarate.

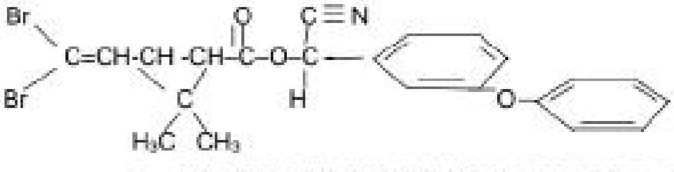
4. DECAMETHRIN/DELTA METHRIN / DECIS

This was first introduced by " **ROUSSEL UCLAF** " and reported by **MICHAEL ELLIOTT**.

This is bromine and cyanide containing synthetic pyrethroid.

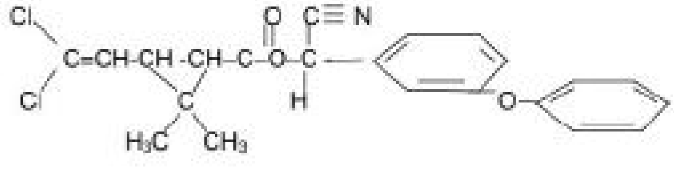
Properties:

1. It is a colourless crystalline powder.
2. It is stable having no degradation even after 6 months.
3. It is insoluble in water. Soluble in organic solvents .Non-phytotoxic, proved effective against insects which are resistant to conventional pesticides.
4. It is not effective against mites.



5. CYPERMETHRIN/CYMBUSH/ RIPCORD/BARRICAD

Dcihloro CMA + Cyano-3- Phenoxy benzyl alcohol



Lecture: 24 Synthetic organic insecticides – Cyclodiene –Diels- Alder reaction – structure , properties

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ORGANO CHLORINE INSECTICIDES

The organo chlorine insecticides are classified into two categories

1. **Chlorinated Hydrocarbons Eg.** DDT, BHC, Methoxy chloar, Lindane
2. **Cyclodiene compounds Eg.** Aldrin , Dieldrin, Endrin, Endosulfan

CYCLODIENE INSECTICIDES

Major characteristics:

1. These are polychlorinated compounds
2. Must contain at least one bicyclic ring
3. Must contain at least one Endomethylene bridge
4. prepared by Diels Alder Additive Reaction
5. HCCP (Hexa Chloro Cyclo Pentadiene) is the basic raw material required for their synthesis.
6. Highly persistent
7. Very effective contact insecticide

Disadvantages:

1. Highly toxic to mammals
2. Long persistence in the environment

DIENE: An alkene that has two double bonds in its molecules.

CONJUGATED DIENE: The compound in which the two double bonds are separated by one single bond.

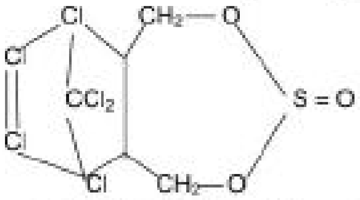
Eg. 1,3 Butadiene , $CH_2{=}CH-CH{=}CH_2$

DIELS –ALDER REACTION:

A type of chemical reaction in which a conjugated diene adds to a suitable compound containing one double bond (dienophile) to give a ring compound .It is named after the German chemist **OTTO DIELS & KURT ALDER** who discovered it 1928.

ENDOSULFAN /THIODAN

An important cyclodiene insecticide used very extensively.

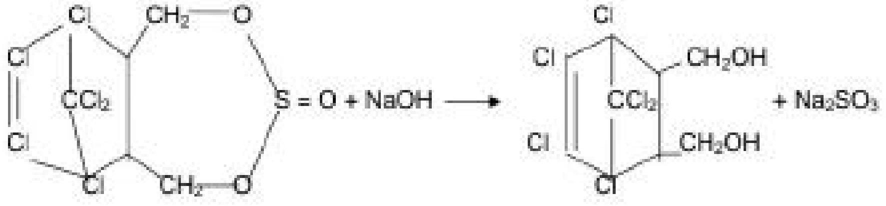


6,7,8,9,10,10- hexa chloro –1,5,5a,9,9a- hexa hydro 6,9 methano-2,4,3,-benzo dioxo thiepin -3- oxide.

Properties:

1. It is a mixture of two isomers α and β in 4:1 ratio.
2. Technical grade is an amorphous powder.
3. It is insoluble in water but soluble in most of non-polar organic solvents.
4. Readily decomposed by alkali to form endosulphan alcohol and inorganic sulphite .

Reaction:



5. It is a stomach and contact poison
6. It is highly toxic to mammals with an LD_{50} value 40-110 mg/kg body weight.
7. Formulated as dust , granules etc.,
8. It is metabolized to sulphate in the metabolism of insects, plants and animals.

Mode of Action of cyclodiene compounds:

They inhibit the activity of Respiratory enzymes. This leads to disruption of oxidative phosphorylation. The symptoms of poisoning in insects are:

1.Hyper sensitivity,
2.Hyper activity
3. Violent burns and
4 .Collapse of insects finally.

Lecture: 25 Organo phosphorus insecticides – Discovery – Advantages – Classification –Mode of action .Structure , properties and uses of Dichlorvos (DDVP)

ORGANO PHOSPHORUS INSECTICIDES

Organo phosphorus compounds constitute a variety of Agrochemicals and as a group they rank first in consumption .They were discovered as toxic nerve gases by the defence labs of Germany during II World war. Insecticidal properties of organo phosphorus compounds were identified by GERHARD SCHRADER (1937) .These also act as Acaricides, Nematicides, Defoliants and Desiccants .These are good substitute for Nicotine.

Advantages of organo phosphorus compounds:

1. These are required in very small quantity.
2. These are quickly decomposed leaving no toxic residues
3. These are very quickly metabolized in vertebrates and tendency to be excreted
4. These have wide insecticidal spectrum.
5. Some of these are systemic in nature
6. Some do have Nematicidal action in addition

Classification of organo phosphorus compounds:

1. Derivatives of phosphoric acid (H_3PO_4) :
   Eg. DDVP(Dimethyl dichloro vinyl phosphate) or Dichlorovos or Nuvan
   Phosphomidan (Dimecron)

2. Derivatives of thiophosphoric acid (H_2PO_3S):
   Eg. Methyl parathion, Parathion, Diazinon, Dursaban

3. Derivatives of dithiophosphoric acid ($H_2PO_2S_2$):
   Eg. Malathion, Phasolone(zolone), Phorate (Thimmet)

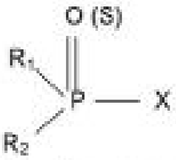
4. Derivatives of pyrophosphoric acid Eg.
   Eg.TEPP (Tetra Ethyl Pyrophosphate), Pestox –III,Sacradan

5. Derivatives of phosphorous acid
   Eg. Falone

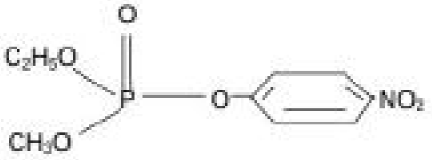
Mode of action of organo phosphorus (O.P.) insecticides:

Acetyl choline esterase is a key enzyme of nervous system and is responsible for hydrolyzing acetyl choline to acetic acid and choline .By doing so, the enzyme helps in carrying nerve impulses to brain. When O.P. insecticides are applied ,the central phosphorus atom of O.P. insecticides phophorylates the active site of acetyl choline esterase enzyme and inhibits the enzyme activity .As a result acetyl choline cannot be hydrolyzed to acetic acid and choline to carry nerve impulses to brain .Thus O.P. insecticides disrupt the nervous system in susceptible animals and insects.

General structure of O.P. insecticides:



Where R_1 and R_2 are short chain alkyl groups (CH_3, C_2H_5) or alkoxy (CH_3O, C_2H_5 O) or alkyl thio (CH_3OS, C_2H_5 OS) groups and X is any labile group which will be metabolized *invivo*

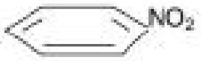


Ethyl Methyl Parathion

Where ,

R_1 is C_2H_5 O (Ethoxy)

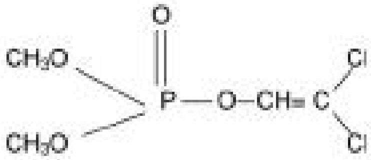
R_2 is CH_3O (Methoxy)

X is 

1. DERIVATIVES OF PHOSPHORIC ACID:

Most of the derivatives of phosphoric acid insecticides are vinyl esters of the acid

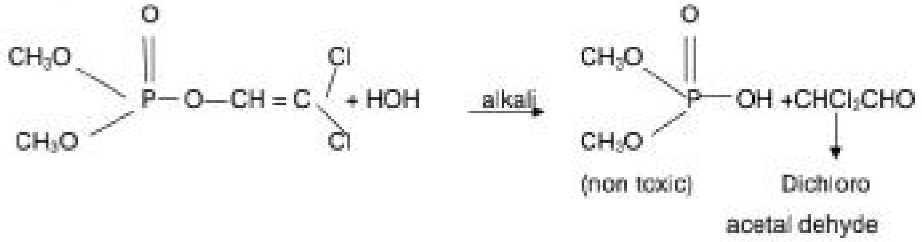
A) DDVP/ Dichlorovos / Nuvan



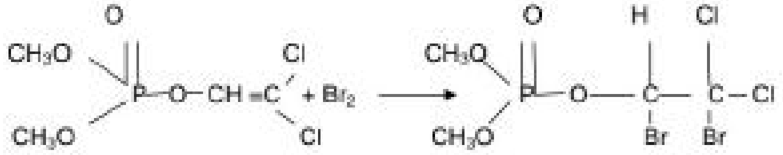
O, O, di methyl O-2,2-dichloro vinyl phosphate .This was introduced in 1955.

Properties:

1. It is a colourless liquid
2. It is moderately volatile and does have considerable fumigant action
3. It is water soluble to the extent of 1 % but highly soluble in organic solvents.
4. It is stable to light and heat .However in the presence of water it gets hydrolyzed to form Dimethyl phosphoric acid (DMPA). This acid acts as a catalyst for further degradation of DDVP .That is why DDVP is formulated with 2 to 4 % epichlorohydrin.



5. The degradation products of DDVP are quickly lost by further decomposition. Thus, use of DDVP poses no residue hazard.
6. DDVP has a vinylic double bond and responds to addition reaction with halogens or hydrogen particularly with bromine .With bromine it reacts as follows.



(O,O- dimethyl-O-1,2 dibromo-2,2-dichloro ethyl phosphate)

Incidentally, this compound is also an effective insecticide and sold as Naled or Dibrom

7. It is a contact and stomach poison - Suitable for the control of sucking insects , flies and mosquitoes etc ,
8. It is moderately toxic to mammals with a L.D.$_{50}$ value of 80 mg/kg body weights of rats.

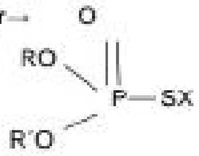
Lecture: 26 Thiophosphoric acid derivatives –Thiolo and thiono isomers . Structure and activity relationships of thiophosphoric acid derivatives, structure, properties and used of Methyl parathion.

DERIVATIVES OF THIO PHOSPHORIC ACID AND INSECTICIDES

Replacement of one 'O'(oxygen) atom by 'S' , in the phosphoric acid derivatives produces thiophosphoric acid insecticides with such replacement, the mammalian toxicity is decreased markedly but the insecticidal toxicity remains unaltered more or less.

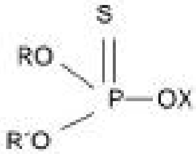
As insecticides, thiophosphoric acid derivatives are of two types

1) .**Thiolo isomer→**



(more toxic to mammals than thiono)

2) .**Thiono isomer→**



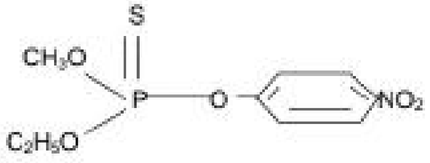
- Thiolo isomers are more toxic than Thiono isomers.
- Thiono isomers can be converted to Thiolo isomers (Isomerisation) by heat and by chemical reagents or by oxidase enzymes.
- Conversion is called as "PISCHEMEUKA" rearrangement.

Structure, Activity Inter Relationship Of Thiophosphoric Acid Derivatives

Most of the insecticides of thiophosphoric acid derivatives are mixed esters of formula

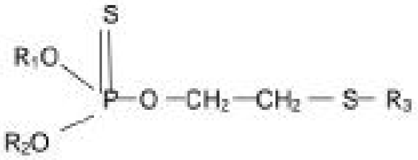
Where **R_1** and **R_2** are short chain alkyl groups and ***Ar*** is aromatic nucleus.

Eg.

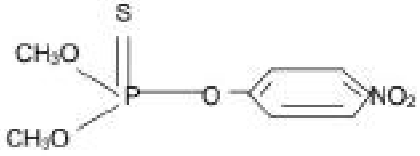


Methyl Ethyl Parathion

1. Most effective insecticides are those in which both R_1 and R_2 are aliphatic radicals and the total number of C atoms in R_1 and R_2 put together does not exceed 4
2. If both R_1 and R_2 are methyl groups → minimum insecticidal activity
   If R_1 is methyl and R_2 is Ethyl → medium insecticidal activity
   If R_1 and R_2 are Ethyl groups → maximum insecticidal activity
3. Both insecticidal activity and mammalian toxicity are increased remarkably, if a nitro ($-NO_2$) group is introduced in 4th or para position of the aromatic ring.
4. Introduction of same nitro ($-NO_2$) group in second and third position of the aromatic ring decreases the insecticidal activity markedly.
5. Introduction of another group (besides $-NO_2$ group at 4th position) into the aromatic ring decreases insecticidal activity, while mammalian toxicity decreases considerably.
6. Introduction of three or more groups, into the aromatic ring decreases both insecticidal activity and mammalian toxicity.
7. If at all, a second group is to be introduced it should be introduced only in third position of the aromatic ring .
8. Introduction of other groups like cyano ($-C\equiv N$) or sulfoxide (S=O) or Sulfone (O=S=O) in fourth position also exhibits increased insecticidal activity but the mammalian toxicity is also increased dangerously, often prohibiting their use.
9. Some times, the replacement of aromatic ring by heterocyclic ring also produces very effective insecticides like dursaban and diazinon.
10. Most of the compounds with the following formula are systematic insecticides.



Methyl Parathion /Metacid /Folidol-80

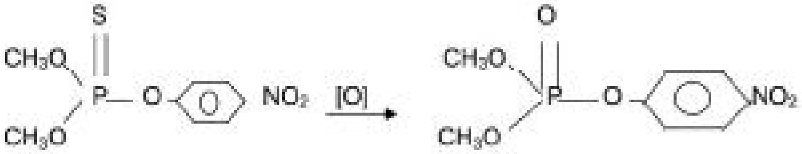


Chemical name: O,O – dimethyl O-4-nitrophenyl thiophosphate

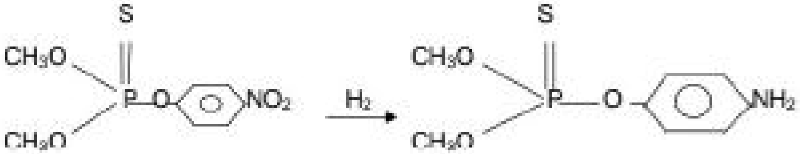
Properties:

1. It is a white crystalline substance.
2. Its water solubility is only 55 mg / l, highly soluble in organic solvents.
3. It is quickly hydrolyzed in alkaline medium to produce 4- nitrophenol (yellow coloured) as an important product to determine the purity of methyl parathion.

4. Oxidizing agents and oxidase enzymes oxidase the P=S groups to P=O forming methyl paraoxone which is more toxic than methyl parathion.



5. Reducing agents reduce the nitro group [NO_2] to [NH_2]group making he compound non-toxic.



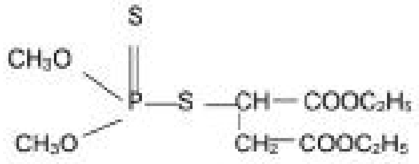
6. Methyl parathion is an effective alkylating agent and alkylates a number of biochemical substances such as amines and thiourea .Most of the compound is lost by methylation before it reaches the enzyme acetyl choline esterase. This explains the low mammalian toxicity of methyl parathion.
7. It is relatively safe compound for mammals
8. Formulated as EC and dusts

Lecture:27 Dithiophosphoric acid derivatives – structure, properties and uses of Phorate and Malathion

DITHIOPHOSPHORIC ACID INSECTICIDES

In the change from Thiophosphoric to dithiophosphoric acid derivative insecticides, the toxicity of the compounds decreases, but chemical stability of the compounds increases.

1. Malathion / Carbophos

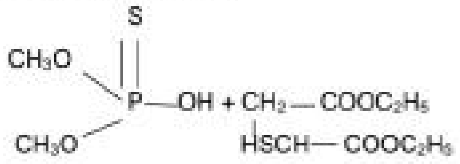


Chemical name: O, O dimethyl –S-1, 2 dicarboethoxy ethyl dithiophosphate

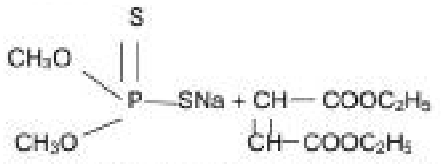
Properties:

1. Colourless liquid
2. Almost water soluble, but soluble in most of organic solvents.
3. It is moderately volatile and does have fumigant action.
4. It is hydrolyzed in both acidic and alkaline medium but in different direction.
5. In insects ,it is oxidized by oxidases to form the more toxic malaoxon

In acid medium, the products are dimethyl thiophosphoric acid and diethyl mercapto succinic acid.



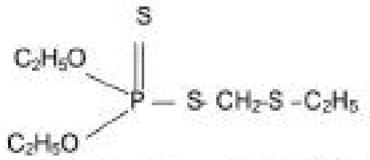
In alkaline medium, the products are dimethyl dithio –phosphoric acid and diethyl furmerate.



But in vertebrates, it is detoxified by loss of ethyl groups to form malathion acid which is non toxic, that's why it is safe for mammalians.

6. Malathion is moderately persistent i.e., 20 days
7. It is a general purpose contact insecticide
8. It is one of the safest insecticides .L.D.50 value is 500-1500 mg /kg body weight .Its use thus permitted in live-stock management, public health, house hold and storage.

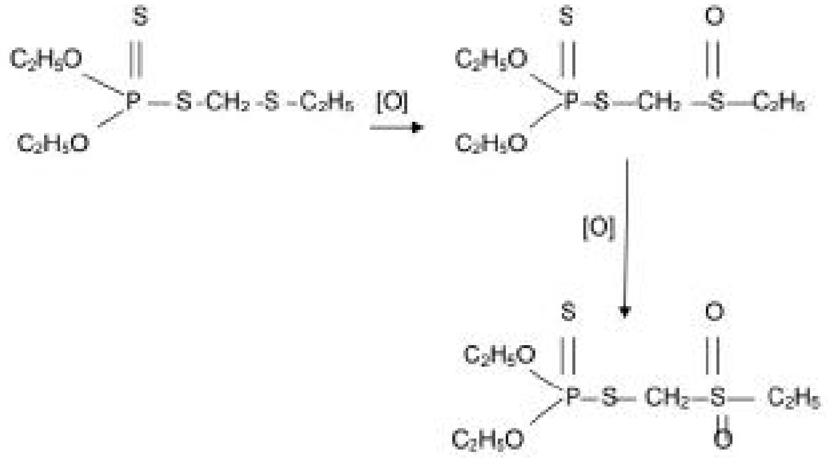
2. Phorate (Thimet)



Chemical Name: O, O- diethyl –S- (ethyl thio methyl) dithiophosphate.

Properties:

1. It is transparent oil.
2. Almost water insoluble but soluble in organic solvents.
3. It is slightly volatile and does have an unpleasant odour
4. In alkaline medium, it is rapidly hydrolyzed to form the respective acid and alcohol.
5. Phorate is oxidized to its sulphoxide and sulphone.Both are more toxic and more persistent than phorate .The reaction takes in dry soils and explains the relatively long life of phorate in soils.



6. Phorate is a very effective systemic insecticide . Very suitable for the control of chewing and sucking insect pests. It is used also as a nematicide.
7. It is extremely toxic for mammals .L.D. 50 is 1.1 to 2.3 mg /kg.
8. Phorate is formulated mainly as granules (10 G)

Lecture: 28 Carbamate insecticides –Chemistry, discovery and mode of action, structure ,properties and uses of Carbofuran

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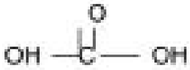
CARBAMATE INSECTICIDES

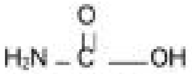
In production and consumption, this rank - II, apart from the insecticides, this act as fungicides, herbicides and acaricides .Eg. Carbaryl, Carbofuran, Aldicarb etc.,

Carbamates are the derivatives of carbamic acid, may be considered as molecule of urea in which an amine (NH_2) group is replaced by a OH group (or) a molecule of carbonic acid in which OH group is replaced by a NH_2 group.

$CO_2 + H_2O \longrightarrow H_2CO_3$



$$OH - \overset{\overset{O}{\|}}{C} - OH$$



$$H_2N - \overset{\overset{O}{\|}}{C} - OH$$

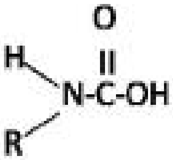
Carbamic acid

Carbamates are in fact esters of carbamic acid. Carbamic acid can be esterified by either aliphatic or aromatic alcohol forming alkyl or aryl carbamates.

Further, one or two H atoms of the NH_2 group may be replaced by aliphatic or aromatic radicals i.e., N-alkyl or N- aryl carbamates.

In general, N-alkyl aryl carbamates are good insecticides

General structure of Carbamate:



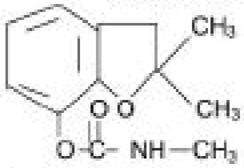
Where R is alky radical like CH_3 , C_2H_5,C_3H_7 etc.,

Ar- is aromatic radical like phenyl, Naphthyl etc.,

N-alkyl aryl carbamate

Carbofuran /Furadon

It is very effective systemic insecticide and very suitable as a soil insecticide .It is also used as nematicde.

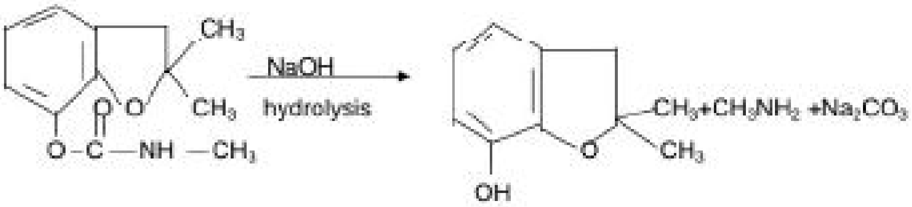


Chemical name: (2,2-dimethyl 2,3-dihydro benzofuranyl- 7-N-methyl carbamate)

Properties:

1. It is a white crystalline substance.
2. Poorly water soluble, but soluble in organic solvents.

3. Some what stable in neutral and slightly acidic medium, but readily decomposed in alkaline pH, when the ester bond is readily degraded to produce the alcohol (2,2 dimethyl 2, 3 dihydro benzofuranol)and methyl amine



It is thus not compatible with alkaline agricultural materials like, lime or Bordeaux mixture. Hence, it should not be mixed with agricultural chemicals of alkaline nature

4. Carbofuran is highly toxic for mammals. L.D.50 value for Rats is 5 mg /kg body weight.
5. It is formulated as granules (3G).

Lecture: 29 Fungicides –Definition –Systemic and non –systemic –Classification of fungicides based on chemical nature with examples –structure and properties and uses of copper oxy chloride and Zineb

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FUNGICIDES

Fungicide is a chemical substance that has the ability to kill fungi and is thus an antifungal substance. Some fungicides act on the "surface" near the site of application and these fungicides are called non-systemic fungicides.

A systemic fungicide is a fungi toxic compound which when applied to any part of the plant is absorbed by plant tissues and is translocated either upward or downward or both and exert toxicity in the fungi directly or indirectly through its metabolite at a site away from its application .

Classification of fungicides

I. Based on the chemical nature

1.Sulphur containing fungicides :

A).Inorganic: Eg .Lime sulphur; powedered sulphur

B). Organic: Eg. Zineb, Maneb, Thiram and Vapam

2. Copper containing fungicides:

Eg.Bordeaux mixture [Ca (OH) $_2$ + $CuSO_4$]

Eg. Burgundy mixture [$CuSO_4$] + Na_2CO_3

Eg. Cheshnut compound [$(NH_4)_2CO_3$+$CuSO_4$]

3. Mercury containing fungicides:

A).Inorganic: Eg. Hg Cl (Mercurous chloride or Calomel)

Hg Cl_2(Mercuric chloride)

B) .Organic: PMA (Phenyl Mercuric Acetate)

EMC (Ethyl Mercuric Chloride)

4. Quinones : Chloranil ; Dichlone

5. Heterocyclic nitrogenous compounds : Captan , Captafol, Folpet

6. Benzimidazoles: Eg. Carbendazim, Thiobendazole, Benomyl

7. Oxanthins: Eg.Carboxin ; Oxycarboxin

8. Morpholines: Tridemorph ; Dodemorph

9. Thiophanates:

These are derivatives of thio aliphanic acid

$[H_2N-\overset{S}{\overset{\|}{C}}-NH\,COOH]$

Eg. Topsin and Topsin -M

10. Organophosphorus fungicides: Kitazin; Hinosan

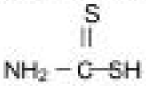
11. Pyrimidines : Ethrimol, Dimethrimol; Triarimol

12. Miscellaneous : PCNB(Penta Chloro Nitrobenzene)

13. Antibiotics: Streptomycin, Cycloheximide, Chloroneb, Triphenyl acetate

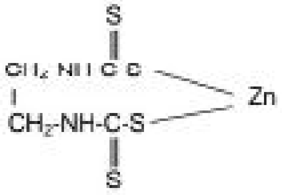
1. ZINEB

Chemical Name: Zinc ethylene bis dithiocarbamate



$NH_2 - \overset{\overset{S}{\|}}{C} - SH$

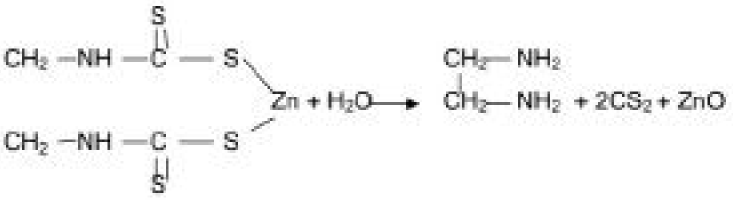
Structure:



This is a widely used 'S' containing fungicide

Properties:

- It is a white crystalline substance ,decomposes before melting point which is usualy between 140 and 160 °C
- It is insoluble in water as well as organic solvents, but highly soluble in pyridine.
- Zineb containing 74 % moisture, under unfavourable conditions, may decompose with the evolution of explosive CS_2 . So it should be stored in well ventilated place at low temperature.



- Zineb brakes down in the plants, within 10-15 days of its application, resulting in the formation of volatile products like $ZnSO_4$, which is used as a source of micronutrient zinc.
- Its $L.D._{50}$ value is 2000 to 5000 mg /kg or 2-5 grams per kg body weight.

2. COPPER OXY CHLORIDE/ BLITOX/FYTOLAN

(It is the most widely used copper based fungicide)

Copper oxy chloride: $Cu\ (OH)_2 .\ Cu\ Cl_2$

Properties:

1. It is a green coloured powder ,insoluble in water
2. It is mixture of cupric hydroxide and cupric chloride
3. It is marketed in the form of Wettable Powder containing 88 % COC which is equivalent to 50 % copper.

Lecture: 30 Structure, properties and uses of Carbendazim, Captan, Carboxin and tridemorph .

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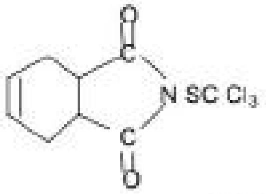
3. CAPTAN



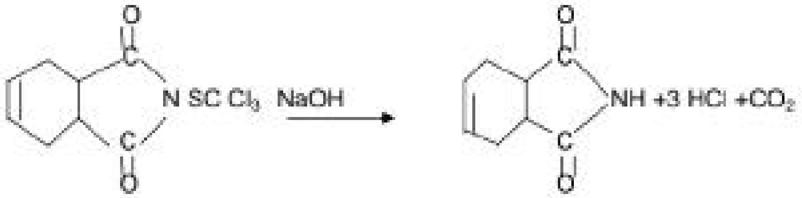
N-Tri chloro methyl thio tetra hydro phthalamide

SC Cl_3 →thio phosogene group responsible for fungicidal action of the compound.

This is a widely used, broad spectrum protective fungicide and used as seed dresser and also for seed disinfection. It is a heterocyclic nitrogenous compound

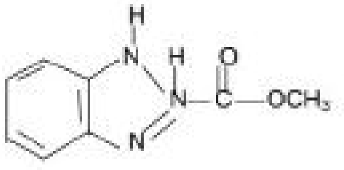
Properties:

1. It is a white crystalline substance, almost odourless.
2. It is insoluble in water (slightly) and most soluble in organic solvents .
3. Capton is hydrolyzed particularly in alkaline medium. That's why it should not be mixed with agricultural chemicals of alkaline nature



4. L.D.$_{50}$ value is 9000 mg /kg or 9 grams per kg body weight .

4. CARBENDAZIM / MBC



Chemical name: 2 methyl benzimidazole Carbamate

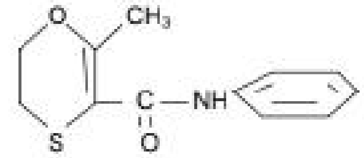
It is a potent broad spectrum, systemic fungicide against powdery mildew and soil borne fungi, but ineffective against phycomycetes.

Properties:

- It is a whitish grey powder with a faint acid odour
- It is insoluble in water, slightly soluble in organic solvents but highly soluble in acetic acid.
- Carbendazim is stable even at 50 ^{0}C for a period of two years. But in alkaline medium it decomposes rapidly.

- The fungi toxicity of Carbendazim is clearly due to benzimidazole nucleus. It exerts its toxicity by inhibiting fungal DNA synthesis or Cell division or nuclear division .The interference with DNA synthesis is probably due to structural similarity with purine bases namely Guanine and Adenine.
- Its L.D.50 Value is 6400 mg /kg body weight.

5. CARBOXIN /VITAVAX

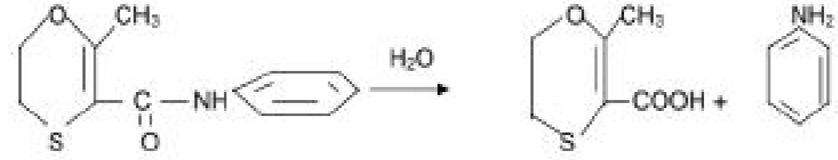


Chemical name: 2,3,dihydro 6 methyl 5 phenyl carbonmyl 1,4,oxathin

It is a very effective systemic fungicide against basidiomycetes which include rust, smut and bunts of cereals .It is also used as seed dresser .It is the most widely used member of oxathin group. The other important member of the group is its sulphon analog i.e., that is oxycarboxin (Plantavax).

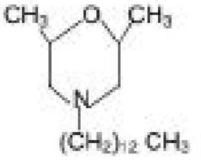
Properties:

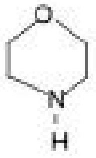
- It is a white crystalline substance with two crystalline forms .One form is melted between 91.50to 92.50 ^{0}C and another is melted between 98 and 100 ^{0}C.
- It is insoluble in water and highly soluble in inorganic solvents.
- It is oxidized in soils plants and water to the corresponding sulphoxide
- On long standing in water Carboxin is converted to corresponding carboxylic acid



- In most susceptible fungi it inhibits the activity of succinate dehydrogenase
- Its L.D.50 value is 3,200 mg/kg body weight

6. TRIDEMORPH/ CALIXIN





Morpholine

Chemical name: 2, 6 dimethyl 4 tridecyl 1,4 morphaline

It is an effective systemic, eradicant fungicide mainly against mildews and ensures long lasting protection. Replacement of tri decyl group at 4th position by a cycic dodecyl group results in the formation of dodemorph, the other important member of this group

Properties:

1. It is faint yellowish liquid
2. It is immiscible with water, but miscible with organic solvents.
3. It is fairly stable compound because of the absence of very reactive functional groups in its structures .It does not degrade even for two years under normal storage
4. It has considerable fish toxicity also
5. It effects the permeability of fungal cell membranes resulting in the leakage of cellular material
6. Its L.D.50 value is 1250 mg /kg body weight.

Lecture: 31 Herbicides –Classification of herbicides based on chemical nature with examples .Selectivity of herbicides briel nt on mode of action of herbicides (Respiration ,mitochondrial activity ,photosynthesis , protein and nucleic acid metabolism

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HERBICIDES

I. Classification of herbicides based on chemical nature

1. Aliphatics : Dalapon , Acrolein , TCA (Tri Chloro Acetic Acid),

   Allyl alcohol

2. Amides and acetamides : Alachlor, Butachlor , Propanil , Diphenamid
3. Arsenicals : MAA(Methane Arsenic Acid),

   DSMA (Disodium Methyl Arsenate)

4. Phenyl acetates and Benzoics : Dicamba, 2,3,6 trichlorobenzoic acid
5. Carbamates : Propham , Swep, Barbam
6. Phenols : Penta chloro phenol (PCP) , Dinoseb
7. Bipyridilliums: Paraquat , Diquat
8. Triazines : Atrazine ,Simazine and Propazine
9. Triazoles : Amitrole, Amitrole – T
10. Diphenyl ethers : Nitrofen , Oxyfluorfen
11. Thiocarbamates : Benthiocarb , Triallate
12. Substituted urea: Manuron ,Diuron , Metaxuron
13. Dinitroanilines : Trifluralin, fluchloralin
14. Nitriles : Bromoxynil , Dichlobenil
15. Pyridazinones: Pyrazon, Oxypyrazon
16. Uracils : Bromacil, Terbacil
17. Phenoxy acids : 2,4-D, 2,4,5-T
18. Miscellaneous : Picloram, Glyphosate
19. Inorganic herbicides: Borax, Sodium chlorate,

    Ammonium sulfamate.

    Mercurous chloride, Ferrus sulphate .

Selectivity of herbicides

Selectivity refers to the ability of a herbicide to kill a target plant in a mixed plant population.

Activity refers to the ability of a herbicide to control a weed. Selectivity of a herbicide play an important role in developing the chemical weed control.

Selectivity is achieved physically, chemically, mechanically, environmentally and metabolically.

Each herbicide has its own physical and chemical properties like water solubility, absorptive force, vapour pressure and polarity which contribute to the selectivity of the herbicide.

Before exerting toxicity to a target plant the chemical should be absorbed and translocated .For example, hydrophilic herbicides because of high surface tension of water molecules, tend to form large spherical droplets which don't readily wet the waxy cuticle of the leaf surface. This results in poor and improper wetting of the foliage and as a consequence, the herbicide activity reduced. In case of lipophilic herbicides they enter the waxy cuticle better than the hydrophilic ones but translocation within the plants is very slow in the water continuum. This in turn plays a crucial role in conferring selectivity and activity. A very important factor of the selectivity of the herbicide is the plant morphology and anatomy. Thus, thin cuticle permits greater absorption of herbicide compared to thick cuticle. Similarly plants with larger size and greater number stomata absorb higher amount of herbicides and make the plants more susceptible.

The most important factor governing the selectivity of herbicides is differential metabolism of a chemical in plants. In tolerant plants , the chemical is inactivated in one or more pathways .In certain plant species , detoxification of the herbicide takes place at a rate slower than that of accumulation resulting in the plant mortality , while in others it is much faster , enabling the plants to be tolerant. Several species of leguminous plants are resistant to the phenoxy butyric acid herbicides because they lack β-oxidases to convert *invivo* to the active phenoxy acid derivatives. Therefore 2,4, DB is a selective post emergence herbicide in legumes .

Mode of action of herbicides

Most of the herbicides act by inhibition of one or more of the following biochemical processes

1. I. Respiration and Mitochondrial Activities
2. II. Photosynthesis
3. III. Protein and Nucleic acid metabolism
4. IV. Synthesis of hydrolytic enzymes

I. Respiration and mitochondrial activities: Mitochondria are cellular organelles responsible for the oxidation of respiratory fuels and conservation of energy emanating thereof in the form of ATP. The process thus involves eth synthesis of ATP from ADP and transport of electrons from the substrate to the molecular oxygen.

Herbicides inhibit these processes by uncoupling the reaction of ATP formation or interference with electron transport and energy transfer. Uncouplers usually act on the membranes of mitichandria where phosphorylation takes place.

Dalapon and Propanil are important herbicides of this category. Dalapon is reported to impair glucose metabolism by interfering glycolysis and Kerb's cycle in susceptible plants. Propanil interferes with the oxidation of malate and succinate in Kerbs cycle and also with electron transport and ATP generation in mitochondria.

Ii.photosynthesis: The events of photosynthesis can be divided into two phases

A. Light phase:

The phase in which light energy is conserved resulting in the formation of NADPH and ATP. Light phase involves the Hill reaction, the usual photosynthetic electron transport system and two photosystem like P.S.I and P.S.II which differ in the distinctive optimum wavelength and the ratio of Chlorophyll a to Chlorophyll b. The photosynthetic electron transport chain has three segments, a short segment from H2O to PS-II , a central chain from P.S-II to P.S.I and the a segment from PS-I to NADP+ .

The reaction involving the evolution of oxygen form H_2O and simultaneous reduction of the electron acceptor as depicted in the following equation is called the Hill reaction

$$H_2O + A \xrightarrow{\text{Light}} AH_2 + \frac{1}{2} O_2$$

Where A is the Hill reagent . In photosynthetic systems , the eventual Hill reagent is NADP+ . Thus

$$NADP^+ + H_2O \xrightarrow{\text{Light}} NADPH + H^+ + \frac{1}{2} O_2$$

The transfer of electrons from H_2O to $NADP^+$ is however not direct and involves a number of intermediaries and both P.S.I and P.S.II.

B. Dark phase:

The phase in which CO_2 is reduced by NADPH and ATP.

A large number of herbicides inhibit photosynthesis principally by inhibiting or blocking or enacting

a) The Hill reaction and the production of oxygen from H_2O in P.S.II Ex Ureas, Uracils, Nitriles and Dphenyl ethers.
b) The transfer or transport of electron in P.S-II Eg. Niriles and Ureas
c) Removal of electrons from the electron transport chain from Ferredoxin in P.S.II eg.Bypyridiliniums.
d) The non-cyclic photopohprylation or ATP synthesis Eg. Ureas , Triazines , Uracils, Nitriles

Iii. Protein and nucleic acid metabolism: The various steps of protein synthesis are i) amino acid activation ii) chain initiation iii) chain elongation iv) termination.

Herbicides like barbam , a carbamate ,inhibits protein synthesis , the degree of inhibition is related to the susceptibility of the species to the herbicide C.D.A.A.(N,N-diallyl -2-chlo acetamide) inhibits the incorporation of exogene aminoacids in protein chain elongation .

Nucleic acids inhibition (both DNA and RNA) is considered to be the primary mechanism of dinitroaniline herbicides like trifluralin and fluchloralin, while diphanamid inhibits RNA synthesis.

iv.Inhibition of the syntheis of hydrolytic enzymes:

During seed germination, enzymes are activated, synthesized and stored insoluble foods degraded, soluble foods translocated, nutrients mobilized and synthetic reaction related to growth take place at a faster pace. One of the major metabolic processes that needs take place during this time at a faster rate is the production of hydrolytic enzymes such as amylases, proteases ,lipases ,phosphatases ,esterases etc., some of these hydrolases are under the control of the gibberellins .Aleurone layers of the cereal grain are the seats of production of these enzymes .During imbibition of the seeds ,embryo supplies the harmone gibberllic acids to the aleurone which then induces the synthesis of polyribosomes , and nucleic acids .An effect of the herbicides on any one or more of these events would lead to the other events as well , consequently effecting the eventual germination of the seed.

A number of pre- emergence herbicides particularly amides and thiocarbamates exert action by inhibition of one or more these events.

LECTURE-32 Structure, properties and uses of 2,4 D, Atrazine ,Butachlor Glyphosate and Benthiocarb

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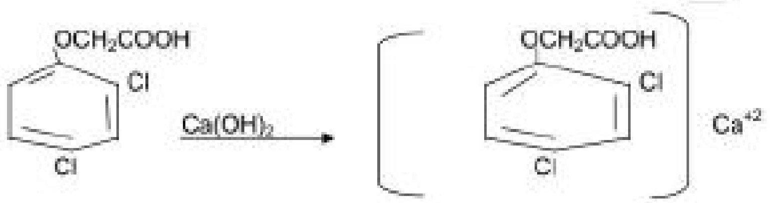
(1) 2, 4-D (2, 4 – Dichlorophenoxy acetic acid)

It is a most important member of the phenoxy acid family and is used for the control of broad leaved dicotyledonous weeds.

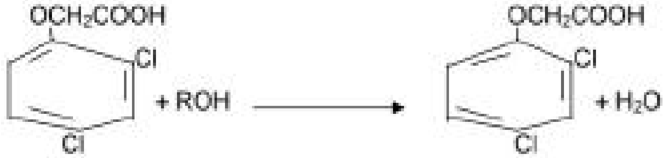
It is a white crystalline substance, insoluble in water but soluble in organic solvents like ethanol and acetone. Technical product emits a characteristic smell of 2,4 dichlorophenol present as an impurity .

With organic and inorganic bases 2, 4 –D forms stable salts .In fact 2,4-D formulated in the form of metal or amine salts .



2,4-D Calcium salt

2,4-D reacts with the alcohols to form esters which are more effective than its salts .



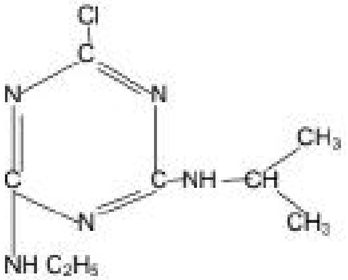
2,4-D ester

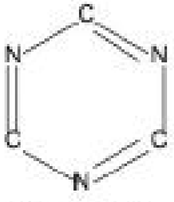
2, 4-D is formulated in the form of its esters also. Practical use is now being made of ethyl, isopropyl, butyl, heptyl and octyl and isocrotyl esters of 2, 4-D for its commercial use.

L.D.$_{50}$ value of 2,4-D for experimental animals is in the range of 375 to 1000 mg /kg body weight (oral) .It is thus a compound of medium toxicity to mammals .

2. ATRAZINE

It is selective pre –emergence herbicide for the control of grass and broad leaved weeds in maize, sorghum, sugarcane, pine apple and orchards and also as a non-selective herbicide along the railway tracks.





Triazine ring

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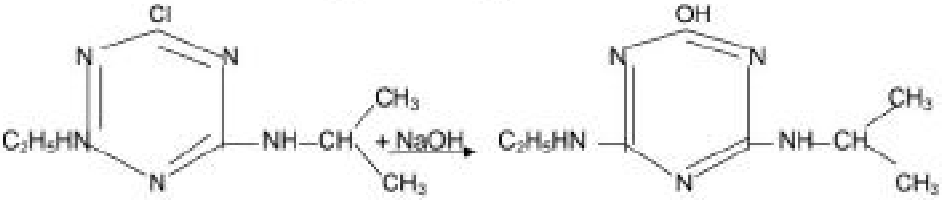
Chemical name:

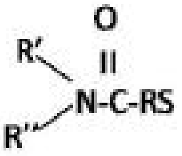
Atrazine is 2-chloro- 4 – (ethylamino) -6 -(isopropylamino) –S- triazine

1. It is a white crystalline substance .It is almost insoluble in water.
2. when boiled with NaOH , the chlorine at 2nd position is split of f resulting in the formation of 2- hydroxyl – 4- (ethyl amino) 6- (isopropyl amino) – S triazine which does not have any herbicidal properties .

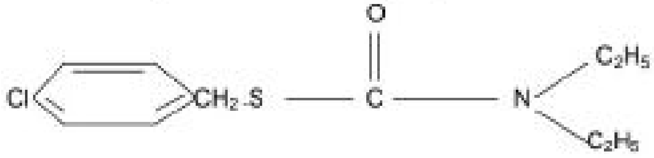


3. It is a highly persistent herbicide
4. It is very safe compound for mammals and L.D.50 value for rats is 3000 mg /kg body weight.

4. BENTHIOCARB/BENDIOCARB/THIOBENCARB



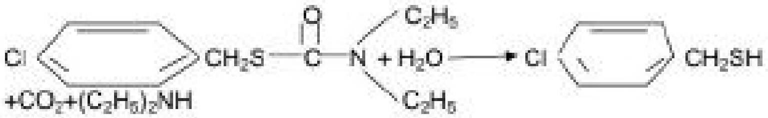
it belongs to thiocarbamates groups and derivatives of thiocarbamic acid.



Chemical name: S-(4-chlorobenzyl) N, N- diethyl thiocarbamate.

Benthiocarb is very popular for the control of broad d leaf and aquatic weeds in rice .

It is a white crystalline substance . The low water solubility compels its use either in suspension or emulsions. It is moderately persistent in soil. In true solution it is rapidly hydrolysed under alkaline medium to produce 4- chlorobenzyl mercaptan and diethyl amine among others.

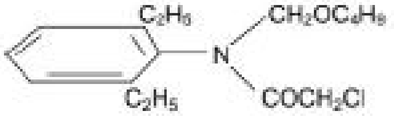


It is moderately volatile and its entry to the underground shoot tissues of the plant mainly through vapour phase .Its L.D.50 value for experimental animals is between 2200 to 3100 mg /kg body weight.

BUTACHLOR

Belongs to amides/ acetamides/ anilides

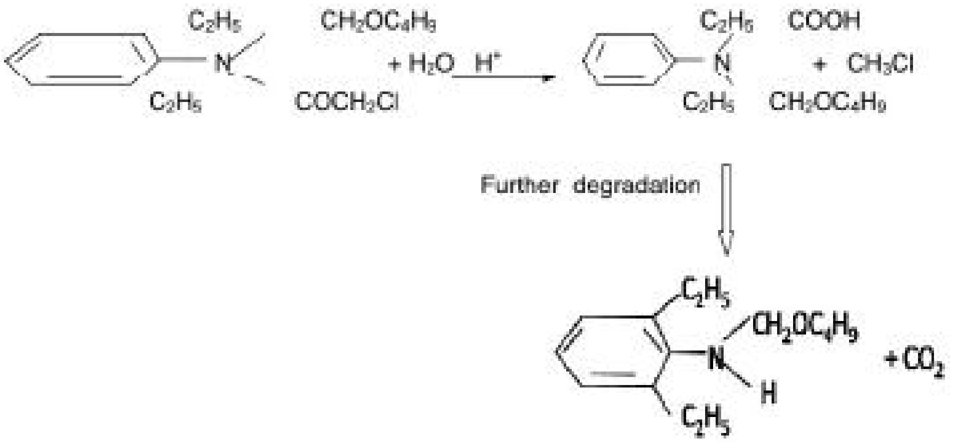
acetanilide



Chemical name: N-(butoxy methyl) -2-chloro- 2 , 6 - diethyl acetanilide .

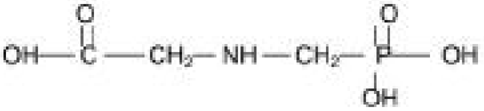
1. Butachlor is used extensively in India in the form of granules in rice as a post emergence herbicide.
2. Butachlor resembles alachlor another promising herbicide of this group, which has $-CH_2OCH_3$ instead of $-CH_2OC_4H_9$
3. It is a white crystalline substance, it is insoluble in water but soluble in aromatic solvents .

4. Amide linkage is very prone to cleavage and in acidic medium , it is broken to produce the corresponding carboxylic acid and the aliphatic chloride .



5. Crop species resistant to Butachlor, the compound is presumably detoxified by this pathway. Other detoxification pathways too operate simultaneously.
6. Butachlor is practically non-toxic for mammals. L.D.50 Value for experimental animals is more than 5,500 mg/kg body weight

GLYPHOSATE



$$\mathrm{OH-\overset{\overset{O}{\|}}{C}-CH_2-NH-CH_2-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-OH}$$

N-Phosphomethyl glycine

Properties :

- The herbicidal activity of glyphosate was discovered in 1971 and introduced as an isopropyl ammonium salt by Monsanto.
- Glyphosate is a broad spectrum selective post emergence herbicide used for effective control of rhizomatous and deep rooted perennial weeds.
- The susceptible plants are show growth inhibition with in 4-7 days of application followed by general foliar chlorosis and necrosis .
- Extensively used in plantation crop such as tea ,coffee ,rubber , oil palm etc., orchard crops , vine yards , pine apple sugarcane and in non-cropped areas such as banks of irrigation channels ,derange ditches, road sides and industrial and recreation.

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Dharmendra Kumar

[redacted]

UNIT-1.2

CHEMISTRY OF FRUITS AND VEGETABLES

Generally, the fruits and vegetables are made up of the following constituents. H_2O, CHO, fat and lipids, proteins, Amino acids, vitamins, minerals, viz.,P, K, Ca, Mg, Fe, organic acids, pectins, pectic enzymes, tannins, pigments, odorous compounds.

Water

It is the major constituent i.e. 75-95% in fresh fruits and vegetable. It is also present in leaves, stalk (or) stem and ranges from 70-80%. As the plants attain maturity, the water content gets reduced. The moisture content varies at the stage of crop growth, variety of crop, irrigation schedule and harvesting time.

CHO

They are sugars (or) polyhydroxy aldehyde (or) ketones. Fruits will have generally monosaccharide. The pentoses will be more in apple, guava, lime, grapes.

Disaccharide in non-reducing sugars such as sucrose, lactose and maltose

Triasccharide - Ramnose

Polysaccharide – Starch.

The sweetness of the fruit is decided by the type and quantity of sugars present in the fruit. It varies for e.g.

Sucrose – 100%
Glucose – 75%
Fructose - 173%
Maltose - 72%
Lactose - 16%

Total sugars in riped fruits (in %)

Apple	6 –17	Guava	3-10
Banana	11-12	Grapes	2-19
Mango	14	Pineapples	8-18
Orange	4-12	Lime and lemon	1-14
Papaya	9	Tomato	2-4

Reducing and non-reducing sugars in fruits (%)

Fruit	Reducing	non-reducing
Apple	6-11	1-7
Mango	3-5	7-8
Papaya	7	<1
Orange	3-6	2-5
Lime	1-3	<1

Types of sugars in fruits (%)

Fruits	Glucose	Fructose	Sucrose
Apple	1.6	6.1	3.6
Banana	5.8	7.0	-
Grapes	8.0	8.0	-
Orange	2.4	2.4	5.0
Lime	<1	<1	<1
Pineapple	2.3	1.4	8.0
Tomato	1.6	1.2	-
Pomegranate	5.5	6.1	-

Classification of CHO: Sugars

Monosaccharide – e.g. Glucose and Fructose. In some cases it is equal, glucose is > fructose and in some cases fructose is > Glucose. Sometimes arabinose will also be higher.

Disaccharides –e.g. Sucrose – more in sugarcane

Sugar derivatives contain the sugar acids and the polyhydroxy alcohols.

Sugar acids:

i. Saccharic acid

ii. Mucic acid

iii. Gelacturonic acid

iv. Gluconic acid

v. Glucoronic acid

Polyhydroxy alcohol

i. Sorbitol

ii. Glycerol.

II. Structural CHO

It contains many polysaccharides such as the galacton and Arabinon. They are the polysaccharides (i.e. homo and hetero) are the cellulose, hemicellulose and the gumes. Arabinose, xylon.

III. Pectic substances are groups of compounds comprising pectin, protopectin and pectic acid.

IV. Protopectin

Organic acids are the important constituents responsible for the taste and flavour of the fruits.

Different types are:

I. Aliphatic volatile acids.

i. Formic acid

ii. Acetic acid

iii. Butyric acid

II. Aliphatic mono carboxylic acids

i. Alcoholic acids

Glycolic acid

Lactic acid

Glyceric acid

2. Aldehydric acid

Glyoxalic acid

3. Ketonic acid

Pynuric acid

Oxaloacetic acid

III. Aliphatic dicarboxylic acid

1. Oxalic acid – present in banana

2. Succinic acid – all fruits

3. Maleic acid – apple, grapes

4. Fumaric acid – green apples

5. Tartaric acid – Tamarind, grapes

iv. Tricarboxylic acid

Citric acid

Isocitric acid

Cisaconitic acid

v. Aromatic acid

Benzoic acid

Salicylic acid

Coumaric acid

Quinic acid

Skimic acid

V. Amino acids:

All the fruits : Glutanic acid, Aspartic acid

Apple : Aspartic, glutamic, β alanine

Banana : Aspartic, glutamic, hystidine

Tomato : Glutamic, Tryptophan

VI. Protein content in different fruits (%)

Generally it is very low in fruits. It varies with species of crop, season, cultural practices followed by the influence of environmental factors.

Apple	**0.2**	**Mango**	**<1**
Banana	**1.1**	**Pineapple**	**<1**
Grapes	**1.3**		
Tomato	**1.2**		
Guava	**0.8**		
Avocado	**2.1**		
Dates	**2.2**		

VII. Enzymes

Role: It helps in ripening

Pectinase → act on pectin and covert them into methyl alcohol and poly galacturonic acid.

Cellulase → act on cellulose and convert them into methyl alcohol and simple proteins. This reaction is responsible for softening while ripening.

Amylases → act on starch, maltose and convert then into simple sugars

Phosphorylases → act on starch and maltose and convert them into phosphorylated sugars.

Invertase → Inversion of sugar

Lipases → act on fats.

Peroxidases → Involves in the oxidation and reduction

Phenolases → Acts on phenolic compounds

Proteases → act on proteins.

VIII. Fruit lipid

Fruit lipid contains very high amount of fat. e.g. Butter fruit – Avocado → 60% fat. Besides this, soybean contains 16%, potato 5%, Lipids gets converted to protein as oligoproteins.

IX. Volatile compounds

Characteristic odour of any fruits is due to the volatile compounds.. They will less than 100 ppm in concentration but they are esters, alcohols, aldehydes and ketones. Presence of these compounds will give characteristic smell.

Apple – Ethyl 2 methyl butyrate

Grapes – Methyl anthranilate

Banana – Amyl acetate and isopentyl acetate

Grape fruit – Terpenes

Lemon – Hydrocarbon containing isoprene

Orange – limonine

X. Fruit phenolic compounds

These are responsible for colour, flavour and taste. These phenolic compounds give both desirable and undesirable qualities. The fruit phenolic compounds include flavonoids and the cinnamic acids. The major flavonoids are the anthocyanins, the leucoanthocyanins, the flavonols, flavones. The presence of these phenolic compounds in fruits gives an astringent taste.

XI. Fruit pigment

Pigments give colour such as carotenoids, chlorophylls, anthocyanin and anthoxanthin. The yellow, orange and red colour of the mango, papaya, tomato, carrot, peach, apricot and red pepper is mainly due to the presence of carotenoids. Carotenoids contain hydroxy groups called as Xanthophylls. This is the specific colour of yellow maize, papaya, mandarin orange. Carotenoids are water insoluble but some are fat soluble. Flavonoids are widely distributed in plants and are water solublr and they consist anthocyanin which gives red, blue, purple colour to the fruits. Anthoxanthins are responsible for yellow colouration.

XII. Vitamin

Yellow coloured fruits generally contain vitamin A. e.g. Papaya, Mango. Vitamin C- Citrus fruits and high in west Indian cherries. Guava – 200 mg/100 g, Banana – 10-30 mg/100 g, Melon fruits - 23-35 mg/100 g, Orange – 50 mg, Apple – 2-10 mg, Tomato – 25 mg, West Indian cherry – 500 – 1000 mg/100 g.

Besides A and C some fruit contains β-carotein → the precursor of vitamin A. Some fruit contains Nicotinic acid, folic acid and thiamine.

Mango – Vitamin A-total soluble solids – 20-26%.

Pulp ratio – 60%, reducing sugars – 9.8%, Non. Reducing sugars –7.4%

Carotenoids – 1675-11,536 mg/100 g

Among mangoes, Alfonso contains more carotenoids.

Vitamin A – 10-36%, Acidity – 0.15 – 29%

Different stages of maturity

Juvenile stage – up to 21 days – only cellulose materials are present.

Adolescent stage – 21-49 days – development of aroma takes place and CHO content gets increased.

Climactaric stage – Climataric fruits, respiration takes place even after the harvest. e.g. Mango, Papaya, Banana.

Non-climataric – Respiration will be less after harvest. eg. Apple, grapes, Date.

Climataric stage – 49-77 days. In this the sucrose content gets accumulated.

Finally the Senescence stage – more than 77 days decrease in glucose and sucrose content.

Banana

Total soluble salts– 17-21%, total sugars – 16-25%, acidity – 0.1-0.2%

Stages:

Inflorescence stage – up to 130 days, young inflorescence contains N up to 80% and important amino acids are alanine and arginine. After 130 days the amino acids content gets reduced. 75% of soluble N is Aspergin, glutamin, hystidine. Dry matter production takes palace in 80-100 days period. Dry matter will be around 25%. Starch gets accumulated after 100th day. Hydrolysis of starch is taking place up to 130 days and after that gets converted to glucose, fructose and sucrose. Generally the acidity gets reduced as the fruits get ripened. Insoluble pectin gets decreased after 100 days. Then the soluble pectin gets decreased. As the fruit gets ripened, chlorophyll gets disappeared and the yellow pigment dominates.

Apple : TSS -> 16-17%, glucose 1.7%, Fructose –6.1%, Sucrose – 3.6%
Among amino acids dominant ones are Aspargin, Aspartic acid, Glutamic acids and B-alanine. Protein content is very low 0.2%. Important organic acids present are maleic acid, however the green apple contains more of fumaric acid. Sugars - more glucose and fructose are present.

PAPAYA :

Solo variety – More of vitamin A. More cheap and more nutritious. It is poor man's apple.

Immature papaya fruit will have more of milky latex which has papain very much used in pharmaceutical industries and also used by hotels for making meat softer. It is also used in tanning industry – juice, pulp. It has contain Fe-17 mg/100 g, Ca – 0.5/100 g, carotein 666 mg/100 g, vitamin 57 mg/100g.

Papaya seed contains one toxic principle called carpin. It contains some aromatic compounds such as Ethyl butyrate and ethyl acetate, methyl butyrate and methyl acetate.

Guava

It contains more moisture 76-88%, acidity 0.2-0.6% CHO – 8.1 –14.5%, Vitamin C 38-300 mg/100 g, carotein – in unriped fruit –150 mg/100g in case of riped fruit – 480 mg/100 g. Fat content – 0.2%, fruit fiber – 0.7%, volatile compounds – butyl and ethyl alcohols and Protein 0.6-2%

In premature stage – contain more fructose and glucose upto 5% and later stages it gets reduced to 0.2%.

Grapes

Grape is a non-climataric fruit that is why harvesting is done when the berries are fully riped.

Paneer, musket, seedless, Thomson, Anab E sahi

CHO = glucose and fructose ranges 200 g/l of Juice.

In unriped fruit the glucose content is less than 8.5%. It contains the pentoses (Arabinose and xylose). The organic acid present in grapes is maleic acid which influences the taste and flavour. Industrial use of grapes:- used in wine industry, juice industry, dried grapes.

Anthocyanin and Tannins are responsible for specific colour such as red vine and white vine. The compounds which give aroma for grapes and wines are Terpenes and Terpenols. The berry of the fruit contains more of free terpenols and bound state of terpenols.

Following are the signs for ripening of fruit :

1. Formation of the waxy layer on the skin of berries
2. They become soft
3. Slight change in colour and browning of cluster stem
4. Berries are easily detached from the stem on pulling.
5. Seeds are loosely attached with the pulp and also become brown in colour.

6. On taste berries are sweet.

7. Juice of berries becomes thick and the refractometer reading shows 18-20.

8. Grapes are harvested by cutting.

9. Yield of grapes varies much due to variety, system of training or pruning, climatic condition, soil type, age of wines and also the cultural practices. A well maintained grape vine is productive for number of years.

Citrus: vitamin C

i. It is non-climataric especially the sweet oranges fail to ripen after they are harvested. When the fruits approach maturity, the skin colour changes from dark to light green then to yellowish. However, the colour change is not reliable criteria; the ripening is decided with TSS, acidity content, TSS-acidity ratio. TSS-acidity ratio is important factor. It gives an idea about the quality of juice and flavour. Fruits should be harvested before they attain over maturity. Sugar content: 0.9 – 3.4%.

The yield varies with the climatic conditions, soil types, varieties and age of plant, pests and diseases, management practices.

Amino acid: Aspartic – glutamic.

Sapota

Cricket ball, PKM, Co

It's climataric fruit which will ripe even after the harvest. The maturity of sapota is judged by following points.

1. **The fruit changes to dull orange (or) potato colour.**
2. **On scratching the fruit it shows a yellow streak but it will be green if the fruit is not matured.**
3. **The skin becomes smooth, free from brown scales.**
4. **The content of the milky latex is reduced then it becomes watery.**
5. **Spine like stigma, at the tip of the fruit drops off, when it attains maturity.**

6. Harvesting is done by twisting the fruit.
7. Up to 30 years gives yield 2000-3000 fruits from a ripened tree.
8. Quality and yield is decided by climate, soil type, cultural practices, age and variety.

Pomegranate

It is non climataric. It starts bearing fruits from 4th year and cultivated upto 30 years.

Pomegranate fruit development and maturity shows the CO_2 evolution from the fruit has been low and non climataric peak (or) measurable ethylene was detected during the maturities. The pomegranate fruit is ready for harvest in 5-7 months. Matured fruits will be yellowish in colour and turns pink and finally red in colour. On tapping it gives a metallic sound, and then it is fully ripened. Yield goes up to 30 years.

CHEMISTRY OF VEGETABLES

Importance of vegetables

i. They play a major role in human nutrition. They acts as a substitute for nutrients

ii. They are important for neutralizing acidity during digestion. They also serve as roughage in human nutrition and thus help in proper digestion

iii. Important source of minerals like Ca, P, Fe, Mg

iv. Important source of vitamins A and C

v. The green and yellow vegetables like carrot, turnip, beans contains appreciable quantities of vitamin A. Dried seeds of beans and peas and legumes contain proteins. Besides vitamin C, the vegetables also have the thiamine, niacin and folic acid. The tomatoes and potatoes contains fairly high amount of vitamin C. The factors that affect the composition of vegetables

i. Genetic variations

ii. Fertilizer and mature application

iii. Soil condition

iv. Climate

v. Cultural

vi. Stage of maturity

vii. Changes that takes place during processing

viii. Changes that takes place during storage

Daily requirement of vegetables for human consumption: 300 g/day person

Crude fiber content:

Cauliflower	**0.74 –1.74**
Chillies and Capsicum	**17.0 – 18%**
Potato and cucumber	**0.2 - 0.67%**
Bhendi	**7.0 - 18%**

CHO:

Tomato	**3-5%**
Carrot	**3-7%**
Cauliflower	**1-4%**
Brinjal	**5-6%**
Cucumber	**2-3%**
Radish	**1-2%**

Reducing sugars:

Tomato	**1-4%**
Potato	**0.2-2.1%**
Brinjal	**0.6-2.0%**
Onion	**2-3%**
Cauliflower	**2.2-4%**

Crude protein:

Peas	**6-8%**
Brinjal	**0.6-2.2%**
Tomato	**0.8-2.7%**

Cauliflower	1.6-2.9%
Radish	0.73-1.3%

Ascorbic acid content (mg/100g):

Peas	30-104
Cauliflower	48-98
Bhendi	9-16
Tomato	25-100
Onion	6-10

β - carotene (mg/100g):

Carrot	0.4-8.5
Cucumber	9-25
Tomato	1.25-1.61

Acidity:

Tomato	0.5-1.6%

Pungency:

Brinjal – Glycoalkaloid is pungent material – 0.5-5 mg/100 g

Chillies – Capsaicin is pungent material – 0.15-0.95%

Onion – Allyldisulphide 13-62 mg/100g

Colouring matter:

Anthocyanin pigment – Brinjal – Violet colour – 0.07-0.75 iu/100 g

Oleoresin – in chillies – 30 – 112 iu /100 g

Capxanthin, Zea cryptoxanthin, β - carotene

Tomato – lycopene red colour	2-5 mg/100 g
Starch in potato	6-10%
Peas	3-12%
Sweet potato – pectic substances	4-7%

Alcohol insoluble solids:

Potato	15-17%

Phenolic compounds:

Potato	**16-24 mg/100g**
Onion	**1-3**
Brinjal	**44-138**
Carrot	**44-86**

Change of colour in fruits is due to

Polyphenol oxidase which is responsible for the change of colour to brown (or) discoloration of the harvested fruits.

In brinjal 2-46 units of protein of Polyphenol oxidase is present In chillies 210-2430 of protein very high.

Ash content:

Carrot	**0.22-0.81%**
Brinjal	**0.38-0.6%**

Brinjal : *Solanum melongena*

It is a good source Ca, P, Fe, Vit B. It consists of 14-19% protein with very high biological values and digestibility coefficient. However, proteins are very low in lysine, Tryptophan, methionine and isoleusine.

Sugars present in brinjal are glucose, fructose and sucrose. It contains vitamin C ranging from 4-12 mg/100 g. It goes as high as 24 mg/100 g. The pigment of brinjal is anthocyanin – otherwise called as nasunin. It also contains the other pigment, lycoxanthin. The bitter principles present in leaves of brinjal are solasodins which is an alkaloid. The edible portion of fruit contains 11% of pectin. It also contains some phenolic compounds such as chlorogenic and neochlorogenic acid.

Enzymes present are polyphenolases which are capable of oxidizing anthocyanin pigment and others are capable of oxidizing chlorogenic acid present in brinjal.

Potato – Solanum tuberosum

Starch content is as high as 65-80% on dry weight basis. Important sugars present are glucose, fructose and sucrose. The non-starch material polysaccharide of the tuber includes cellulose, hemicellulose and pectic substances – 1.8-3.3% on dry weight basis. Pectic substances contain anhydrogalacturonic acid. It also contains polysaccharides like Ramnose, xylose and galactose. The pectic substance includes cold water soluble and hot water soluble and ammonium citrate and ammonium oxalate soluble fractions.

The N content varies from 1.2-2.0% on dry weight basis of the total N, half is present on the form of protein and the N consist free amino acids, oxides, and nitrogenous bases. The important protein of potato is globulin, then this globulin consists two fractions of protein namely tuberin and another is globulin II. The tuberin constitutes 76% of the total protein and globulin II is 1.4% only. The other proteins such as albumin, glutenin and prolamine amounts about 4%, 5% and 1.8% respectively.

The biological value of potato protein is 68% and this protein has low amount of S containing amino acids but however they are rich in lysine. The enzymes present in potato are Phosphorylases and α and β amylases, phosphatases. The vitamins present in potato are vitamin A and vitamin c in larger amounts but in smaller amounts it also contains riboflavin, thiamine and nicotinic acid. Fat content is very low 0.1% on fresh weight basis organic acids present are citric and maleic acid. Among the phenolic compounds the chlorogenic acid and also the tyrosine are common substances present in potato. Tannins, quinones are present in potato skin and they give the particular colour to the potato skin. e.g.,Kuprijothi – variety. Important alkaloid in potato is solanine → Steroidal Glycoalkaloid. It contains so many fractionsα, β and r solanine and also α, β and r choconine. But all these alkaloids get last during boiling. Volatile

compounds present in potato are amyl alcohol, it also includes, H2S, acetaldehyde, methanol, acetone, ethanol, dim ethyl Sulphides.

Bhendi:

These bhendi fruits are very rich in pectin and mucilage compounds. The fruits are rich in Ca and Fe. It also contains a flavanoid compound. Fruits are rich in vitamin A. C and also contains thiamine and riboflavin to some extent also niacin. The seed cake contains large quantity of protein and used as animal feed. Bhendi flower contains flavanol pigments are Goss pectin and Quercetin. It's rich in fiber content.

Tomato

It is an important vegetable grown in Tamil Nadu, Andhra Pradesh, Karnataka. PKM. is important variety. Colors are due to presence of lycopene. It also contains alkaloid → Tomatine. It will be 130-150 mg/100 g. Tomato is commonly called as poor mans apple

It contains	H_2O	94%
	Protein	1%
	Fiber	0.6%
	Fat	0.3%
	CHO	4%

It has minerals viz., Na – 3 mg, Mg – 11 mg, Cu – 0.1 mg, Cl – 51 mg
K – 268 mg ,S – 11 mg, Mn – 0.19 mg, Ca – 11 mg, Fe – 0.6 mg,
P – 27 mg

Vitamins:

Vitamin A	1100 (IU)
Vitamin B	0.2 mg
Vitamin C	23 mg
Vitamin E	0.27 mg

Nicotinic acid	**0.6 mg**

It also contains biotin, maleic acid, citric acid, oxalic acid, sugar content – 1.85 – 4.27%, Acidity – 4.2-10.2 mg/100 ml. Ascorbic acid 21-22.5 mg/100 g. It is also a chief source (or) alternative source for citrus fruits in case of vitamin C. It is commonly used as salad vegetable. Tomato Soup, Ketchup, pickles etc.

Cole crops:

Crops grown in hilly areas and needs cool temperature

Cabbage – Brassica oleracea var. capitata

Chemical compounds: for 100 g of fresh cabbage

Water		**92.1 g/100 g of fresh cabbage.**
Protein		**1.4 g**
Total fat		**2 g**
Total CHO		**5.7 g**
Fiber		**1.5 g**
Vitamin A		**70 IU**
Vitamin B, and B2		**0.04 mg**
Vitamin B6		**0.11 mg**
Vitamin C		**46 mg**
Minerals	**P**	**28 mg**
	Ca	**46 mg**
	K	**227 mg**
	Na	**30 mg**

Cauliflower:

Composition / 100 g of cauliflower

Water	**91.75 g**	**Vitamin A**	**40 IU**
Energy	**31 cal**	**Ascorbic acid**	**70 mg**
Protein	**2.4 g**	**Thiamine**	**0.2 mg**
Ca	**22 mg**	**Riboflavin**	**0.1 mg**

Niacin	**0.57 mg**

Cauliflower was cut into pieces and dried and stored and used in off seasons.

Radish:

Nutritive value / 100 g of modified roots

Moisture	**94.4%**	**Fiber**	**0.8 g**	**Fe**	**0.4 mg**
Protein	**0.7 g**	**CHO**	**3.48 g**	**Na**	**33 mg**
Fat	**0.1 g**	**Ca**	**50 mg**	**K**	**138 mg**
Minerals	**0.6 g**	**P**	**22 mg**		
Vitamin A	**5.1 IU**	**Oxalic acid**	**9 mg**		
Riboflavin	**0.02 mg**	**Calories**	**17 units**		
Vitamin C	**15 mg**				

Radish leaves: chemical composition

Water	**89.1%**	**Fat**	**0.6%**	**Fe**	**0.8 mg**	**Ca**	**0.31%**
Protein	**3.9%**	**P**	**0.06%**	**CHO**	**4.1%**	**Vitamin A**	**81 IU**
Riboflavin	**2.7 mg**	**Vitamin B**	**21 mg**	**Vitamin E**	**21 mg**		
Nictoinic acid	**2.4 mg**						

Moringa:

Oil extracted from dried moringa seeds will have high lubrication value. Besides the leaf protein it also contains many amino acids. Amino acids are expressed in terms of mg/100 g of N.

Chemical compounds of Moringa (composition/100 g)

Particulars	Drumstick	Leaves
Moisture (%)	87	76
Protein (g)	2.5	7.6
Fat (g)	0.1	0.7
CHO (g)	3.7	12.5

Energy K. cal	**26**	**92**
Ca + Mg (mg)	**30**	**440**
P (mg)	**100**	**70**
Fe (mg)	**5.3**	**7**
Carotene (mg)	**110**	**6780**
Thiamine (mg)	**0.05**	**0.06**
Riboflavin (mg)	**0.07**	**0.05**
Niacin (mg)	**0.2**	**0.8**

Amino acids:

Arginine	**6**	**Leusine**	**9.3**
Hystidine	**2.1**	**Isoleusine**	**6.3**
Glycine	**4.3**	**Valine**	**7.1**
Tryptophan	**1.9**	**Phenylalanine**	**6.4**
Methionine	**2**	**Threonine**	**4.9**

Uses: Both drumstick and leaves are used for cooking

Seed oil:

More valuable As lubricant → Watches, Aero plane parts and aromatic industries

Seed: Sedimentation/ coagulating agent. Purification of water (Pollution)

Seed contains following compounds

Moisture	**4**
Oxide protein	**38.4**
Fatty acid	**34.7%**
NFE	**16.4%**
Fiber	**3.5%**
Mineral matter	**3.2%**

Vitamins in vegetables

Vegetable	Vitamin A (IU)	Thiamine	Riboflavin	Nicotinic acid	Vitamin C
Brinjal	124	0.04	0.2	0.04	12
Tomato	320	0.07	0.1	0.4	31
Radish	5	0.06	0.02	0.5	15
Bhendi	88	0.07	0.1	0.6	31
Beans	221	0.08	0.06	0.3	11
Cabbage, cauliflower and carrot	2000	0.1-0.5	0.01-0.1	0.4 – 1.0	1-124
Turnip (greens)	9540	trace	trace	Trace	130

Minerals in vegetables

P – 0.3-0.7%, K = 1-4%, S-0.4%, Ca – 0.5-2%, Mg – 0.1-0.5%, Fe, Mn, Cu, Zn – 50-500 ppm

SPICES AND CONDIMENTS

Commonly used are ginger, turmeric, cardamom, coriander, chillies, pepper, clove, nutmeg, cinnamon, vanilla, cumin seeds.

Pungency is given by alkaloids such as S- compounds called allyltrisulphide – It is present in Onion, Garlic contains – Allyl sulphide

Ginger

It is a modified underground stem. It is commonly used as a spicy material. It contains stain volatile oils, pungent compounds, proteins, cellulose, starch, sugars, minerals and resin compounds.

Starch content varies from 40-60% in a rhizome on dry weight basis. It contains non-volatile pungent oil called as gingerol and this gingerol is obtained by the solvent extraction.

This gingerol is composed of a series of homologous compounds and these are all the condensation products called as gingerone which contains

the straight chain aldehydes. In ginger the aroma and flavour are determined by the presence of volatile oils. The main volatile compound is sesquiterpene hydrocarbon. It also contains the monoterpene hydrocarbons. It also contains the oxygenated monoterpenes. The particular odour of ginger is due to these hydrocarbons. It also contains gingiberene which is commonly present in turmeric.

Colouring pigment in turmeric is curcumin.

Desmethoxv curcumin	24%
Bixethoxy curcumin	15%

Coriander

It acts as flavour, increasing taste, a medicinal value material; dried and ripe seed of coriander contains most steam volatile oils, protein cellulose, pentasons, tannins, calcium oxalate and also other mineral.

Fiber 23-36%, CHO 20%, Fatty oils 16-28%,
Protein 11-17%.

Among the fatty acids, the saponifiable fractions of fatty acids amounts for 90%, among this, the important acid is oxtadecinoic acid.

The major constituent of spicy oil is coriandrol. It is an optically active form of monoterpene alcohol which is called as linalal.

Pepper

Pepper berries contains the steam volatile oil, fixed fatty oils, alkaloids, resins, proteins, cellulose, pentasons, starch and the minerals.

Maximum oil content of dried pepper is 3.8%, this value will be always more for the black pepper than white pepper. The pungent of black pepper is due to alkaloid called as "Piperin". Piperin content ranges from 4-10%.

The fatty oil presence varies from 2-9%, piperin contains almost 95% of total pungent alkaloid present in the pepper. The aroma and the flavour are due to stem volatile oil which comprises more of monoterpene

hydrocarbons. The pepper contains spicy oil called deoresin. The oleoresin is nothing but a spicy oil containing aromatic and pigments. It contains natural antioxidant which enhances the keeping quality.

Composition of pepper: oleoresin Volatile oil content – 15-25 ml/100g, Refractive index at 20°C – 1.45790 – 14890.

The total N content is around 55%, in the form of piperin.

Uses

It reduces fat accumulation in blood veins.

Chillies

It's used as both vegetable and spices. The chilli fruits contain fixed fatty oil, steam volatile oils, pigments, the pungent principles, resins, proteins, cellulose, pentasons, and the minerals. Chilli fruits contains significant amount of quantity of vitamins B, C, E and A → Carotene, when it is present is fresh vegetable. Vitamin C – 340 mg/100 g is fairly high. Pungency is due to "Capsaicin". The Colouring matter of ripened fruit are due to the presence of "Capsanthin". Then the Zeasanthin, glutenin, cryposanthin, α and β-carotene, the dry chillies also contains xanthophylls, the fixed oil in the chilli fruit varies from 9-20%. Then it will have low volatile oil content which ranges 1-2%.

Comp of spices and condiments (%)

Name	Oleoresin	Vol. acid	Active principle (%)
Pepper	10-12	19-35	Piperin 40-60
Chillies	12-16	-	Capsaicin 1-4
Ginger	15-7	25-38	Gingerol 20-30
Turmeric	6-7	18-25	Curcumin 30-47
Cardamom	-	4-5	-
Cinnamon	-	-	Cinnamic aldehyde
Clove	-	70-90	Eugerol
Cumin	-	2.5-4.5	Cumaldehyde
Fenugreek	-	0.2	Trigonelline, Choline

Coriander	-	0.5-2.0	Coriandrinol
Vanilla	-	1.2-2.5	Vanillin
Onion	-	-	Allyl disulphide
Garlic	-	-	Allylsulphide, Allyl trisulphide

Narcotics and Beverages

Narcotics → Substances that produces drowsiness

Crop – Tobacco

i. Chewing type

ii. Flue red Virginia tobacco.

Plant parts → leaves, stems and roots

Alkaloids present in Nicotine are Nicotine, Nor-Nicotine, Anabasin.

Smoking qualities of Virginia tobacco regimes, following contents

Nicotine	0.5-1.7
Sugar	0.8-0.9
K	3-4%
Cl	0.25-0.29%

The smoking qualities are also assessed by the following ratio of contents

ratio of total N

ratio of Soluble N

ratio of total ash

ratio of water soluble ash

Beverages

2 types

i. Used for chewing: eg. Betel vine, Areca nut, Cocoa

2. Used for drinks: e.g. Tea, Coffee

Betel vine

Oxygenated compounds in betel vine

1. Methyl chevicol	**0.81%**
2. Terphenol	**0.76%**
3. Cincole	**0.68%**
4. Anethole	**0.63%**

Betel vine → the pleasant aromatic flavour is due to the presence of Terpene compounds. Oil content in leaves varies from 0.11 – 0.15, phenol content in leaf – 2.5-8.4%.

Arecanut

Alkaloids : 1. Arecoline (0.12-0.14%)
2. Arecaidine
3. Arecolidine
4. Guvacine

Cocoa

It has highest fat content: 56-58%. It also contains free fatty acids <1% and some chocolate flavour.

Coffee

Colour – due to presence of chlorogenic acid. Alkaloids → Caffeine, Trigonelline.

Ingredients	Green coffee	Roasted coffee
Moisture	**10-12**	**-**
CHO	**60**	**53**
Reducing sugar	**1**	**-**
Sucrose	**7**	**-**
Pectin	**2**	**-**
Hemicellulose	**15**	**13**

Fiber	**20**	**22**
Oils	**13**	**15**
Protein	**1.2**	**1.2-1.3**
Ash	**4**	**4**
Chlorogenic acid	**7**	**4.5**
Trigonelline	**1**	**1**
Caffeine	**1**	**1.2**

Colour of coffee sometimes changes to bluish green and this is due to the presence of oxidative product of chlorogenic acid. The aroma of coffee is due to the presence of sulphur compounds and also due to pyrazines.

Tea

The tender leaves are used. There are two types of tea, green dust and green powder. The major constituent of tea is

Thiamine → It is glutamyl ethyl amyl.

Tea also contains caffeine → 2.5-4.5%, Tannins – 2.4%

Amino acid – 2.1%. Amadora → Combination of amino acids and sugars in green leaves. Taste of tea flavour is due to presence of catechins.

There are 3 different types of catechins

i. L. epicatechins

ii. L. gallo catechins

iii. Gallyl esters of L. epicatechins.

Flavour of tea is due to presence of pyrazine, furones, pyrroles, 2, 4 hepta dianol.

Composition of different parts of tea plants

1. Bud	**4.9% pectin**
2. 1st leaf	**6% pectin**
3. 2nd leaf	**4.7% pectin**
4. Stalk of plant	**7% pectic acid**

Nutritional composition

Zinc	**22-63 ppm**
Cu	**22-25 ppm**
Fe	**40-180 ppm**
Pb	**1 ppm**

ESSENTIAL OILS

These are complex mixtures of the odorous and the steam volatile compounds deposited by the plant in the sub cuticular spaces of glandular hairs and also in the cell organelles.

These essential oils are present mainly in spices and medicinal plants.

Compounds of essential oils are Monoterpene and Sesquiterpene

It also contains mixtures of aldehyde, ketones, esters, phenyl terpenes, and camphor and benzene derivatives.

Essential oils are classified as alcohol groups, → e.g. geraniol.

Aldehyde	**e.g. citrol.**
Ethers	**e.g. Anethole**
Hydrocarbons	**e.g. pinine**
Ketones	**e.g. Piperitene**
Phenols	**e.g. Eugenol.**

Advantage

Presence of Essential oils enhances hygienic conditions. It will not allow rancidity. Free from bacteria, and other catalytic enzymes. It do not impart colour to the product and free from tannins. It is stable.

Uses:

Mainly used in the preparation of cosmetics for giving fragrance.

Examples for essential oils

1. Rose oil	**Geraniol**	**68-81%**
	Citronellol	**26-35%**

2. Jasmine oil

Esters of benzyl acetate	**32-74%**
Linalol	**30-45%**
Methyl anthranilate	**0.4-3.5%**
Indole anthranilate	**1.7-2.7%**

Geranium oil :

Oil	**0.15%**	
Geraniol	**56.7%**	**unsaturated terpenols**
$(C_{10}H_{18}O_7)$		

Lemon grass oil :

Oil	**0.28-0.5%**
Citrol	**85-95% $(F_{10}H_{16}O)$**

Palmrosa oil :

Free geraniol	**80%**
Combined geraniol	**15%**

Export: Geranium, Lemon grass, Palmrosa oil.

Patchouli oil

Oil	**1.3%**

Citronella oil

Eucalyptus oil	**Hilly region**
Cinchona oil	**Nilgiris**

Medicinal and aromatic plants:

Pharmaceutically and economically important

1. Solanum sp:

Solasodine and solanine 2% (prevents diarrhoea)

2. Cassia absus –

Chaksine iodine

3. *Vinca rosea*

Leaf alkaloid:	**Vinblastine** **Vinceristine**
Root alkaloid:	**Ajmalicine** **Serpentine**

Pyrethrum: Chrysanthemum sp.

Flower contains: Pyrethrin I, Pyrethrin II and Pyrethrolone

All are being used as insecticide and biopesticides

***Chimona ledge Riana* :**	**Quinine – Antimalarial.**
Datura innoxia	**Hyercyanine**
Aloe barbadensis	**Aloin compound**
Artemesia annua	**Artemisinin, Santonin**
Daisuorea delloides	**Tuber**
Daiscorea floribunda	**Diogenin, codinine**
Digitalis lanata	**Acetyl oligonin**
Glycyrhiza glabra	**Gly cirrhizin**
Papaver somniferum	**Codinine, morphine – drug called opium → Large, number of alkaloids have been isolated such as norprotein, narceine, papaverine etc.**
Rauvolfia serpentine	**Serpentine, Rescinamone, Ajamline**

Onion and garlic also posses medicinal properties they contain lackrymatory factors responsible for tears in eyes.

Allyldisulphide – onion
Allyl sulphide – garlic

CHEMISTRY OF FORAGE CROPS

Chemical compounds and nutritional properties of forage crops

Legume Forages, cereal Forages, Tree Forages, Grasses

Legume Forages: **Lucerne, Berseem, Cowpea**

Cereal Forages: **Sorghum, Maize, Cumbu, Rice, Ragi, wheat**

Grasses: **Guinea grasses cumbu Napier, Buffalo grasses, Dinanath, Kolukattai, Hariyali.**

Tree Forages: **Agathi, Desmanthus, Subabul, Velimasal**

Composition of forage crops:

Moisture – green Fodder - 70-75%, Dry fodder → 1/10th of its weight, CHO → Nitrogen free extract → Soluble portions of CHO also contains some organic acids, very easily digestible materials, it also has crude fiber, mainly present as cellulose, hemicellulose and lignin (35-75% → Digestible capacity).

Forage protein – 80-90% forms crude protein

Generally, Grass protein is inferior in quality wise to that of legume protein. Forage contains 3-25% crude protein.

CO.2 fodder grass contains crude protein 8.92%, Crude fat 1.76%, Total ash 14.0%, Ca 0.59%, P 0.29%, Mg 0.38%, K 1.86%.

Fats → Energy source and mainly used for maintaining health of animals.

Minerals → Depend upon fertility status of soil in which it is grown. Mainly Ca, Mg, K were required in larger quantity whereas micronutrients such as B, Cu, Fe, Mn, Zinc, Mo, Na, Co, Cl also needed in comparatively lesser amount. Almost all the forage crops contain all these elements.

Growth factors

Enzymes, hormones, vitamin B – complex C, E and K are present in Forage crops and vary in amount.

Toxic substances

Oestrogens, coumarins, saponins, Alkaloids, cyanogenitic glycosides, nitrates, oxalic acids, selenium, mimosine

Nutritional factors

Factors that determine quality aspects of forage crops.

True Digestible Nutrition (TDN)

$$\text{Protein Digestible Nutrition (PDN)} = \frac{\text{Digestible Portion of crude fiber}}{\text{Crude fiber} \times 2.25}$$

$$\text{Nutritive ratio (NR)} = \frac{\text{Digestible CHO} + \text{Digestible ether extract} \times 2.25}{\text{Digestible crude protein}} \quad \text{or}$$

$$NR = \frac{DC + DE \times 2.25}{DCP}$$

Metabolic energy = Heat in the food – Heat last through urine and other materials.

$$\text{Protein quality} = \frac{\text{(\%) digestible crude protein} + \text{(\%) digestible true protein}}{2.25}$$

Biological value of proteins → It is the amount of nitrogen in dietand amount of N in excreta of an adult animal are measured and the percentage of N retained by the animal from the quantity of N absorbed from the diet.

Nutrition content for forage crop

Cumbu Napier hybrid grass

Digestibility - 50%

Ca - 0.8%

Fe - 250 ppm

Mn - 150 ppm

Cu - 15 ppm

General composition of green Forage

Sorghum, Cumbu, maize, Ragi, Varagu and Other green grasses.

Crude protein – 5.2-10.6%

Crude Fiber – 28-37 %

Ca - 0.9%

P - 0.5%

Nutritional content in the straw

Crude protein - 2-8%

P - 0.5%

Ca - 0.9%

Crude fiber goes as high as 60%

Nutritional Content in (Silage → preservations of green Forages and some additives such as molasses are added to increase it's nutritive value).

Crude protein - 3-8%

Crude fiber - 24-44%

Ca - 0.4%

P - 0.5%

Nutritional content of leguminous Forage crops

Cowpea, Lucerne, Berseem

Dry matter 11-20%

Moisture 80%

Crude protein 12-24%

Cellulose	**21-33%**
Non digestive protein	**37-57%**
Hemicellulose	**7-21%**
Lignin	**4-10%**
Silica	**1-2% (Induces more resistance in plants)**
Ash	**10-13%**
Soluble CHO	**60-85%**
Crude fiber	**35-75%**

Toxic principles

Oestrogens

These are phenolic compounds which causes infertility in animals.

Coumarins → These are phenolic compounds mainly present in legumes, its presence causes reduction in palatability of forage corps. It causes bleeding in animals, causes anticoagulation.

Saponins → they occurs mainly as glycosides when these undergo hydrolysis, they releases sapogenins. Commonly present in Lucerne and Jowar. Its presence causes excess salivation. Causes vomiting, diarrhoea, damages liver and kidney systems.

Alkaloids → Alkaloid content exceeds 0.5 mg/kg then it will become toxic to animals.

Typtomine in grasses → grazing animals in let loose cases

Perololine – grazing animals

Pyrolizidine → Seen in all livestocks

Cyanogenic glucosides – HCN

Secondary metabolites which release the cyanides, nitrites, isothiocyanates → Mainly present in young sorghum and ratoon sorghum crop. HCN react with haemoglobin in blood to form methanoglobulin which causes reduction in O_2 content.So O_2 content intake is affected causing death.

Alkaloids affect liver, kidneys and lungs.

Nitrate nitrogen will become more toxic in the animal stomach (Rumen) is reduced to nitrite which also interfere with the O2 intake in the blood. It will never become toxic when they exceed 0.3-4% but it creates the accumulators of nitrates.

On hydrolysis of this cyanogenic glycosides they yield to molecules of glycosides, and one each of benzaldehyde and hydrocyanic acid. This hydrocyanic acids gives problems for animals. Hydrocyanic acid present in sorghum is Dhurrin.

Oxalic acid → Calcium oxalate, Na oxalate, K oxalates will interfere with Ca metabolism. When Ca metabolism gets affected, this oxalate gets accumulated in the kidney and also affects brain tissues. Above 3% of concentration it will become toxic to animals. Generally the oxalates are present in grasses.

Xelenine →In Ray little quantity of 4 ppm causes toxicity to animals. Commonly present in Lucerne. Leads to abnormal growth of muscle, in animals. Its toxicity is detoxified in the presence of sulphur compounds.

Mimosine → It is an amino acid present in tree fodder such as Lucerne. When leaf is fed alone in more amount causes 50% toxicity. Problem causes due to its presence is less of hairs, causes excessive salivation, stunted growth, leads to formation of goiter.

Post – harvest changes in Horticultural and Agricultural produces

There are 2 different types of reactions are taking place.

1. Constructive	2. Destructive
Synthesis takes place	Degradation takes place
Maintenance of mitochondria	Destruction of chloroplast
Formation of carotenoid	Breakdown of chlorophyll
Anthocyanin – colour	
Inter conversion of sugars	Stand hydrolysis
Synthesis of starch → Glucose, fructose and sucrose	
TCA cycle	Destruction of acid
Formation of flavour and	Oxidation of substrate
Volatile compounds – Taste	
Formation of amino acids	Solubilization of pectins
Building blocks of protein	
Formation of ethylene pathway	Ethylene induces cell wall softening
Takes place generally before harvest	takes place after harvest

Post harvest – General changes

- Moisture loss
- Weight loss
- Lesser enzymatic activity
- Catabolism – destruction – things gets lost
- Alterations in proximate and ultimate constituents
- Changes in nutritive values
- Changes in texture, taste, flavour, aroma
- Changes in pH value
- Changes in consumer acceptability

Moisture

Moisture content should be loss 10-15% when the seeds are stored after harvest, there will be accumulation of metabolites such as ammonium, HCN, essential oil and degradation of acetones.

Loss of amino acid

Decrease in quality, above 40% of harvested products in world is lost through post harvest deteriorates. Tomato, banana, Mango etc. Many of the chemical changes with occur to induce changes in flavour, taste, texture, odour, after harvest. It will not be in the case of grains. So the grins can be stored. In grains moisture content will always be less and also in preserved fruits cereals, seed legumes are stored for a long time when the moisture to at optimum level. But there will be changes taking place at the time of germination. Because these grains are biological products, that's why they germinate and respire. Accumulation of metabolites leads to dormancy in seeds. Dormancy is an crop factor and once when the dormancy to broken, seed will germinate because of decomposition of the seed. Low viability the vigor of seeds is due to the production of volatile compounds such as methanol. With glucose metabolism, we can manipulate the seed deterioration quality.

Post harvest changes in Horticultural crops

3 important processes taking place

1. Transpiration
2. Respiration
3. Ethylene production

Transpiration

It leads to loss of water, 65-95% loss. There's loss in moisture which leads to shrinking, withering of tissues of the plant parts that leads to loss in weight.

Respiration

Broadly classified as climateric and non climateric fruits. Climatric fruits respire more in non-climatric fruits -> less respiration. cli. fruits → Ex. Mango, Papaya, Apple, tomato, banana. Non – climatric fruits → Ex. orange, Grapes, pomegranate (Fruits are allowed to ripe in tree itself).

Respiration is the enzymatic oxidation of sugars leads to the production of CO2, H2O and Energy that leads to catabolic activities. Because of this response aroma, taste and lowering of the self – life. In non – climatric fruits, keeping quality will be more.

Ethylene production

Ethylene production leads (or) induced changes in permeability of the mitochondria in the membranes. It will enhance more ATP movement through its permeability. The respiration activity also increased due to production of ethylene compounds.

Three different stages – controlled by enzymatic activities

1. Unriped stage 2. Riped stage 3. Over ripening stage

The ripening is highly influenced by pectin compounds.

Pectin → protopectin unripe –protopectin Pectin Ripe – pectin Pectic Proteins

RNA High Low Low
Synthesis

Ethylene synthesis Low High High

During ripening of fruits starch is converted into glucose, fructose, sucrose. Because of transpiration and respiration, the moisture content gets altered, loss in wt, ultimate change in proximate and ultimate compounds,

reduction in ascorbic acid content total soluble solids gets increased and acidity gets decreased, sweetness gets increased.

CHO + O_2 → CO_2 + H_2O + energy

In the case of immature plants parts there's more TCA cycle activities whereas the case of matured plants parts more of hexose monophosphate pathways is increased. Citric acid, tartaric acid in grapes gets changed to lactic acid and CO2 and biodegration of fruit juice leads to formation of soluble sugars. It gives to lactic acid and converted to acetic acid – citric acid succinic acid.

Lactic acetic citric – succinic acid.

Starch converted to ethanol and acetyl COA.

Glucose → Succinate → Fumerate → Acrylase → Ethylene + CO_2

Because of transpiration and respn there will be some alternately in the flavour, aroma, taste and enzymatic activities. Besides over ripening leads to decrease of nutritive values and finally the consumer acceptability. Changes due to enzymatic activity especially due to Hydrolases enzymes

1. **Carbohydrates → act on CHO, starch and sugar fractions**
2. **Pectinases – Pectic compounds – mainly involved in ripening of fruits.**
3. **Proteases 0 Amino acids.**
4. **Chlorophyllases enzymes chlorophyll – colour changes**

Chlorophyll + H_2O chlorophyllases phytol + chlorophytol phytol is due photo chemical oxidations whereas the chlorophyll is due to storage and senescence (process of being old).

Degradation of green colour. Because of degradation leads to change of carotenoids and carotenoids becomes unstable and converted to anthocyanin due to influence of light and O_2 and gives red colour due to lycopene in anthocyanin.

Softening of tissues and textural changes

Its due to enzymes called ethylene methyl esterase, polygalacto uronase, protopectinases.

Flavour production → If once produced the acidity gets decreased and sweetness gets increased. Tannins, phenols, flavonoids gets increased because of flavored products.

Changes in CHO

Starch hydrolysis takes place leading to simple sugars. Such as glucose, fructose and sucrose.

Changes in lipids

Because of rancidity of fats, the lipid changes.

Protein synthesis

Because of protein synthesis, highly influenced by proteases, proteolytic enzymes. Due to this linoleic acid gets decrease and palmitic, linolenic acid gets decreased.

Vitamins

Vitamins content gets decreased; org. acid content also get decrease quality gets decreased.

Changes in pH

It can be prevented.

1. By keeping the produce in refrigerators (or) cold condition.
2. Lowering O_2 decrease and increase CO_2 content in storage
3. By using 2, 4- dinitrophenol
4. By using ethylene inhibitors
5. By using sugar inhibitors such as benzimidozole.

6. **Spraying of 0.5% $CaCl_2$.**
7. **Storing in perforated polythene bags**
8. **Use of antioxidants (Tocopherol)**

POST HARVEST CHANGES IN SUGARCANE

Non-reducing sugar become reducing sugar by inversion. Harvesting at right time reduces the sugar loss. There should not be any delay in harvesting once it attains maturity.

After harvest, it should be immediately transported for the factory for crushing. The juice also should not be kept unused. Age of sugarcane 10-12 months and the juice is processed immediately.

Changes

1. Conversion of sucrose to glucose and fructose – inversion (Invertase acted upon this).

2. Sucrose should be retained for maximum output

3. Reduction in sugar output varies 5% - 150% if the canes are not crushed within 4 day after harvest.

Depending upon situation the reduction even goes as high as upto 50%.

If the harvest is delayed after 9 days of its maturity, loss of sugar will be 37%.

Sugar recovery also reduced by 11% (for opt. and 9 days)

In the case of sugarcane juice, besides inversion, microbial degradation leads to more acidity of juice and more viscosity will be there and the sugar crystal formation is effected and finally the quality gets deteriorated.

Enzymes involved are acid invertase and neutral invertase which are involved in inversion processes. In the case of early maturing cane varieties the sugar gets accumulated it attains maturity and there will be sudden (or)

till drastic reduction because of the soluble active invertase enzymes therefore sugar recovery gets reduced.

The sucrose gets translocated and gets accumulated in the sheath of cane will become index for identifying the maturity stage. If it is not harvested at right time, the change of pH also influences the recovery of sugar etc, it should be prevented.

If you want to avoid sugar loss
Harvest at right time
immediate transport
Crushing at right time
Should be immediately bundled and kept under shade (or) should be sprayed with water do increase the humidity and chemicals such as sodium meta silicate 20-30 moles / l of water.
Topping of sugarcane based on net sugar recovery.
Red rot (or) sett rot of sugarcane will immediately spread if not harvested at right time.
Green and dry leaf ratio also influences the sucrose content reducing sugars will be low at early growing stage but towards the end of growth stage the sucrose content will gel increase and attains peak (or) maximum at right maturity stage and after that the sucrose content gets reduced if not harvested at right time.

There will be decrease in N, P and ash content and increased in K, Ca content with increase in sucrose content at maturity stage.

Post harvest changes in oil seed crops
i. Ground nut, 2. Castor, 3. Sunflower 4. Gingelly, 5. Mustard

The case of oil seed the synthesis of lipids starts at the early mid stage of the seed development. Most of the accumulated starch is the storage protein and the lipids.

In case of groundnut, the crude fat and crude protein content gets increase with the decrease in free fatty acids and free amino acids at the time of maturity. The sugars and the starch content also the activity of hydrolytic enzymes gets decreased at the time of germination of oil seeds. At the time of germination, the favorable environment with water and temperature the seed started germinating and at the time of germination the starch content rapidly gets mobilized and the endosperm becomes completely liquefied. The cell walls of are get dissolved. The cytoplasm and protein deposits also get dissolved in those things are made available for the germinating seed and growing seedling. The elongation of radical and plumule are made.

Chemistry of pesticides

Pesticides

Definition

The comprehensive term "pesticides" relates to compounds used for the control of pests of all descriptions including plant and those directly hazardous to the health of man and animals.

The term pesticide also embraces compounds for the control of rodents, slugs, snails and household and stored product pests.

Pesticides

These are chemicals designed to combat the attack of various pests on agricultural and horticultural crops.

They fall into three major classes

Insecticides

Fungicides

Weedicides (weed killers)

A pesticide is described as a chemical (or) biological agent that eliminates (or0 dissuades the pest life for the benefit of man.

The pesticides are generally classified into various groups based on pest organism against which the compounds are used, their chemical nature, mode of action and mode of entry.

1. Insecticides

Compounds used to control various insects / pests attacking field crops, farm animals, stored products and human being eg. Endosulfan, Malathion, Carbaryl, carbofuran and synthetic pyrethroids.

2. Rodenticide

The chemicals that are exclusively used to control various rats e.g. zinc phosphide, warfarin, thallium sulphate, alpha-naphthol Thoreau and bromodialone.

3. Acaricides

These are chemicals used to control mites feeding on various crops and animals. Some insecticides are found to kill the mites that are said to have acaricidal activity. The term acaricide is applicable to agents capable of killing the eggs of mites also e.g. Dicofol, tetradifon, chlorofenzon, chlorophenoltuon, azinphos (methyl), binapacryl and sulphur.

4. Avicides

These are chemicals used to repel birds like quails, baya, house sparrow, crows, parakeets and pigeons which often become pests of field and orchard crops. eg. TMTD (Tetra methyl thiuram disulfide), Anthraquinone. Most of the insecticides are highly toxic to birds.

5. Molluscicides

These are chemicals used to kill the snails and slugs in agriculture and public health service. Eg. Metaldehyde, Nitrosamide, copper sulphate, pentachlorophenoate and Trifenmorph.

6. Nematicides

These are chemicals used exclusively for the control of nematodes. They are classified as fumigant and non – fumigant nematicides.

The fumigant groups of compounds are injected into the soil mainly as per plan application eg. D.D. (Dichloropropane Dichloropropene), DBCP (Nemagon) (dibromochloropropane), ethylenedibromide.

The non fumigent nematicides are suitable for post planting treatment eg. aldicarb, fensultothion, carbofuran mocap, phorate, thioxazim, disulfoton and Vc 13.

Some organophorous insecticides like parathion, Malathion phosphamidon, diazinon, Dimethoate also possess nematicidal properties. Oxamyl is a nematicide which can be sprayed to control foliar nematodes.

7. Fungicides

The term fungicide means any agent capable of killing fungi.

Chemicals which inhibit, inactivate (or) destroy the ability of fungi to grow and reproduce are referred as fungicides. Fungicides are exclusively used to control plant diseases caused by fungi.

Eg. Copper oxychloride, bordeaun mixture, sulphur, dithiocarbamates like manoczeb, thiram, zineb and propineb, pthalamides like captan, captatol and folpet, organophosphorous compounds like edipheriphos and systemics like carbendazim.

8. Bactericides

These are exclusively used to control the diseases causes by plant pathogenic bacteria. E.g. Streptomycin sulphate and aurecomycin.

9. Herbicides

These chemicals are used to control the weeds and undesirable plants in crop and plantations. These are again classified as pre-emergence and post emergence herbicides, eg. 2, 4-D butachlor, benthiocarb, pendimethalin, atrazine, fluchloralin, anilophos and paraquat.

10. Chemosterilants

Chemicals which deprive insect species of their ability to reproduce are known as chemosterilants.

Such chemicals when administrated orally to the insect (or) by contact with them produce irreversible sterility without affecting their mating behavior.

They are classified into a. alkylating agents.

b. Antimrysboliyrd c. Miscellaneous eg. Tepa, Amithopterin. hempa and hemel. However, they are seldom used in practice due to their hazardous nature.

Pheromones → chemicals with attract the insect and secreted by external entries by an animal (or) insect and produce the specific response in a receiving individual on the particular species mainly for mating synthetic hormones are available for attracting the opposite sex.

Repellants

Chemicals which cause insects to move away from the source are referred as repellants.

Pesticide – Classification

Insecticides	Fungicides	Herbicides
1. Organochlorine	1. Control of diseases	1. Selective
2. Organo phosphorus	2. Seed disinfectants	2 Non-selective
3. Carbonates		
4. Synthetic pyrethroids		

Herbicides are also classified based on methods of use and their effect on plant as follows.

a. Contact herbicides

b. Systematic herbicides

c. Herbicides acting on root system of plants (or) germination seeds.

Fungicides

Suphur compounds Copper compounds Mercurial compounds Others

1. **Inorganic**
2. **Org**

1. **Inorganic**
2. **Organic**

1. **Quinones**
2. **Organotin**
3. **Antibiotics**

4. **Heterocyclic N compounds**

Insecticides

Inorganic

1. Arsenic trioxide
2. Arsenic pent oxide
3. Arsenate's
4. Fluorine insecticides

Organic

Natural org insecticides

Synthetic org. insecticides

Natural organic I	Synthetic organ I
1. Nicotine	1. Organo chlorine compounds
2. Not – nicotine	2. Organo phosphorus compounds
3. Anabasine	3. Carbamates
4. Pyrethrum	4. Synthetic pyrethroids
5. Rotenone	5. Miscellaneous
6. Allethrin	

Insecticides are classified based on

1. Mode of entry
2. Mode of action
3. Chemical nature

1. Mode of entry

- a. stomach poison
- b. Contact poison
- c. Fumigant
- d. Systematic poison

a. Stomach poison

The insecticide applied on the leaves and other part of the plant when infested act in the digestive system of the insect and bring about the kill.

These chemicals penetrate the intestinal membrane and cause deranged metabolism. The stomach poison should be palatable for the pest species and be able so bring about the kill quickly.

Most chlorinated hydrocarbons and organo phosphorus compounds act as stomach poison.

A bacterial toxin of Bacillus thurngiensis belongs to this group.

b. Contact poison

The toxicant which brings about the death of the pest species.

By means of contact with the wan monolayer and getting adsorbed on the surface of the cuticle of the body, and also penetrates into the body through the vulnerable sites viz., membranes, bases of sefae and tracheal system on its body is said to be a contact poison.

All suitable insecticides like chlorinated hydrocarbons, many organophosphates, carbamates and synthetic pyrethroids act as contact insecticides.

c. Fumigant

Most of the fumigants are respiratory poisons and act in gaseous phase. All lands of insects can be controlled irrespective of their feeding habits. Eg. Hydrogen cyanide, aluminium phosphide, EDB and insecticides like DDVP, lindane phorate have got fumigant action. Fumigants enter through the spiracles.

D. Systemic poisons

These chemicals when applied to plant (or) soil are absorbed by foliage (or0 roots are translocated through vascular system into the plant and any insect particularly that sucking form feeding will get poisoned and killed and such forms are called as systematic insecticides. Eg. Methyl elemeton, belimethoate, phosphamidon, phorate, carbofuran and aldicarb.

2. Mode of action

a. Physical poisons
b. Protoplasmic poisons
c. Respiratory poison
d. Nerve poison.

a. Physical poison

Toxicant which brings about the kill insects by exerting a physical effect is a physical poison. Heavy oils, tar oil etc cause the insects particularly scale insects to die of asphyxiation i.e. exclusion of air.

Inert dusts effect a loss of body moisture by lacerating the epicuticle due to their abrasiveness as in aluminum oxide (or) absorb moisture from the body due to their hygroscopic nature as in charcoal.

b. Protoplasmic poison

A toxicant responsible for precipitation of protein especially destruction of cellular protoplasm of midgut epithelium is said to be a protoplasmic poison.

e.g. Heavy metals like Hg, Cu, Fatty acid, Formaldehyde, ethylene oxide, flwrine and arsene compounds.

c. Respiratory poison

A chemical which blocks cellular respirations as with the fumigants hydrogen cyanide, eartron monoxide etc. is said to be a respiratory poison. They inhibit the enzyme activity.

d. Nerve poison

A chemical associated with its solubility in tissue lipid and functions actively by interfering with nervous system like inhibiting acetyl choline esterase, altering impulse transmission and causing death is called as nerve poison.

e.g. Organophosphate, carbomate, Organochlorine (DDT, Lindane), botanicals like pyrethrum, Nicotine, synthetic pyrethroids etc.

3. Chemical nature

a. Inorganics

b. Organics

- i. Hydrocarbon oils
- ii. Animal origin
- iii. Organic compounds of plant origin
- iv. Synthetic org. compounds

1. Ditritrophenol
2. Organothiocyanates
3. Chlorinated hydrocarbons
4. Organophosphorous compounds
5. Carbonates
6. Synthetic pyrethroids
7. Microbial toxicant
8. Nuclear polyhedrosis viruses (NPV)

a. 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 fluoaluminate, sodium flusilicate), sulphur, lime, barium carbonate, thallium sulphate and zinc phasphosole. However except sulphur and zinc phosphide others are not in use.

b. Organics

1. Hydro carbon oils

Mineral oils – petroleum oils – coal tar oils fussil fuels. Geosole oil, anthracene, oil in its natural stage itself will become toxic to plants and used as solvents, diluents.

2. Animal origin

Oils from animal beings Ex.: Marine annelids.

Lumbrianerias heteropoda, lumbrianaris braviciara are found to possess insecticidal properties. Insecticide derived from LH and LB are called Nereistoxin. Common name for animal origin P is cartap.

3. Plant origin

Toxicants derived from plants and used for control of insects. Eg. Pyrethrum, rotenone, derris, Nicotine ryania, Acorus, Neem.

4. Synthetic org. compounds

Very commonly and frequently used insecticides to control pests. It has broad subgroups in it (refer front page).

a. These dinitrophenols are derivatives of 4, 6-dinitro 2 alkyl phenols of these salt and esters are used as insecticides. They act as stomach and contact poison also affect the ovicidal effect of eggs. The commonly used dinitrophenols DNOC-Dinitro organic compounds, Dinocap-acaricide (mites),

BINAPACRYL – commonly called morocide. It is not systemic acaricide and controls the spider mites very effectively.

B. Organothiocyanates → These are org compounds possessing iso thiocyanates. They are known to possess insecticidal property very quick knock down effect. The group common one is lord – controls aphids, thrips, red spider mites. Contact insecticide – thanite.

C. Chlorinated hydro carbons → (Other wise called Organochlorine)

They are potent nerve poisons which will have very quick known down effects and very high residual toxicity. It undergoes slow degradation.

Chlorinated hydrocarbons Organophosphorus
DDT
BHC
Chlordane, Aldrin, Dieldrin, Hepta chlor, Toxaphene, Endrin, Endosulfin.

These are phytotoxins to some of cucurbitaceae plants which are highly susceptible. They are very very toxic to fishes.

d. Organophosphorus (OP)

Commonly acts as nerve poison, inhibit choline esterase poisoning due to OP compounds generally causes chloinergic symptoms. In insects it

causes the hyperactivity. Tremors consulsion (fits), paralysis. All these things finally leads to death.

Dichlorous, phosphamidon, Monocrotophos, Dicrotophos, chlorofenvinphos, methyl parathion, fenthion, fentrothion, chloropyriphos, methyl demeton, quinolphos, malation, phasalone, phorate, profenphos.

Carbamates

These carbamates are the esters of carbamic acid, these mainly acts as nerve poison chemicals. it inhibits chloiesterase which inturn causes cc medicated synaptic transmission. Through nerves.

Eg. Carbaryl
Carbofuran
Aldicarp
Oxamyl
Methamyl

Synthetic pyrethroids

These will have very good knock down effects and relatively less toxic to higher org. (or) animals over usage of insecticides is SP develops resistance in insects.

eg. Cypermethrin
Decamethrin
Permethrin
Ethofen pox (trebon)

Microbial toxicants

Bacillus thuringiensis Bacterial toxins, act as stomach poison, causing death, causes gut infection, very effective against lepidopteron insects.

Nuclear polyhedrosis viruses (NPV)

Larva infected by virus is made to mingle with other larva and after the death of this entire larva they are washed in water and sprayed on crops.