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Plant Metabolites and Systemic Pathways: A Defence Mechanism Against Insects

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Introduction

Plants and insects have coexisted for over 350 million years, engaging in a continuous co-evolutionary battle. Both have developed strategies to overcome each other's defences, leading to an evolutionary arms race. This dynamic has resulted in plants evolving sophisticated defence mechanisms capable of recognizing non-self-molecules or signals from damaged cells—similar to the immune systems of animals—triggering immune responses against herbivores. To deter herbivore attacks, plants deploy specialized defences, including morphological structures and the production of secondary metabolites and proteins. These compounds exhibit toxic, repellent, or antinutritional effects on herbivores. Secondary metabolites (SMs) are small molecules synthesized by plants to enhance their ability to compete and survive in their environment, often influencing interactions with other organisms. All plants possess the capacity to produce secondary metabolites, with Angiosperms being particularly prolific producers. These metabolites are primarily derived from five precursor pathways and include diverse compounds such as terpenoids, flavonoids, and anthraquinones (War *et al.*, 2012).

Nature of secondary metabolites

The formation of secondary metabolites and their storage sites are restricted to certain developmental phase of the plant, specific organs, tissues or specialized cells. The formed or synthesized secondary metabolites were stored in two ways. It is also called as compartmentation of secondary metabolites. They were

1. **Intracytoplasmic** – Secondary metabolites were stored in vacuoles and plastids. Usually, they were hydrophilic in nature.

   Examples- In sorghum, glucoside dhurrin is stored in vacuole, whereas simple phenyl propane's and flavonoids were stored in chloroplast.
2. **Extra cytoplasmic-** Secondary metabolites were stored in cellwalls, pollen walls etc., Usually, they were lipophilic in nature.

Examples- Terpenes were restricted to store in resin ducts and Furanocoumarins were stored in oil tubes.

Distribution

The synthesized secondary metabolites not distributed evenly throughout the plant both in terms of qualitative and quantitative and also in space and time. SM are not synthesized or accumulated in any specific group of cells at all times during the life of plant.

Example - cyanogenic glycosidic dhurrin distributed in epidermal layer of cells, whereas catabolic dhurrin distributed in mesophyll tissue

Concentration of secondary metabolites altered by many factors like diurnally, climatic, edaphic factors and also the exposure to microorganisms, grazing animals etc., (Kojima *et al.*, 1979).

Functions of secondary metabolites

- They act as plant growth hormones- examples auxins, cytokinin's, abscisic acid etc.,
- Wound healing hormones- traumatic acid

Example - Tetracyclic triterpene cucurbitacin present in *Cucurbita* is highly toxic to generalist feeders and also responsible for healing the leaf feeding damage by squash beetle.

- Insect pollinators are attracted to secondary metabolites: eg- flavonoids, carotenoids and volatile terpenoids
- They act as chemical signals in the ecosystem and as antibiosis agents against insects and pathogens (Tallamy, 1991).

Biosynthetic pathways of secondary metabolites

Excluding the primary process of sugar and protein biosynthesis there are three major pathways for the production of secondary metabolites in plants.

They are

1. The acetate- malonate pathway
2. The acetate – mevalonate pathway
3. The shikimic acid pathway

1. Acetate – mevalonate pathway

- ✓ Terpenoids and steroids are biosynthesized by this pathway
- ✓ Angiosperms produce all type of terpenoids and steroids as a major defense strategy against herbivores

Terpenoids

- ✓ Largest, structurally diversified, naturally occurring SM
- ✓ The allied terpenoid compounds are steroids.
- ✓ Structure is complex in nature- composed of isoprene repeating unit
- ✓ They are lipophilic substances
- ✓ Certain types of terpenoids occur as conjugates with sugar (e.g., iridoids)
- ✓ Act as toxicants, feeding deterrents, ovipositional deterrents

Types of terpenoids

1. Monoterpenoids (10c)

- Widely distributed in higher plants.
- Volatile, lipophilic and give characteristic odor.
- Accumulate in resin ducts, secretory cavities and epidermal glands.
- Monoterpene derivatives toxic to insect are pyrethroids, present in leaves and flowers of Chrysanthemum species- neurotoxins, hyperexcitation, uncoordinated moment, paralysis
- In conifer resins- α-pinene, β-pinene, limonene and myrcene- defensive chemical against bark beetles (coleoptera: Scolytidae)
- Citronellol- oviposition deterrent to the leaf hopper (*Amrasca devastans*)
- Limonene and geraniol were present in flowers, they attract the attract pollinators (Saxena and Basit, 1982)

2. Iridoids

- Cyclopentane monoterpene derived compounds.
- Structural similarity with iridodial and iridomyrmecin. They are defensive secretions of ants belonging to Iridomyrmex.
- Present in 57 plants families of Dicotyledonae.
- Iridoid glycosides are deterrents or toxic to a variety of generalist insects
- Antifeedants to grasshopper and lepidopteran larvae.
- Act as feeding stimulants – e,g., Euphydryas sp (Bowers *et al.*, 1991)

3. Sesquiterpenoids (C-15)

- Aliphatic or cyclic isoprenoid compounds.

Types

a) Drimane skeletal type- potent feeding deterrents.

- Drimane dialdehydes inhibit the feeding of *Spodoptera exempta, S. littoralis and Leptinotarsa decemlineta and Myzus persicae.*
- It blocks stimulatory effect of glucose, sucrose and inositol on chemosensory receptor cells locate on the insect mouth parts.

b) Sesquiterpene lactones-largest group, mainly present in Compositae family (Asteraceae)- localised in glandular hairs or in the latex ducts.

- Poisonous to lepidopterans, flour beetles and grasshoppers- exact toxicity is not known.
- Examples – alantolactone, cumambranolide etc., (Gershenzon and Kreis, 1999).

c) Gossypol –phenolic, cadinene type sesquiterpene dimer with two aldehyde residues.

- Present in pigment glands, leaves and flowers of cotton plant.
- Toxic to herbivores – antibiosis to *Heliothis virescens* and *Spodoptera sps.*
- Toxicity – complexation with proteins in the gastrointestinal tract, causing a reduction in their digestibility or with digestive enzymes – loss of enzymatic activity

4. Diterpenoids (c20)

- Nonvolatile, present in the resins of higher plants.
- Resin diterpenes of pine- resistance to pine bark beetle *Dendroctonous frontalis*
- Higher levels of abietic and levopimaric acids- increase mortality, reduce growth and extend development time of sawfly larvae

5. Triterpenoids – tetracyclic and pentacyclic compounds

- Cucurbitacin's – isolated from Cucurbitaceae family
- Cucs B – predominant compound followed by Cucs D, G, H, E, I, J, A, C, F and L.
- Feeding deterrents – cucumber leaf beetles (*Phyllotreta spp. Phaedon spp, Cerotoma trifurcata*), stem borer and red spider mites.
- In contrast, spotted cucumber beetle *Diabrotica undecimpunctata howardi* are immune to the toxic.
- Cuc B – powerful host recognition cue and stimulates feeding

2. Acetate – malonate pathway

- ✓ Acetyl coenzyme acts as a precursor
- ✓ Produces – fatty acids, lipids, esters etc., and formation of plant aromatic compounds from polyketides.
- ✓ Polyketides – protect plants from bacterial and fungal infection.

Biological functions

- ✓ Linoleic and linolenic acid- healing of damaged tissues through their degradation.

- ✓ Unsaturated fatty acid (18:3)- pollen of clover acts as food marker for bees.
- ✓ The fatty acids, wax, esters – in leaf cuticle – acts as a protective layer against insect, fungal, and bacterial attack.

3. Shikimic acid pathway

- ✓ Shikimic acid was first isolated from *Illicium anisatum* (Illiciaceae).
- ✓ Pathway restricted to plant kingdom.
- ✓ Produces aromatic compounds from carbohydrates.
- ✓ Examples – phenolic compounds, coumarins, secondary aromatic compounds.
- ✓ Tryptophan, Tyrosine and phenylalanine are the precursors

a) Phenolic compounds

- Aromatic in nature, contains phenolic hydroxy groups
- Phenylpropanoids are important and essentially compounds in higher plants.
- The two main types of phenolic polymers in plants are- lignin and tannins
- Formed by single pathway but differs in both chemical and biological properties**.**

Lignins

- Integral cell wall component in vascular plants
- Polymerization of the cinnamyl alcohols

Functions

- Provide mechanical strength- aerial shoots
- Mechanical barrier and unpalatability- restrict the attack of MO's and herbivores.

Tannins

- Compounds with an astringent taste.
- Protein binding agents

Functions

Avoid astringent food- digestion – coagulation of mucoproteins in their oral cavity

Coumarins

- Localized in roots and seed coats.
- More than 300 coumarins – reported from 9 families of monocots and 70 families of dicots

Functions

- Toxic to – Bacteria, viruses, fungi, vertebrates etc.
- Simple coumarin- ovicidal to Colorado potato beetle, toxic to mustard beetles.
- Furanocoumarins –capable of binding to pyrimidine bases of DNA.

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