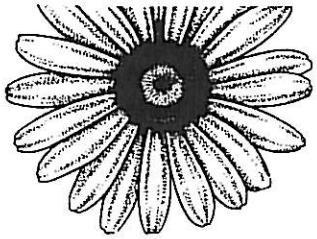
PYRETHROIDS



Natural pyrethrum has seldom been used for agricultural purposes because of its cost and instability in sunlight. Over the past two decades many synthetic pyrethrin-like materials have become available. They were originally referred to as *synthetic pyrethroids*. Currently, the better nomenclature is simply *pyrethroids*. These are very stable in sunlight and are generally effective against most agricultural insect pests when used at the surprisingly low rates of 0.01 to 0.1 pound (4.5 to 45 grams) active ingredient per acre (ai/A).

The pyrethroids have an interesting evolution, which is conveniently divided into four generations. The **first** generation contains only one pyrethroid, allethrin (Pynamin®), which appeared in 1949. Its synthesis was very complex, involving 22 chemical reactions to reach the final product.

The **second** generation includes tetramethrin (Neo-Pynamin®, 1965), followed by resmethrin (Benzofuroline®, in 1967) which is 20 times as effective as pyrethrum; then bioresmethrin, 50 times as effective as pyrethrum (1967), Bioallethrin® (1969) and finally phenothrin (Sumithrin®, 1973).

CINERIN I

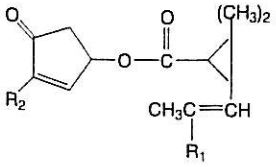
$R_1 = -CH_3$

$R_2 = -CH_2CH=CHCH_3$

CINERIN II

$R_1 = -C(=O)-OCH_3$

$R_2 = -CH_2CH=CHCH_3$



PYRETHRIN I

$R_1 = -CH_3$

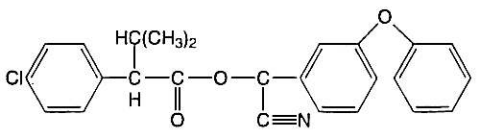
$R_2 = -CH_2CH=CHCH=CH_2$

PYRETHRIN II

$R_1 = -C(=O)-OCH_3$

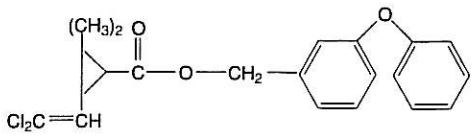
$R_2 = -CH_2CH=CHCH=CH_2$

ESFENVALERATE (Asana®)



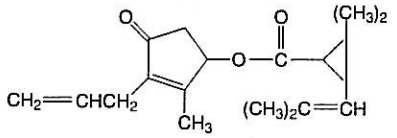
cyano(3-phenoxyphenyl)methyl-4-chloro-α-(1-methyl-ethyl)benzeneacetate

PERMETHRIN (Ambush®, Pounce®)



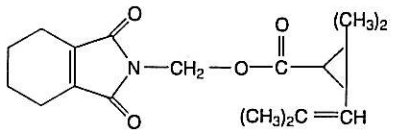
m-phenoxybenzyl (±)-*cis, trans*-3-(2,2-dichlorovinyl-2,2-dimethylcyclopropanecarboxylate

ALLETHRIN (Pynamin®)



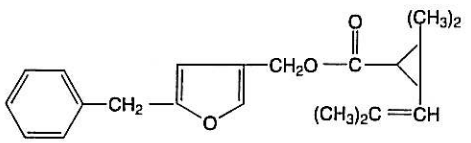
2-methyl-4-oxo-3-(2-propenyl)-2 cyclopenten-1-yl 2,2-dimethyl-3-(2-methyl-1-propenyl) cyclopropane-carboxylate

TETRAMETHRIN (Neo-Pynamin®)



(1,3,4,5,6,7-hexahydro-1,3-dioxo-2*H*-isoindol-2-yl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate

RESMETHRIN (Benzofuroline®)



(5-phenylmethyl-3-furanyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl cyclopropanecarboxylate

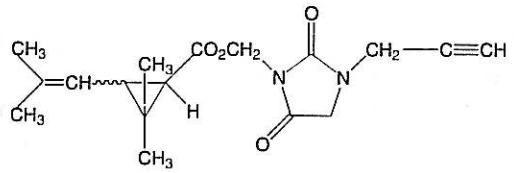
The **third** generation includes fenvalerate (Pydrin®, discontinued, Bellmark®) and permethrin (Ambush®, Astro®, Dragnet®, Flee®, Pounce®, Prelude®, Talcord® and Torpedo®) which appeared in 1972-73. These became the first agricultural pyrethroids because of their exceptional insecticidal activity (0.1 lb ai/A) and their photostability. They were virtually unaffected by the ultraviolet in sunlight, lasting 4-7 days as efficacious residues on crop foliage.

The **fourth** and current generation, is truly exciting because of their effectiveness in the range of 0.01 to 0.05 lb ai/A. These include bifenthrin (Capture®, Talstar®), *lambda*- cyhalothrin (Demand®, Karate®, Scimitar® and Warrior®), cypermethrin (Ammo®, Barricade®, Cymbush®, Cynoff® and Ripcord®), cyfluthrin (Baythroid®, Laser® and Tempo®), deltamethrin (Decis®, Deltagard®, K-Othrine®), esfenvalerate (Asana®, Hallmark®), fenpropathrin (Danitol®), flucythrinate (Cybolt®, Payoff®), prallethrin (Etoc®), tau-fluvalinate (Mavrik®, Klartan®), tefluthrin (Evict®, Komet®, Force® and Raze®), tralomethrin (Scout X-TRA®, Tralex®) and *zeta*- cypermethrin (Mustang®, Fury®). All of these are photostable, that is, they do not undergo photolysis (splitting) in sunlight. Because they have minimal volatility they provide extended residual effectiveness, up to 10 days under optimum conditions.

Recent additions to the **fourth** generation pyrethroids are acrinathrin (Rufast®), imiprothrin (Pralle®) which received U.S. registration in 1998 and the newest *gamma*-cyhalothrin (Pytech®) which is in development.

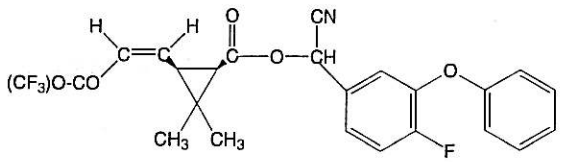
The pyrethroid structures resemble each other to some extent, as seen in the illustrations. Most of them are not significantly improved with the addition of pyrethrin synergists. The pyrethroids share similar modes of action, resembling that of DDT, by keeping open the sodium channels in neuronal membranes. There are two types of pyrethroids, Type I and Type II. Type I, among other physiological responses, has a negative temperature toxicity action. That is, they are more effective when the temperature is

IMIPROTHRIN (Pralle®)



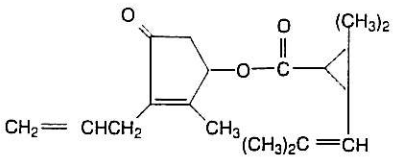
[2,5-dioxo-3-(2-propynyl)-1-imidazolidinyl]methyl 2,2-dimethyl-= 3-(2-methyl-1-propenyl)cyclopropanecarboxylate

ACRINATHRIN (Rufast®)



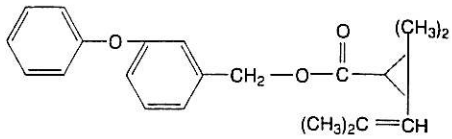
cyano(3-phenoxyphenyl)methyl 2,2-dimethyl-3-[3-oxo-3-[2,2,2 trifluoro-1-(trifluoromethyl)ethoxy]-1-propenyl]cyclopropanecarboxylate

***d-trans*-ALLETHRIN (Bioallethrin®)**



2-methyl-4-oxo-3-(2-propenyl)-2-cyclopenten-1-yl 2,2-dimethyl-3-(2-methyl-1-propenyl) cyclopropanecarboxylate

PHENOTHRIN (Sumithrin®)



(3-phenoxyphenyl)methyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropane-carboxylate

lowered. Type II, in contrast have a positive temperature toxicity, showing increasing kill with increase in temperature. More about this is given in Chapter 17, Modes of Actions for Insecticides.