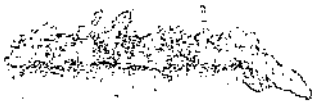
P A R T III

I N T R O D U C T I O N



In the earlier parts, the preparation and characterisation of some new organotin compounds have been reported. Since, triorganotin compounds exhibit a wide range of biological properties, some attempts will be described in the subsequent pages of the biological properties of some selected compounds, described in preceding pages. A brief review of some important biological properties (antifungal and acaricidal) may be given here.

Search for new pesticides is essential as even successful pesticides can loose their effectiveness due to growth of resistence of pests towards those pesticides. Moreover, consideration of environmental pollution may lead to discontinuance of some successful pesticides. In the search of new pesticides, organometallic compounds are increasingly gaining importance. Organomercurials have played an important role until recently as successful biocidal agents. But due to high mammalian toxicities and possibilities of biomethylation of mercury compounds, the use of organomercury compounds are now a days severely restricted and may ultimately be totally discontinued. Organotin compounds may replace organomercury compounds in some of their biocidal applications.

The principal advantages of the organotin agrochemicals which mainly possess prophylactic action (1) are their relatively low phytotoxicity, their generally low toxicity to non-target organisms and the lack of resistance by croppests to these chemicals.

Furthermore, triorganotin compounds undergo degradation in the environment eventually, to form harmless inorganic tin residues.

A. Antifungal Activity

As pointed out earlier, the first investigation in the field of antifungal activity of organotin compounds were carried out by van der Kerk and Luijten in 1954 (2). It was found by them that only triorganotin (R_3SnX) derivatives are the powerful fungicides. A number of tetra-, di-, and monosubstituted organotin compounds were tested and all showed very little or practically no activity, compared to triorganotin derivatives.

Zedler and Beiter (3), Hartel (4), Kubo (5) and Kaars Sijpestijn (6) have also studied the antifungal activity of triorganotin derivatives against a number of plant pathogenic fungi.

Although many phytopathogenic fungi prove to be highly sensitive to organotin compounds in vitro, some parasitic fungi e.g. Phytophthora in festans on potato, Corcospora beticola on sugar beet and Septoria apii on celeriac etc are at present successfully controlled by organotins under field conditions.

Experiments with a series of organotin compounds on obligate parasitic fungi have been carried out by Hartel (4) and by Tempel (7). The former found that Peronospora on grape is more effectively suppressed by tributyl tin than by trimethyl tin or triethyl tin compounds. Against powdery mildew on cucumber the triethyl tin

derivative appeared to be optimally active whereas the tributyl and triphenyl tin derivatives were the most effective compounds against powdery-mildew on barley and the tripentyl and trihexyl tin derivatives against apple mildew.

In the symmetrical trialkyltin series the propyl and butyl compounds generally are the most active derivatives, the presence of these particular groups are not the necessary condition for high activity. This becomes manifest when unsymmetrical trialkyl tin acetates were tested (8). From these investigations of van der Kerk and Luijten, it was concluded that among the trialkyl tin acetates, maximum activity is associated with a total number of 9 to 12 carbon atoms in the alkyl group regardless of the nature of the individual group.

Regarding the triaryl tin compounds, tri-m-tolyltin acetate and tri-p-tolyltin acetate appeared to equal triphenyltin acetate in activity, whereas tribenzyl and tris (2-phenyl-ethyl)tin acetate were also considerably active (9).

Interesting independent work by Hartel (10) with trialkyl and triaryl tin compounds showed that in the laboratory, trialkyl and particularly tributyl tins are better fungicides than triaryl tin compounds but that the reverse is true in the field. This has been ascribed to the lower stability and the higher volatility of the former. Moreover, triaryl tin compounds are less phytotoxic than trialkyl tin compounds.

In the early 1960's the first organotin compound, triphenyltin acetate was introduced under the trade name, 'Brestan' commercially by Farbwerke Hoechst A.G. and shortly later Philips Duphar N.V. introduced triphenyl tin hydroxide under the trade name 'Du-Ter' (11). In 'Brestan Super', triphenyl tin acetate is combined with manganese ethylene bis dithiocarbamate (maneb). A similar preparation of Fisons Pest Control, called 'Fennite', combines triphenyl tin hydroxide with maneb . A number of commercial preparations based on these active ingradients are at present marketed under different trade name. The organotin fungicides have almost completely ousted the formerly dominating inorganic copper fungicides for the control of certain diseases of potato, sugar beet and celeriac. Later on, it was also found that a number of important tropical plant diseases viz. those in coffee, rice, groundnut, banana and onion can be controlled successfully (12) by organotins.

The problem of toxic residues from sprays with organotin compounds has been thoroughly investigated. An important feature is the relatively short half life of the compounds on plant leaves in the field. In potato tubers, less than 0.1 mg of tin per Kg was found after the foliage had been repeatedly sprayed with triphenyl tin acetate, after ... days

In Kenya, for controlling the leaf rust disease of coffee, copper based fungicides are used extensively at present. But many farmers are concerned that a build up of copper may occur in the soil after many years of repeated spraying with copper fungicides,

resulting the growth inhibition of cultivated plants. Hence, alternatively, 'Du-Ter Extra' [47.5% W.P. (Wettable powder) active ingredient triphenyl tin hydroxide] has been recommended by the Kenyan Coffee Research Foundation for the treatment of leaf rust and also as an anti-feedant for the giant looper caterpillars that attack the foliage of Coffee plants (13).

Recently Smith et al (14) reported organotin pyridine-2-carboxylates and substituted triazine derivatives (100 ppm) can control coffee leaf rust and coffee bacterial blight disease in vitro.

From the available literature it seems that much work has not been done for controlling the plant pathogenic fungi by using organotin compounds. Srivastava (15) reported that diphenyltin dichloride is the most active fungi toxic agent against Collototrichum falcatum , among diaryltin dichlorides and their activities on complexation, formation with 2,2'-bipyridyl and 1, 10-phenanthroline are slightly increased. Mehrotra (16,17) reported the fungicidal and bactericidal properties of some new organotin compounds. Ram Kishun et al (18) tried to control the bacterial leaf spot of sunnhemp by using the organotin preparation 'Brestan-60' and 'Du-Ter', and found that the compounds failed to inhibit the growth of the causal organism Xanthomonas Patelii in vitro. Mohanty and Mohapatra (19) found the high effectiveness of 'Brestanol' (triphenyl tin chloride) for controlling the blast disease of fingermillet. 'Brestan-60' with high effectiveness for controlling the tikka disease of ground nut and early blight of potato have

been reported by Addy (20). In the present investigation, some organotin compounds were used for determining their antifungal activity against some fungal species *in vitro*.

B. Miticidal Activity

Mites like insects are another important and significant type of pest of crops and plantation, causing serious losses both in terms of quality and quantity of product. The insect pests have received sufficient attention while mites have long remained rather neglected probably due to their microscopic size and obscure nature, even though they have the potentiality of causing extensive damages in agriculture. Majority of mites feed on plants causing various types of direct damages like loss of chlorophyll, appearance of stipplings of bronzing of foliage, stunting of growth producing plant deformities and reduction of yield. Many of these are known as vector of plant viral diseases causing heavy loss to growers.

The plant mites have drawn attention to the workers since the time of Homer who first referred to them as early as 850 B.C. Linnaeus in 1758 listed nearly thirty species in his book "Systema Naturae". The importance was further realised in 19th and 20th centuries through the outstanding works of Kramer Megnin Canestrine, Berlese, Oudemans, Evans (1957), Evans et al (1961), Krantz (1970), Hughes (1976), Gupta (1985). Jeppson et al (1975) brought out a comprehensive book on mites injurious to economic plants (25).

Mites have a high reproductive potential, may have several generation during a season, regarded as genetically plastic organism and new races are formed continually, it undergoes continuous chemical selection. It was found at after the repeated use of a pesticide group resistance occurs quite rapidly. When resistance develops to currently used acaricides, new compounds presumably with different modes of action are required which will last for sometime to protect crops from mite nuisances.

The principle of mite control and the different chemicals used for this purpose have been discussed elaborately by Jeppson (1965) (26).

Sulphur vapour had been used as an acaricide for quite sometime successfully. However, under certain conditions it shows phytotoxicity to the host plant, same in the case with petroleum oil and dinitrophenol. The use of synthetic organic pesticide started during 1940's. The first to be used was "Neotran". Later several others, as 'Ovex', 'Aramite', 'Deneton', 'Chlorobenzilate', 'Dicofol', 'Fenson', 'Dioxathion ', 'Tetradifon', 'Carbophenothion', 'Ethion', 'Binapacryl', 'Movestan', 'Galecron', etc appeared.

The principles involved in the chemical control of the mites are basically the same as applicable in case of insects. Use of improved agricultural practices application of DDT and reduction of predator population due to random use of broad spectrum pesticides are some of the reasons which necessitated to the adaptation of more improved chemical control of the mites.

Acaricides are some what specific in their action. A certain pesticide may be effective for a certain group of mites but may be quite ineffective against a related group. The acaricides not only kill by direct contact and penetration through its integument but also as stomach poison and as fumigant. Therefore, before a pesticide is spread some factors such as its mode of action, its translocation property if any, its residual property, the plant on which it is to be sprayed, the stage of the mite to be sprayed, climatic condition prevailing before and after spraying, population migration in relation to rainfestation etc. should be considered to assess the efficacy of the acaricide.

At present there has been much criticism of the use of some groups of acaricides because of adverse ecological effects. The organo chlorines have been found to be most hazardous and several countries have either banned or restricted their uses. The use of less persistent organophosphorous compounds is also under hard scrutiny. In this connection the search for an alternate class of acaricides with different mode of action, specific and less harmful to the environment is being carried out in different countries for a long time. In the year 1968 a major break through in the field of agriculture was obtained with the development of a completely new type of miticide - 'Plictran'. The product based on trycyclohexyltin hydroxide was introduced into the U.S. market as a result of the joint research effort by Dow and M & T Chemicals (27,28).

As it has been discussed earlier organotin compounds were already known for their biocidal uses and the commercial success of 'Plictran' encouraged other research workers in this area. Species specificity of organotin derivatives suggests that when R = C_6H_{11} (cyclo) or $PhMe_2CH_2$ of a R_3SnX compound, the compound would be a powerful selective miticide. This led to the introduction of the few other organotin miticides. These are 1-tricyclohexyl stannyl 1,2,4-triazole ('Peropal') (29) and bis (2-methyl 2-phenyl propyl tin) oxide (30) commonly referred to as bis (neophyltin) oxide ('Vendex' or 'Torque').

'Plictran' is a specific contact acaricide with a moderate initial toxicity and with repellent anti feeding properties. The duration of protective action lasts for 20 days or more. It was first registered for the control of mites in apples and pears etc. Now it is registered in many European and in other third world countries as an acaricide on citrus, stone fruits and hops as well as apples and pears. The commercial formulation consists of wettable powders which are readily dispersed in water. The active ingredients are applied at a very low concentration e.g. at rates of 2-3 ounce per 100 gallon of spray (15 to 22.5 gm/100 litre water) registered in the U.S. market (31,32,33). 'Plictran' was found to be very effective in controlling red spider mite in lady's finger compared to "Monocroptophos" 36 WSC, 'Carbendenzim' 50 WP and urea. It's efficacy was not diminished when mixed with other agro chemicals. The safety of 'Plictran' to the Coccinillid mite predator, Stethorus sp. was also confirmed during the investigation (34). 'Plictran'

was tested (35) for its effectiveness in comparison to Malathion, oxydemeton methyl and wettable sulphur against Tetranychus cucurbital. A significant reduction of mite population was observed in plots treated with 'Plictran' 50 WP after 1,3,7,10 days of spraying while others did not give any control of the pest; no phytotoxicity of the treated plants was observed. Prevention of Panonychus ulmi and apple-rust mite with 'Plictran' along with 'Vendex' was very significant (36). Evaluation of 'Plictran' against the pink tea-mite (Acaphylla theae) was as effective as standard 'Dicofol' and 'Ethion' (37). 'Plictran' had toxicological parameter to those of chlorine and sulphur containing preparations and had a high ovicidal activity and was highly toxic to mobile phases of the spider mite (38). Periodic application of 'Plictran' caused no resistance development even after ninety consecutive generation and was effective against spider mite population resistant to others especially phosphorous-containing acaricides. The use of 'Plictran' was recommended in rotation with 'Dicofol' and 'Arex', where a resistance to phosphorous-containing and chlorine containing acaricides had developed. Spraying Cotton plants (39) with Zool, 03% Plictran per hectare controlled spider mite by 96% to 96.3% and prevented oviposition, and also showed low toxicity to beneficial entomo-acariphages. This phenomenon was also observed (40) on Strawberries in Southern California when 'Plictran' at 0.25 and 0.75 lb/acre was applied to Tetranychus urticae. Significantly fewer T. urticae occurred in plots receiving 'Plictran' at 0.75 lb/acre than at 0.25 lb/acre. The yields were greater than that of untreated control.

Similar result was obtained (41) when 'Murfite' (Cyhexatin + Murfite mixture; 300 + 160 g/ha) and Cyhexatin (250 g/ha) was applied in the strawberry crop yield with cyhexatin. Residue bioassays with 'Plictran' (42) along with 'Propargite', 'Dicofol', 'Carbophenothion', 'Hexakis' and 'Abamectin' were conducted against three populations of two spoted spider-mites. Behavioural responses (Wulf-off and spin-down) was significantly greater than that of control with 'Plictran', 'Hexakis' and 'Carbophenothion'. Cyhexatin was compared for its toxicity (43) to 'Chloropropylate', 'Azinophosmethyl', 'Methidathion', 'Fervalerate' and 'Benomyl' against 'Panonychus ulmi Tetranychus urticae, Aculus fockeri, Aculus finlandicus. For all above Plictran was highly toxic at the level of their LC_{95} values and the application concentrations used in orchards. Studies on the efficacy of three acaricides (44) on lady's finger revealed that the best result was obtained with 'Plictran' (350, 400 g/ha) and its effect lasted even after 14 days of spraying. One week after spraying all other treatments 'Plictran' (200, 250, 300 g/ha) were found to be on per with others and may even superior to 'Dicofol' 18.5 E.C. and 'Ethion' 50% E.C.

"Peropal" is most effective against the members of Tetranychidae. At 0.004, 0.02 and 0.1% concentration it caused 160% mortality of Tetranychus urticae sprayed once at 0.025% and 0.0025% it persisted long enough to kill 100% of T. urtical population. It mainly acts as contact poison with a merked repellent effect (45). Green house experiments were performed (46) to establish a comparison

of the effectiveness of 'Peropal' against three 'Tetranychus urticae' strains of varying sensitivity to conventional acaricides. Results showed that 'Peropal' was effective against a number of mite species (46).

'Vendex' applied (47) at 2-3 lb/acre to citrus orchards controlled citrus rust mites upto four months. It is also effective against organophosphorous and organochlorine resistant mites showing low toxicity to beneficial mites and honey bees.

As a consequence of wide application of organotin acaricides it is a evident that some resistance might be developed by the mite towards these acaricides. It has been found that (48) Tetranychus urticae failed to develop resistance against 'Plictran' and 'Peropal' over 100 generations even after treated for 40 times whereas over after 18-23 generations resistance to 'Actellic' and 'Etaphos' increased 360 and 1000 fold respectively.

Acaricides show variations in effectiveness against eggs and adults. The egg is generally highly resistant to usual contact acaricides as the eggs have a complex protective membrane surrounding the embryo, which possess difficulty in the penetration of the acaricides, thus it becomes difficult to destroy the eggs along with the adults. But if the eggs are not destroyed completely there remain the chance of rainfestation. So it is important to assess the effectiveness of acaricides as an ovicides i.e. they should possess lethal action on the eggs, as indicated by the cessation of embryonic development.

E X P E R I M E N T A L

Materials and Methods:

A. Fungicidal Activities

(i) Compounds:

Triphenyltin N-hydroxy succinimide, triphenyltin N-hydroxy phthalimide and tributyltin N-hydroxy phthalimide reported in earlier section, have been tested for fungi toxicities.

(ii) Organisms:

(a) *Helminthosporium oryzae*

Breeda de Haan — causal organism of brown leaf spot disease of rice.

(b) *Alternaria solani* (E II and Mart) Jones and Grout — causal organism of early blight disease of potato.

(iii) Culture Media:

Solid media [malt extract agar (21)]:

20 g malt extract (Difco) was boiled in water till dissolved. 20g agar agar (Kobe-Japan) was added and boiled until agar agar was well dissolved. 0.05g chloramphenicol was suspended in 5 ml of 95% alcohol and added to the medium as anti bacterial agent. The volume of the medium was then made upto 1 litre by addition of water. pH of the medium was adjusted with sodium hydroxide to 6.5. Medium was sterilized at 15 p.s.i. for 20 minutes.

4. Anti fungal Activities of selected Compounds in vitro.

Anti fungal activities of the compounds were tested following the growth inhibition studies.

Growth inhibitions were studied following the poisoned food technique (22). Acetone solution of suitable quantity of the compounds in sterile distilled water was incorporated into melted malt agar so as to get the desired concentrations of the compound in the media. Media with desired concentrations of compound were poured in petri plates and after solidification were inoculated at the centre with uniform discs (7 mm) of mycelia, punched out with a sterile cork borer from the advancing zone of a culture test fungus. Three replications on each test with appropriate control under same conditions were maintained. The petri plates were then incubated at 30 ± 1°C in dark. Linear growth of the fungal discs were measured after regular intervals and the percentage of inhibition over control was calculated following the equation

$$\frac{C-T}{C} \times 100$$

[where C = control, T = treated] given by Vincent (23).

5. Determination of ED_{50} and ED_{95}

The ED_{50} [effective dose for 50% inhibition] and ED_{95} [effective dose for 95% inhibition] values (μg/ml) were calculated by least-squares regression analysis using computer.

B. Phytotoxicity on Rice

(i) Seed Sample:

Healthy rice seeds of PUSA 2-21 variety collected from Chinsurah Rice Research Farm, Hooghly, West Bengal, were used in the present investigation.

(ii) Compounds:

Triphenyl tin N-hydroxy succinimide, Triphenyl tin N-hydroxyphthalimide and Tributyl tin N-hydroxy phthalimide were used for determining their phytotoxic effect on rice.

(iii) Effect on seed germination :

Healthy rice seeds were dipped in compound suspension of 100, 50 and 25 ppm concentration for 1, 4 and 8 hours. For control, water with requisite amount of acetone was used. The treated seeds were then placed on moist three layered filter paper in closed petriplates. Plates were incubated at 30 ± 1°C. 100 seeds were maintained for each treatment. After 8 days the germinated seeds were counted. Seeds producing a root or a coleoptile were recorded as germinated. Three replications of each test with appropriate control under same conditions were maintained.

C. Miticidal Activities

(1) Compounds:

Tricyclohexyltin N-hydroxy phthalimide, Tetracyclohexyl 1:3 di-N-hydroxy succinimido distannoxane, Dicyclohexyltin diphenyl glycolate and plictan.

(ii) Organism : Green mite

(iii) Determination of acaricidal activity

(a) Collection of specimens

The mite infested leaves or plant parts were brought to the laboratory in polythene bags after tightly closing the mouth of the bag with a rubber band.

(b) Mounting for microscopical examination

Before examining under microscope, high degree of transparency in the mite is needed. This was done by placing the specimen to be examined on a slide and putting a drop of lactic acid over it. The slide was then gently warmed for a few seconds, which reduced the normal opacity of mites, appendages extended. It was then carefully examined under the microscope.

(c) Rearing

Mite was reared in the laboratory in large numbers for experimental purpose. Rearing was one by two methods. These were cultured in bean seedlings, kept in pots. The adult mites were picked up from the infested leaves or plant parts and transferred to the leaves of potted seedlings or the infested plant parts were kept on top of the seedlings. When the detached part dried up the mites migrated to the leaves of the potted seedlings. Petroleum jelly was applied arcund the base of the stem to prevent the escape of the mites.

The other method used were keeping excised leaves of the host plant in petridish (15 cm diameter) over a cotton pad super saturated with water. Leaf was periodically changed and water was added daily to maintain a thin film of water at the margin of leaf to prevent the escape of mites. Mites were transferred on to the leaves by picking up with a fine brush moistered with water.

(d) Slide-dip method for contact toxicity assessment

This method was originated by Voss (56) improved by Dittrich (57). Adult females of known ages were used for the screening. This was done by collecting eggs over 4-5 hours and rearing adults of a new generation which appeared 6-7 days later, at temperature ranging from 27°C to 29°C.

For the test, microscope slide was covered with a strip of double-sided scotch-tape and twenty adult females were stuck on to the tape, on the dorsal side, in two rows of ten. The prepared slides were dipped, for 5 seconds in serial concentrations of the compound being tested. Slides were drained, by placing on edge for 15 minutes, at room temperature. Mortality counts were made after 24, 48 and 72 hours. Mites not showing movement of appendages when touched by a fine brush were recorded as dead. Three tests were conducted at each dosage level. The treated slides were placed on the top of a moist cotton-pad in petri-dishes, which contained water to maintain the humidity. For the control set, slides were dipped in distilled water for the same length of time.

(e) Method of assaying contact plus stomach toxicity

The method followed here was that of Mansour and Plant (58). The mites were released on fresh leaves and sprayed with the different concentration of the compound. Each test was replicated thrice and mortality counts were made after 24, 48 and 72 hours.

(f) Determination of LC_{95} and LC_{50}

The LC_{50} and LC_{95} [lethal concentration for 50% and 95% mortality] (μg/ml) were calculated as earlier using least square regression analysis using a computer.

R E S U L T S

A. FUNGICIDAL ACTIVITY

The triorganotin compounds, particularly triphenyl and tributyltin derivatives, show excellent fungicidal activities. In the fungi toxicities, the anionic part (X) of R_3SnX does not influence the activity considerably. Though more work is necessary, it seems the triorganotin moieties, as expected, retain its fungicidal properties in Triphenyl tin N-hydroxy phthalimide, Triphenyl tin N-hydroxy succinimide and Tributyltin N-hydroxy phthalimide against Alternaria solani and Helminthosporium oryzae.

The results obtained have been tabulated as follows:

TABLE - I

Effect of Triphenyltin N-hydroxy Succinimide on growth of Alternaria solani

Concentration (µg/ml)	Percentage of Growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
1.56	100.00	100.00	100.00
1.25	100.00	100.00	98.92
0.63	97.90	92.50	86.90*
0.31	93.42	78.90*	72.70*
0.13	71.40*	62.50*	55.00*
0.06	56.30*	49.11*	40.00*
0.03	42.20*	35.24*	29.07*
ED_{50}	0.05 µg/ml	0.07 µg/ml	0.09 µg/ml
ED_{95}	0.38 µg/ml	0.71 µg/ml	0.96 µg/ml
Regression constants : $Y = mx + C$			
m	48.66	43.65	44.98
C	115.52	101.62	95.86
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - II

Effect of Triphenyltin N-hydroxy phthalimide on growth of *Alternaria solani*

Concentration (µg/ml)	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
6.25	100.00	100.00	100.00
3.13	100.00	100.00	96.86
1.56	100.00	99.20	91.11
1.25	100.00	98.16	87.75*
0.63	97.12	87.31*	78.32*
0.31	82.60*	73.35	64.24*
0.13	65.30*	60.21*	52.34*
0.06	50.72*	46.26*	40.12*
0.03	36.28*	32.90*	29.28*
ED_{50}	0.06 µg/ml	0.08 µg/ml	0.11 µg/ml
ED_{95}	0.56 µg/ml	0.94 µg/ml	1.90 µg/ml
Regression Constants : $Y = mx + C$			
m	44.42	41.22	36.69
C	106.77	95.97	84.72
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - III

Effect of Tributyl tin N-hydroxy phthalimide on growth of Alternaria solani

Concentration µg/ml	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
3.13	100.00	100.00	100.00
1.56	100.00	100.00	99.90
1.25	100.00	99.90	93.61
0.63	98.19	96.20	89.20*
0.31	84.48*	83.12*	82.97*
0.13	67.21*	65.50*	62.11*
0.06	51.50*	49.50*	46.19*
0.03	34.10*	33.71*	33.10*
ED_{50}	0.06 µg/ml	0.06 µg/ml	0.07 µg/ml
ED_{95}	0.47 µg/ml	0.51 µg/ml	0.69 µg/ml
Regression constants : Y = mx + C			
m	50.30	49.59	45.20
C	111.39	109.28	102.04
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - IV

Effect of Triphenyltin N-hydroxy Succinimide on growth of *Helminthosporium oryzae*

Concentration (µg/ml)	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
15.63	100.00	100.00	100.00
12.50	100.00	100.00	99.34
10.00	100.00	100.00	97.79
6.25	100.00	95.95	95.20
3.13	96.82	87.14*	75.50*
1.56	78.20*	65.21*	58.00*
1.25	73.43*	58.96*	52.22*
0.63	49.31*	38.64*	33.43*
0.31	34.00*	21.29*	15.24*
0.13	11.62*	3.11	1.59
0.06	0.00	0.00	0.00
ED_{50}	0.35 µg/ml	0.88 µg/ml	1.15 µg/ml
ED_{95}	2.98 µg/ml	4.25 µg/ml	6.38 µg/ml
Regression constants Y = mx + C			
m	61.29	65.83	60.50
C	65.86	53.58	46.27
r	0.99	0.99	0.99

* Data have been used for regression analysis.

TABLE - V

Effect of Triphenyltin N-hydroxy phthalimide on growth of *Helminthosporium oryzae*

Concentration (μg/ml)	Percentage of inhibition over control after		
	24 hrs	48 hrs	72 hrs
6.25	100.00	100.00	100.00
3.13	100.00	100.00	98.48
1.56	93.20	86.90*	82.71*
1.25	87.50*	80.90*	76.25*
0.63	74.70*	66.90*	64.90*
0.31	56.25*	53.48*	49.09*
0.13	37.50*	32.12*	30.23*
0.06	24.61	18.20*	14.04*
0.03	8.26	6.11	4.12
.02	0.00	0.00	0.00
ED_{50}	0.21 μg/ml	0.28 μg/ml	0.33 μg/ml
ED_{95}	1.73 μg/ml	2.31 μg/ml	2.79 μg/ml
Regression Constants : $Y = mx + C$			
m	49.36	48.85	48.28
C	83.26	77.26	73.47
r	0.99	0.99	0.99

*Data have been used for regression analysis

TABLE - VI

Effect of Tributyl tin N-hydroxy phthalimide on growth of *Helminthosporium oryzae*

Concentration (µg/ml)	Percentage of growth inhibition over control after		
	24 hrs	48 hrs	72 hrs
6.25	100.00	100.00	100.00
3.13	100.00	100.00	98.22
1.56	100.00	94.02	88.50*
1.25	100.00	87.50*	84.17*
0.63	100.00	84.21*	75.09*
0.31	98.00	72.10*	66.46*
0.13	85.85*	60.00*	50.60*
0.06	77.00*	51.00*	39.49*
0.03	66.00*	40.00*	28.03*
0.02	52.01*	32.03*	15.21*
ED_{50}	0.01 µg/ml	0.06 µg/ml	0.13 µg/ml
ED_{95}	0.18 µg/ml	1.64 µg/ml	2.22 µg/ml
Regression Constants: $Y = mx + C$			
m	40.51	31.73	36.03
C	124.93	88.16	82.46
r	0.99	0.99	0.99

* Data have been used for regression analysis

SUMMARY OF THE RESULTS

TABLE - VII

ED_{95} Values in μg/ml for growth inhibition against *Alternaria solani*

Compound	ED_{95} values μg/ml		
	24 hrs	48 hrs	72 hrs
Triphenyl tin N-hydroxy succinimide	0.35	0.71	0.96
Triphenyl tin N-hydroxy phthalimide	0.56	0.94	1.90
Tributyl tin N-hydroxy phthalimide	0.47	0.51	0.69
Tributyltin (24) acetate	0.77	0.78	0.98

TABLE - VIII

ED_{95} Values (μg/ml) for growth inhibition against *Helminthosporium oryzae*

Compound	ED_{95} values μg/ml (.. hrs)		
	24	48	72
Triphenyl tin N-hydroxy succinimide	2.98	4.25	6.38
Triphenyltin N-hydroxy phthalimide	1.73	2.31	2.79
Tributyltin N-hydroxy phthalimide	0.18	1.64	2.22
Tributyltin (24) acetate	0.38	0.71	0.96

B. PHYTOTOXICITY ON RICE

The *in vitro* tests of fungicidal activity have limited value to the agricultural pesticide chemist because it circumvents the important consideration of phytotoxicity. A fungicide which causes serious phytotoxicity under varied environmental conditions would be a total failure.

TABLE - IX

Effect of triphenyl tin N-hydroxy succinimide, Triphenyltin N-hydroxy phthalimide and Tributyltin N-hydroxy phthalimide on rice seed germination

Compound	Conc. (µg/ml)	Percentage of germinated seed, treated for		
		1 hr	4 hrs	8 hrs
Triphenyl tin N-hydroxy succinimide	100.00	86	84	76
	50.00	88	88	82
	25.00	88	88	86
Triphenyltin N-hydroxy phthalimide	100.00	86	82	78
	50.00	86	82	82
	25.00	88	84	82
Tributyltin N-hydroxy phthalimide	100.00	72	70	64
	50.00	88	84	80
	25.00	88	86	82
Control		91	91	91

C. MITICIDAL ACTIVITIES

It has been pointed out earlier, that Tricyclohexyl tin compounds show excellent miticidal activities. In present investigation, Tricyclohexyl tin N-hydroxy phthalimide, Tetracyclohexyl 1:3 di-N-hydroxy succinimido di stannoxane (obtained from reaction of Tricyclohexyl tin hydroxide and N-hydroxy succinimide) Dicyclohexyl tin diphenyl glycolate (obtained from Tricyclohexyl tin hydroxide and diphenyl glycolic acid) were prepared. Some preliminary experiments were carried out with these compound against one (non identified) green mite, collected from trees of the locality. It may be pointed out here that these results were preliminary in nature, hence no positive conclusion could be made so far about the miticidal activities of these compounds, except that the miticidal activity is substantially reduced compared to 'Plictran' (Tricyclohexyl tin hydroxide) due to the nature of these ligands. It was somewhat surprising that the Tetracyclohexyl 1:3 di-N-hydroxy succinimido distannoxene gave comparable activity to Tricyclohexyl tin N-hydroxy phthalimide. Further investigation are necessary to draw useful conclusions about the miticidal activities of these compounds. However, we present here the results of experiment carried out so far.

TABLE - X

Contact toxicities of Tricyclohexyl tin N-hydroxy phthalimide for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	60	65	67.5
20	50	55	55
10	40	42.5	45
5	32.5	32.5	35
2.5	20	27.5	27.5
1.2	17.5	22.5	27.5
0.6	0.5	7.5	7.5
LC_{95} (µg/ml)	672.77	571.42	494.70
LC_{50} (µg/ml)	20.98	15.43	13.36
Regression Constants : Y = mx + C			
m	29.8812	28.6883	28.6935
C	10.4971	15.9076	17.6897
r	0.9912	0.9905	0.9813

TABLE - XI

Contact toxicities of Tetracyclohexyl 1:3 di N-hydroxy succinimido di stanoxane for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	57.5	67.5	72.5
20	55	60	62.5
10	55	55	57.5
5	40	45	47.5
2.5	30	35	40
1.2	27.5	30	32.5
0.6	7.5	20	22.5
LC_{95}	738.02 µg/ml	501.21 µg/ml	382.27 µg/ml
LC_{50}	13.50 µg/ml	8.22 µg/ml	6.31 µg/ml
Regression Constants : Y = mx + C			
m	25.8965	25.2143	25.2553
C	20.7270	26.9208	29.7813
r	0.9494	0.9948	0.9957

TABLE - XII

Contact toxicities of Dicylohexyl tin diphenyl glycolate for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	50	55	57.5
20	45	47.5	50
10	42.5	45	45
5	30	35	35
2.5	12.5	12.5	1.5
1.2	0.25	7.5	10
LC_{95} (µg/ml)	779.9025	641.1089	420.7501
LC_{50} (µg/ml)	30.3411	23.6638	21.7674
Regression Constants : Y = mx + C			
m	31.9147	31.4060	34.9863
C	2.7014	6.8455	3.1951
r	0.9576	0.9578	0.9218

TABLE - XIII

Contact plus stomach toxicities of 'Plictran' for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	83.34	90.00	90.00
20	76.67	83.34	86.67
10	56.67	63.34	66.67
5	46.67	53.34	60.00
2.5	16.67	33.34	36.67
1.2	13.34	23.34	26.67
LC_{95}	65.19 µg/ml	50.31 µg/ml	33.71 µg/ml
LC_{50}	7.57 µg/ml	4.78 µg/ml	3.89 µg/ml
Regression Constant : $Y = mx + C$			
m	48.1501	44.0426	48.0012
C	7.6448	20.0535	21.6632
r	0.9756	0.9885	0.9875

TABLE - XIV

Contact plus stomach toxicities of Tricyclohexyltin N-hydroxy phthalimide for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	50	63.34	73.34
20	36.67	46.67	56.67
10	36.67	40.00	53.34
5	26.67	33.34	40.00
2.5	13.34	16.67	23.34
1.2		13.34	20.00
LC_{95}	—	579.29 µg/ml	217.90 µg/ml
LC_{50}	—	20.88 µg/ml	10.45 µg/ml
Regression Constants : Y = mx + C			
m	25.9445	31.1819	34.1194
C	6.3622	8.8475	15.2194
r	0.9682	0.9876	0.9861

TABLE - XV

Contact plus stomach toxicities of Tetracyclohexyl 1:3 di N-hydroxy succinimido distannoxane for Green mite

Concentration (µg/ml)	Percentage of mortality after		
	24 hrs	48 hrs	72 hrs
50	50.00	56.67	63.34
20	43.34	50.00	63.34
10	43.34	46.67	50.00
5	16.67	20.00	33.34
2.5	3.34	06.67	13.34
LC_{95}	639.81 µg/ml	326.84 µg/ml	190.15 µg/ml
LC_{50}	34.08 µg/ml	23.26 µg/ml	14.05 µg/ml
Regression Constants : Y = mx + C			
m	35.3368	39.2104	39.7813
C	4.1569	3.5886	4.3338
r	0.9667	0.9745	0.9762

R E F E R E N C E S

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APPENDIX

Chemical name of the active ingredients of some commercial pesticides.

	Trade name	Chemical name of the active ingredient
1.	Breston	Triphenyltin acetate
2.	Du-Ter	Triphenyl tin hydroxide
3.	Brestanel	Triphenyl tin chloride
4.	Dicofol	2,2,2-Trichloro-1,1-bis(4-chlorophenyl) ethanol.
5.	Tetradifon	4-chlorophenyl 2, 4, 5-trichlorophenyl sulphone.
6.	Carbophenothion	S-4-Chlorophenyl thiomethyl 0,0-diethylphosphorodithioate.
7.	Ethion	0,0,0,0-Tetraethyl S, S'-methylene bis(phosphorodithioate)
8.	Binapacryl	2-Sec-Butyl-4,6-dinitro phenyl 3-methyl but-2-enoate
9.	Galecron	N-(4-chloro-o-tolyl)-N-N dimethyl formamidine.
10.	Aramite	2-(4-tert-Butyl phenoxy) 1-methyl ethyl 2-chloro ethyl sulphite.
11.	Chlorobenzilate	Ethyl 4,4'-dichlorobenzilate.