27. CHARACTERISTICS, PREPARATION AND USE OF SYNTHETIC PYRETHROIDS-FENVALERATE AND CYPERMETHRIN

Synthetic pyrethriods

Pyrethrum is derived from the dried flowers of the plant *Chrysanthemum cinearіaefolium.* The name given to the active insecticidal components of the dried flowers is known as pyrethrins. Chemically pyrethrins are organic esters formed by the combination of two carboxylic acids and three keto alcohols.

The synthesis of chrysanthemic acids and of cyclopentenolones opened up the possibility of obtaining synthetic pyrethroids, a remarkable class of insecticides.

The outstanding properties of pyrethrins are

- ✓ Rapid action
- ✓ Low mammalian toxicity
- ✓ Broad spectrum activity
- ✓ Lack of persistence
- ✓ Repellency

Allethrin is the first of its kind prepared by esterification of synthetic chrysanthemic acid with the alcohol allethrolone.

Allethrin had strong insecticidal activity (0.1 µg / insect) and removal of keto group gave another synthetic pyrethroid known as bioallethrin (0.02 µg / insect).

Bioresmethrin is an extremely active insecticide (0.005 µg / insect). This is photosensitive and consequently was not persistent. However when the isobutenyl group of bioresmethrin was replaced by the dichlorovinyl group, the resultant compound is NRDC134 which was more toxic to house flies and mustard beetles than the most known insecticides.

Permethrin was active against houseflies and mustard beetles and showed much greater photostability and consequently was a moderately persistent insecticide. It was the first synthetic pyrethroid effective as a seed treatment against wheat bulb fly.

Decamethrin was prepared by replacement of chlorine atoms by bromine and the introduction of ∝ cyano group from permethrin. This was discovered in 1974 is a potent insecticide known. (0.0003 µg / insect) 50

times more active than Pyrethrin I. This has reasonable photostability and very low mammalian toxicity.

The corresponding chloro derivative as the cis – trans mixture is known as **cypermethrin** which is a broad spectrum insecticide (dose 20-80 g /ha) with good residual activity on plants.

A survey of the esters of furylmethanol led to the discovery of insecticidal activity in a group of phenyl acetic acid esters and Japanese chemists at Sumitoma company introduced **fenvalerate** in 1974. Fenvalerate is a mixture of 4 isomers and is used at 20-150 g ai/ha against a wide range of pests and relatively stable in light.

American Cynamid introduced another phenyl acetic acid esters viz., **flucythrinate and fluvalinate.**

Bromination of the double bonds on decamethrin and cypermethrin gave tralomethrin and tralocythrin. Both are highly active – activity may be due to the *in vivo* conversion in to parent compounds.

Lambda Cyhalothrin has a comparatively high mammalian toxicity (LD 50 (Oral) 60 mg /kg). It is effective at very low doses (5-30 g ai/ha) against major insect pests in many crops. Little hazard to honey bees and this represents an important advantage over OP insecticides which are highly toxic to honey bees. At normal rates cyhalothrin shows low toxicity to birds with no accumulation in eggs or tissues and no effect on earthworms. The half life in soil is 3-12 weeks; in aerobic soils it undergoes extensive mineralization to CO_2. In flooded soil degradation was slower and only hydrolysis products were detected. No phytotoxicity towards major crops and controls a wide spectrum of lepidopteran pests. This is valuable for the control of plant virus vectors.

Tefluthrin is the first pyrethroid effective as a soil insecticide at doses of 12-150 g ai/ha. It is formulated as granules and may also be applied as foliar spray or seed dressing. Tefluthrin kills insects that are resistant to OP and carbamate insecticides. Low mam. toxicity LD_{50} =1500mg/kg.Little hazard to earthworms and birds but highly toxic to fish. Half life in soil is 4-12 weeks and there is no danger of residue accumulation.

Mode of action of pyrethroids

- ✓ The symptoms of insects poisoned by pyrethroids clearly show that the chemical attacks the insect's nervous systems.
- ✓ Pyrethroids cause hyper excitation followed by convulsions and death in arthropods.
- ✓ The rate and mechanism of metabolism has a major influence on the toxicology of a compound.
- ✓ In (rats) mammals pyrethroids are very rapidly metabolized by ester cleavage, oxidation hydroxylation.
- ✓ The synthetic pyrethriods are very expensive to prepare on a tonnage basis.
- ✓ The high insecticidal activity and low mammalian toxicity of pyrethroids are especially significant now that compounds stable to light and oxygen are potentially available.
- ✓ Their toxicity to fish is high. They are rapidly degraded in soil and have no detectable illeffects on soil microflora and microfauna. They are not active against mites.
- ✓ The major symptoms of pyrethroid poisoning in insects may be accounted by effects on the kinetics of nerve membrane sodium channels.
- ✓ The mean open times of these channels are prolonged with consequent hyperactivity of nerves.
- ✓ The synthetic pyrethroids have been found to be useful as early season sprays to control the variety of insects that occur on cotton including boll worms, leaf worms, jassids, thrips and whitefly. They are used in combination with an organo phosphorus insecticide as an ultra-low volume spray.
- ✓ They are non toxic to humans and animals. LD_{50} to rats is around 8000 mg/kg. They are used at only 50 g/ha. The cost/of treatment per hectare is low.