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REVIEW

Organotin compounds in agriculture since 1980 Part I. Fungicidal, bactericidal and herbicidal properties

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The object of this review paper is to provide a guide to agrochemical research involving organotin compounds which has been performed since 1980. The information is presented in tabular form and Part I is divided into main sections as indicated by the title. Each section is then subdivided to cover the various commercial organotin compounds. A final subsection lists investigations involving novel compounds. A table of the contents has been provided to enable ease of reference.

Keywords: Agrochemicals, organotin, triphenyltin, tricyclohexyltin, trineophyltin, fungicide, bactericide, herbicide

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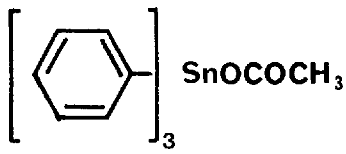
Part 1—Fungicidal, bactericidal and herbicidal properties

INTRODUCTION

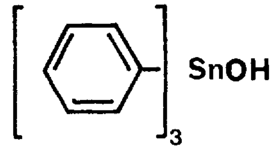
Organotin compounds have a wide range of industrial applications.[1] It has been estimated[2] that some 35 000 tons per year are currently being produced and that of that figure agrochemicals represent 3000 tons per year.[1]

The use of organotins in agriculture was pioneered in the 1950's and early 1960's by van der Kerk and co-workers.[3–7] The first commercial products were introduced during the early 1960's: triphenyltin acetate (fentin acetate: Brestan) by Hoechst and triphenyltin hydroxide (fentin hydroxide: Duter) by Philips Duphar. Both compounds are effective against almost the same range of fungi as the copper fungicides, but at about one-tenth the dosage.[8] They are also recommended for the control of leaf spot on sugar beet and celery, blast on rice, berry disease on coffee and for algal control on paddy rice.[8] A third triphenyltin compound, the chloride (fentin chloride: Brestanol) also produced by Hoechst is now used, although to a lesser extent.[1]

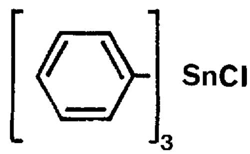
A few years later saw the introduction by Dow of the acaricide tricyclohexyltin hydroxide (cyhexatin: Plictran) which is highly effective in the control of phytophagous mites.[8] Two further organotin miticides were subsequently introduced; bis(trineophyltin)oxide (fenbutatin oxide: Vendex or Torque) by Shell and tricyclohexyltin-1,2,4-triazole (azocyclotin: Peropal) by Bayer. Thus there are currently six commercially available



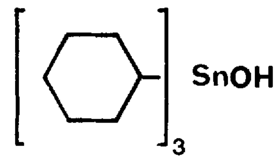
Fentin acetate
mp 118–120°
LD_{50}* (rat) 125 mg Kg^{-1}



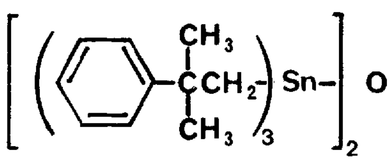
Fentin hydroxide
mp 116–120°
LD_{50}* (rat) 108 mg Kg^{-1}



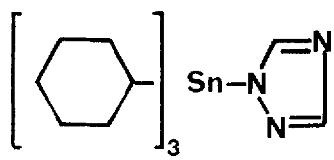
Fentin chloride
mp 105–107°
LD_{50}* (rat) 125 mg Kg^{-1}



Cyhexatin
mp 195–198°
LD_{50}* (rat) 540 mg Kg^{-1}
LD_{50}† (bee) 32 μg Kg^{-1}



Fenbutatin oxide
mp 138–139°
LD_{50}* (rat) 2630 mg Kg^{-1}
LD_{50}† (bee) 100 μg Kg^{-1}



Azocyclotin
mp 219°C
LD_{50}* (rat) 631 mg Kg^{-1}

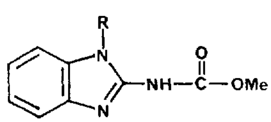
*Oral; †Contact mp in °C.

Figure 1 Organotin compounds used in agriculture.

organotin compounds for agrochemical use; these are shown in Fig. 1. They are supplied by over 16 different companies under a variety of names (see for example the appendix of Reference 1).

In addition, the three triphenyltin compounds, as well as cyhexatin, have also shown antifeedant properties;[1,9,10] indeed these organotin compounds outperform many other feeding deterrents.[9] A second new area where the triphenyltins are showing potential is as chemosterilants. Various kinds of insects, e.g. common house fly, confused flour beetle, Colorado beetle, Mediterranean fruit fly, spiny boll worm and the boll weevil, have shown diminished or no reproduction after feeding on these derivatives.[1] In these latter two possible uses, only very low sublethal concentrations of the compounds are required. It is of interest to note that cyhexatin has recently been found to exhibit fungitoxic activity (see Table 1.5). Acaricidal, antifeedant, chemosterilant and insecticidal properties are covered in Part 2. The main advantages of the organotin agrochemicals have been claimed to be their low phytotoxicity, their generally low toxicity to non-target organisms, and the lack of resistance by crop pests to these chemicals.[1,11] However, there has been some concern with regard to the phytotoxicity of the triphenyltin compounds to certain crops.[1] Also triphenyltin resistant strains of *C. beticola* from sugar beet in Italy,[12] Northern Greece[13] and Yugoslavia[14] have been isolated. *C. capsici* and *G. ampelophagum* have been trained in vitro for resistance to triphenyltins, although in these cases the resistance was of a low order even after 10–14 generations.[15] Regular use of cyhexatin over a period of 7–8 years has resulted in the development of resistance by *T. urticae* (24.9 fold) in pear orchards of Southern Oregon[16] and *P. ulmi* (31.4 fold) in apple and peach orchards of Bulgaria.[17] Similarly *T. urticae* on strawberry and pear crops in the Western USA have shown high to moderate levels of resistance to cyhexatin. In Turkey resistance to this compound is reported to be developing slowly.[19] Cases of cross resistance to azocyclotin and fenbutatin oxide have also been recorded.[17] In contrast, *P. ulmi* from apple orchards in New Zealand, where cyhexatin had been used for ≤ 9 years showed no evidence of resistance.[20] Neither was resistance seen in 90 consecutive generations of *T. urticae* when cyhexatin was periodically applied.[21] Furthermore, resistant organisms can often be successfully controlled by the use of binary compositions of the organotin compound with another active agent.

Organotins are most suitable for use in such binary formulations since they are generally compatible with other pesticides.[8] Indeed, synergism, where the binary mixture performs better than either of its components separately, has been reported for fungicidal,[14,22,23] acarcidal[24–26] and insecticidal[27,28] compositions. Additionally, fentin acetate is active against the soil-borne fungi *A. alternata* and *B. tetramera*, which cause the degradation, and hence loss of activity, of carbendazim(I), the fungitoxic hydrolysis product of benomyl(II), and hence increases the effective lifetime of this fungicide.[29]



I R = H

II R = $NH(CH_2)_3Me$

In general, therefore, the advantages claimed above hold true. In addition, the triorganotin compounds undergo environmental degradation, i.e. the loss of the organic groups from the tin atom:[1,11]

$$R_3SnX \rightarrow R_2SnX_2 \rightarrow RSnX_3 \rightarrow SnX_4.$$

Whether this process proceeds completely to the right, with the formation of harmless inorganic tin residues, is a moot point. What is certainly true however is that the loss of a single organic group from a triorganotin species causes a significant lowering in biological activity, which in turn favours the organotins over many of their competitors.

It has been estimated that only one compound in approximately 10 000 chemical species tested will actually reach commercialisation as a plant protection agent.[30] In spite of such daunting odds it is pleasing to record that there has continued to be much interest in screening novel, i.e. previously untested, organotin compounds. A lot of this work has concentrated on derivatives of the established organotin pesticides, while the remainder has explored the effects of other organotins. A table covering these investigations is given at the end of each main section.

A relatively new approach to disease and pest control is the use of pesticides in combination with biological control agents. Studies involving organotins in combination with predatory mites, entomopathogenic fungi and similar organisms have been performed and are presented in Part 2 of this review.

Other related areas in which organotin compounds are showing potential, but which are not included herein, are: mosquito larvicides,[31–34] control of the snail hosts of schistosomiasis[35–38] and in the chemotherapy of leishmaniasis.[39]

SECTION 1 FUNGICIDAL AND BACTERICIDAL PROPERTIES

The various fungi and bacteria mentioned in this section are presented alphabetically in Table 1.1. The fungicidal and bactericidal investigations of the commercial organotins appear in Tables 1.2–1.5 and are listed alphabetically with regard to the crop on which they were studied. The studies involving novel organotins, Table 1.6, are divided into: triphenyltin derivatives (1.6.1); anionic complexes (1.6.2); mixed organotins (1.6.3) and miscellaneous compounds (1.6.4). These are listed in order of the element directly bound to tin.

Table 1.1 Fungi and bacteria included in Section 1

Fungus/bacterium	Crop	Compounds[a]
Achlya flagellata	fish	H
A. racemosa	fish	H
Albugo tragopogonis	scorzonera	H
Alternaria alternata	brinjal	A
A. brassicae	in vitro	N
A. brassicicola	in vitro	N
A. carthami	safflower	H
A. dauci	carrot	H
A. helianthicola	sunflower	A, H
A. porri	onion	A
A. sesami	sesame	A
A. solani	potato	A
Aspergillus fumigatus	in vitro	N
A. niger	in vitro	N
A. terreus	in vitro	N
Bacillus mesentericus	in vitro	N
B. pumilus	in vitro	N
B. subtilis	in vitro	N
Beauveria bassiana	silkworm	A
Botrytis allii	in vitro	N
Cacao moniliasis	cacao	A
Candida albicans	in vitro	N
Cercospora arachidicola	peanut	A, X
C. beticola	sugar beet	H, C
C. carrotae	carrot	H
C. kikuchi	soybean	H
C. wrighitia	forest nurseries	A, H
Cercosporidium personatum	peanut	A
Chaetomium globosum	in vitro	N
Choanephora	cowpea	A, H
Cladosporium allii-cepae	onion	A, H
C. carophilum	in vitro	N
C. cucumerinum	in vitro	N
Colletotrichum capsi	in vitro	N
C. coffeeanum	coffee berry	N
	in vitro	N
C. dematium	soybean	H
C. falcatum	in vitro	N
C. gloeosporides	in vitro	N
Cryptoccus neoformans	in vitro	N
Diaporthe phaseolorum	soybean	H
Ersiphe betae	sugar beet	A
E. graminis	in vitro	N
E. polygoni	beans	N
	in vitro	N
Escherichia coli	in vitro	N
Fusarium lycopersici	soil-borne	A, H
F. moniliforum	in vitro	N
F. oxysporum	red clover	A
	soil-borne	A, H
F. roseum	red clover	A
F. solani	betel vine	H
Glomeralla glycines	soybean	H
Hemeleia vasatrix	coffee	N
	in vitro	N
Helminthosporium graminium	in vitro	N
H. sativum	wheat	A, C, H
	in vitro	N
H. spp.	rice	N
	in vitro	N
Klebsiella pneumoniae	in vitro	N
Macrophoma mangifera	in vitro	A
Micrococcus agilis	in vitro	N
Microsporum canis	in vitro	N
Myrothrecium roridum	bitter gourd	A
M. verrucaria	in vitro	N
Neovossia indica	wheat	A
Penicillium ilaticum	in vitro	N
P. notatum	in vitro	N
Peronspora destructor	onion	A
Pestalotia palmarum	coconut	A
Phoma betae	sugar beet	A
P. macdonaldii	sunflower	A, H
Phomopsis	sunflower	A, H
Phythium aphanidermatum	sugar beet	A
Phytophthora infestans	tomato	A
P. palmivora	black pepper	A, H
	cacao	A, H
Plasmopara viticola	grape	N
	in vitro	N
Pseudomonas aeruginosa	in vitro	N
P. fluorescens	in vitro	N
P. syringae	coffee	N
	in vitro	N
Puccinia	wheat	A
P. arachidis	ground nut	C
	wheat	C
P. graminis	wheat	N
	in vitro	N
P. recondita	wheat	N
	in vitro	N
Pythium	soil-borne	A, H
Pyrenopeziza brassicae	brassicas	A
Pyricularia penniseti	bajra	H
Rhizoctonia bataticola	forest nurseries	A
R. solani	cowpea	A
	maize	A, H, C
	rice	A
	soil-borne	A, H
	sugar beet	A, H

Table 1 (continued)

Fungus/bacterium	Crop	Compounds[a]	Fungus/bacterium	Crop	Compounds[a]
Saccharomyces cerevisiae	in vitro	N	*Staphlococcus aureus*	in vitro	N
Salmonella typhi	in vitro	N	*Stemphylium solani*	in vitro	H
Saprolegnia hypogyna	fish	H	*Streptococcus faecalis*	in vitro	N
S. megasperma	fish	H	*S. lactis*	in vitro	N
Sarcina lutea	in vitro	N	*Synchytrium psophocarpi*	winged bean	A
Sarocladium oryzae	rice	C, H			
Sclerospora sacchari	maize	A, C	*Trichophyton mentagrophytes*	in vitro	N
Sclerotium rolfsii	ground nut	C			
	linseed	A			
	ragi	H	*Uromyces phaseoli*	pinto bean	N
	straw	A		in vitro	N
Septoria appiicola	celery	H			
Sporotrichum schenkii	in vitro	N	*Xanthomonas malvacearum*	in vitro	N

[a]A = fentin acetate (Table 1.2); C = fentin chloride (Table 1.4); H = fentin hydroxide (Table 1.3); N = novel compounds (Table 1.6); X = cyhexatin (Table 1.5).

Table 1.2 Fungicidal and bactericidal investigations involving fentin acetate

Crop	Disease/causative organism	Comments	Reference
Bitter gourd	Leaf spot *Myrothecium roridum*	Gave only slight reduction in percentage of diseased leaves	41
Black pepper	*Phytophthora palmivora*	Showed good promise as a protectant on leaves. Was a better eradicant than other chemicals tested	42
Brassicas	Light leaf spot *Pyrenopeziza brassicae*	Gave good inhibition of conidial germination and mycelial growth	43
Brinjal	Leafspot and fruit rot *Alternaria alternata*	Was amongst those compounds which proved most effective in inhibiting growth	44
Cacao	*Cacao moniliasis*	In field tests incidence was reduced from 93% to 51%	45
Cacao	*Phytophthora palmivora*	At 2000, 1000 and 500 $\mu g\, g^{-1}$ gave 100, 97 and 93% inhibition of growth respectively	46
Coconut	Gray blight *Pestalotia palmarum*	Activity was shown, but other fungicides performed better	47
Cowpea	Web blight *Rhizoctonia solani* Early season disease	On its own or in combination with Gammalin 20 markedly reduced severity of the disease Gave reduction of incidence	48
Cowpea	Pod rot *Choanephora*	Inhibited mycelial growth	49
Forest nursery seedlings of *Wrighitia tinctoria*	*Cercospora wrighitia*	Was effective to some extent	50
Forest nursery	Soil-borne pathogen *Rhizoctonia bataticola*	Minimised growth at all concentrations tested	51
Linseed	Foot rot *Sclerotium rolfsii*	Was not effective	52
Maize	Sugar-cane downy mildew *Sclerospora saccari*	Seed treatment at 5 $g\, Kg^{-1}$ gave good protection	53
Maize	Banded sclerotial disease *Rhizoctonia solani*	Gave complete inhibition	54
Onion	Downy mildew *Peronospora destructor* Purple blotch *Alternaria porri*	Gave some control of both diseases	55

Table 1.2 (continued)

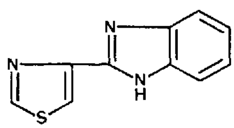
Crop	Disease/causative organism	Comments	Reference
Onion	Leaf blotch *Cladosporium allii-cepae*	In combination with Maneb was most effective in inhibiting spore germination, growth and reproduction of the fungus	56
Peanut	Early and late spot *Cercospora arachidicola* *Cercosporium personatum*	In the field was amongst the compounds which gave best control	57
Potato	Early blight *Alternaria solani*	Plots treated with 1 $Kg\,ha^{-1}$ had minimum infection	58
Red clover	Fusarium wilt *Fusarium oxysporum* *F. roseum*	Was the most effective of eight fungicides in inhibiting mycelial growth in vitro	59
Rice	Sheath blight disease *Rhizoctonia solani*	Infected seeds were treated with 0.1, 0.2 and 0.3%. Slight inhibition of seed germination occurred, but increase in seedling growth and vigour was observed. Viability of the seedlings was maintained for $\leq$8 months	60 60
Rice	Sheath blight *Rhizoctonia solani* Rice blast	Inhibited the saprophytic activity in soil, but other compounds were superior At 1.86 $\mu g\,cm^{-3}$ was most effective in inhibiting spore germination	61 62
Sesame	Alternaria blight *Alternaria sesami*	Under field conditions 250 $\mu g\,g^{-1}$ inhibited spore germination 100%	63
Silk worm	Muscardine disease *Beauveria bassiana*	Was most effective compound tested Inhibited fungal growth at 0.0025%	64
Straw	*Sclerotium rolfsii*	Soil mixing with 100 $\mu g\,g^{-1}$ killed fungus on straw. Was moderately effective in top 2 inches of soil when applied as a drench	65
Sunflower	Leaf spot *Alternaria helianthicola*	At 0.1% concentration gave ca 77% inhibition of growth and spore germination	66
Sunflower	*Alternaria helianthicola* *Phoma macdonaldi* *Phomopsis*	At 100 $\mu g\,g^{-1}$ was fungitoxic to all three	67
Sugar beet	Damping-off disease *Rhizoctonia solani* *Phythium aphanidermatum* *Phoma betae*	Showed good activity particularly against *P. aphanidermatum* and was effective against *P. betae*	68
Sugar beet	Powdery mildew *Erysiphe betae*	In combination with wettable sulphut completely controlled infection	69
Tomato	Late blight *Phytophthora infestans*	Gave promising results in this preliminary study	70
Wheat	Karnal bunt *Neovossia indica*	As a seed dressing was amongst the compounds with highest activity	71
Wheat	Leaf rust *Puccinia*	Combined with maneb gave effective control of leaf rust but not stem rust	72
Wheat	Spot blotch *Helminthosporium sativum*	At 0.05–0.2% produced a reduction in intensity of disease	73
Winged bean	False rust *Synchytrium psophocarpi*	In field trial produced significant reduction of infection	74
—	Soil-borne fungi *Rhizoctonia solani* *Fusarium oxysporum* *F. lycopersici* *Pythium*	Effective against all 4 in the laboratory	75
—	*Macrophoma mangifera*	In vitro was highly effective in inhibiting mycelial growth and stromatal production	76

Table 1.3 Fungicidal and bactericidal investigations involving fentin hydroxide

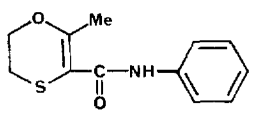
Crop	Disease/causative organism	Comments	Reference
Bajra	Leaf spot *Pyricularia penniseti*	Showed high toxicity to mycelial growth and spore germination	77
Betel vine	Betel vine decline *Fusarium solani*	Second most active compound of 11 on test	78
Black pepper	*Phytophthora palmivora*	Showed good promise as a protectant on leaves	42
Carrot	Foliar diseases *Alternaria dauci* *Cercosporia carrotae*	At 0.4% gave control	79
Celery	*Septoria apiicola*	When formulated with propineb gave best control on test	80
Cocoa	*Phytophthora palmivora*	At 500 $\mu g\,g^{-1}$ completely inhibited growth of the fungus	46
Cowpea	Basal stem rots	In vitro at 200 $\mu g\,g^{-1}$ inhibited growth of all pathogens associated with basal stem rots. Gave effective control in field trials	81
Cowpea	Pod rot *Choanephora*	Inhibited mycelial growth	49
Fish	Aquatic fungi pathogenic to fish *Achlya flagellata* *A. racemosa* *Saprolegnia hypogyna* *S. megasperma*	At $<100\,mg\,dm^{-3}$ inhibited fungal growth on artificial media	82
Forest nursery seedlings of *Wrighitia tinctoria*	*Cercospora wrighitia*	Was effective to some extent	50
Maize	Banded sclerotial disease *Rhizoctonia solani*	A foliar spray of thiabendazole(III) (0.005%), followed by vitavax(IV) (0.1%) and duter (0.05%) was most effective in reducing disease and resulted in increased yields	54
Onion	Leaf blotch *Cladosporium allii-cepae*	Was most effective in inhibiting spore germination, growth and reproduction of the fungus	56
Ragi	Foot rot *Sclerotium rolfsii*	Incidence of infection was markedly reduced when 25 g/ha was incorporated into the soil before sowing	83
Rice	Sheath rot *Sarocladium oryzae*	Controlled disease but brestanol (Ph_3SnCl) was more effective	84
Safflower	Leaf blight *Alternaria carthami*	At 0.05% gave control	85
Scorzonera	White rust *Albugo tragopogonis*	When mixed with tridemorph(V) 4 treatments at 14-day intervals gave most effective control	86
Sesame	Mycoflora of seeds	Gave a broad spectrum effect of eradicating mycoflora	87
Soybean	Pod and stem blight *Diaporthe phaseolorum* Anthracnose *Collectotrichum dematium* *Glomeralla glycines* Leaf blight *Cercospora kikuchii*	Was amongst compounds which gave best disease control and highest yield increases	88
Soybean	Foliar fungi	Did not show much activity	89
Sugar beet	Leaf spot *Cercospora beticola*	At 0.33 $kg\,ha^{-1}$ decreased the severity of the disease	90
Sugar beet	Crown rot *Rhizoctonia solani*	Was most effective at controlling the infection	91

Table 1.3 (continued)

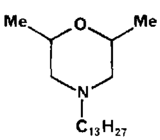
Crop	Disease/causative organism	Comments	Reference
Sunflower	Leaf spot *Alternaria helianthicola*	0.2% concentration gave ca 87% inhibition of growth and spore germination	66
Sunflower	*Alternaria helianthicola* *Phoma macdonaldii* *Phompsis*	At 100 $\mu g\, g^{-1}$ was fungitoxic to all 3	67
Wheat	Spot blotch *Helminthosporium sativum*	Reduction in intensity of disease was achieved using 0.05–0.2% treatments	73
—	Soil-borne fungi *Rhizoctonia solani* *Fusarium oxysporum* *F. Lycopersici* *Pythium*	Was effective against all four fungi in the laboratory	75
—	*Stemphylium solani*	Moderately active in vitro against mycelial growth	92



III



IV



V

Table 1.4 Fungicidal and bactericidal investigations involving fentin chloride

Crop	Disease/causative organism	Comments	Reference
Ground nut	Wilt *Sclerotium rolfsii*	As a seed soak or soil drench offered some control, but other compounds were better	93
Ground nut	Rust *Puccinia arachidis*	Spore germination was totally inhibited even at half-normal dose i.e. 0.05%	94
Maize	Sugar-cane downy mildew *Sclerospora sacchari*	Seed treatment at 5 $g\, Kg^{-1}$ gave good protection	53
Maize	Banded sclerotial disease *Rhizoctonia solani*	Gave complete inhibition of the pathogen	54
Rice	Sheath rot *Sarocladium oryzae*	Three sprays at 0.1% gave good control of the disease and increased yields	84
Sugar beet	Leaf spot *Cercospora beticola*	Was effective when applied at 750 $g\, ha^{-1}$ in 2–4 spray treatments. Root yield was also increased	95
Wheat	Leaf rust *Puccinia arachidis*	At half-normal recommended dose in vitro gave 100% inhibition of spore germination	96
Wheat	Spot blotch *Helminthosporium sativum*	Treatments of 0.05–0.2% reduced the intensity of the infection	73

Table 1.5 Fungicidal and bactericidal investigations involving cyhexatin

Crop	Disease/causative organism	Comments	Reference
Apple	Brown rot	Application of 1.8 g per tree in spray volumes ranging from 0.225–9.0 dm^3 per tree gave complete control	97
Peach	Black spot (apple scab) Powdery mildew		97
Peanuts	Early leaf spot *Cercospora arachidicola*	Complete inhibition in vitro at $\geq 73.5\, \mu g\, cm^{-3}$	98

Table 1.6 Fungicidal and bactericidal investigations involving non-commercialized organotin compounds

1.6.1 Triphenyltin derivatives, Ph_3SnX

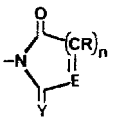
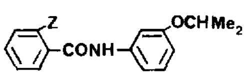
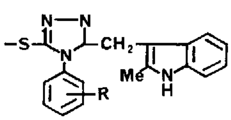
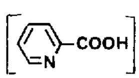
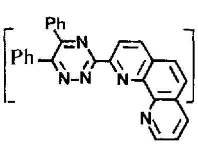
X=	Comments	References
—$(CH_2)_nY$ Y = halogen, NR_2 etc. (Other R_3Sn included)	Fungi: *B. allii*, *P. ilaticum*, *A. niger*, *C. Cucumerinum* Bacteria: *B. subtilis*, *S. lactis*, *E. coli*, *P. fluoroscens* Good activity was claimed	99
 $n = 1, 2$ Y = O, S E = CR′, N	Stannylimides show fungicidal activity	100, 101, 102
—$OCO.C_6H_4.SCN$-4 (and analogues)	Exhibited greater fungicidal activity than fentin acetate against *Xanthomonas malvacearum*	103
—$OCO.CH(Me)(C_6H_3Me_2$-2,3)$NOCCH_2OMe$ acrylated aminocarboxylates	At 0.006% inhibited infestation of wheat by *Puccinia graminis* by 95–100%	104
—OCH_2CH_2OBu	Gave 80–90% inhibition of *A. niger*, *H. sativum* and *A. terreus* at 0.1% concentration and at 10 mg cm^3 inhibited the growth of *B. subtilis*, *B. pumilus* and *S. lutea*	105
—OH in physical combination with benzanilides: 	Fungicidal activity was claimed	106
—SC(SMe)NNC(H) 	Fungi: *A. terreus*, *F. moniliform*, *Helminthosporium* spp. and *C. falcatum*	107
and other Schiff base complexes	Bacteria: *S. aureus*, *B. subtilis* and *B. pumilus*. At 0.1% gave 100% inhibition of fungal growth. Showed high toxicity to bacteria except *B. pumilus*	
	After 1 week gave 80–90% inhibition of *Helminthosporium* spp, *A. terreus* and *A. niger*. Bactericidal activity was comparable to sulphaguanidine, but less than that of tetracycline	108, 109
-1,3-diphenylpropane-1,3-dione complex -quinolin-8-ol complex -quinolin-8-thiol complex	At 100 mg dm^{-3} all 3 had activity similar to fentin acetate against *P. viticola*	110
Ph_3SnCl  adduct and Ph_3SnCl  adduct	Showed excellent levels of control against coffee berry disease (*C. coffeeanum*), coffee leaf rust (*H. vasatrix*) and coffee bacterial blight (*P. syringae*)	111
$Ph_3SnNCSe$[DMA] adduct	Inhibits growth at a minimum inhibitory concentration of 3.125 $\mu g/cm^3$ of bacteria; *S. faecalis* and *E. coli*; and fungi *C. albicans*, *C. neoformans*, *S. schenckii*, *T. mentagrophytes* and *A. fumigatus*	112

Table 1.6 (continued)

X=	Comments	References
$Ph_3SnN_3[L]$ adduct	Parent compound and its complexes were effective in inhibiting growth of *S. faecalis, S. aureus, K. pneumoniae* and *E. coli*, but not *P. aeruginosa*. Similarly, they were active against the fungi: *C. albicans, S. schenkii* and *T. mentagrophytes*; but were inactive against *C. neoforms* and *A. fumigatus*. L = benzimidazole tended to give highest activity	113

1.6.2 Anionic complexes

X=	Comments	Reference
Phosphonium organohalogenostannates(IV) e.g. $[Bu_3PC_{18}H_{37}]^+[Cy_3SnCl_2]^-$(A)	Fungicidal, bactericidal and algicidal properties are claimed. 0.02%A on barley showed <20% infection by *E. graminis* (controls 100%)	114
Triethyl ammonium chloride complexes of triphenylstannyl isoureas e.g. $[Et_3NH]^+[RNHCO(NCN)SnPh_3Cl]^-$	Fungi: *A. niger, C. globosum, C. carpophilum, F. monoliforme, M. verrucaria, P. notatum, S. cerevisiae* and *T. mentagrophytes* Bacteria: *M. agilis, B. subtilis* and *S. aureus* showed higher activity than uncomplexed triphenyl stannyl isoureas	115
Ammonium organohalogenostannates(IV) $[R_4N^+]_2[\overline{(CH_2)_n}SnX_2X_2']^{2-}$ n=4,5; X,X′=halogen,NCS	Exhibit higher activity than either parents towards gram-positive bacteria	116

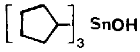
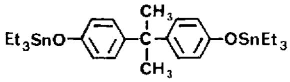
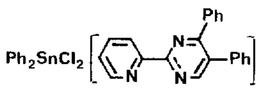
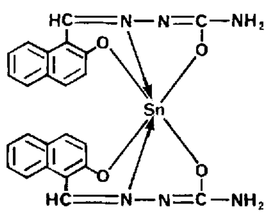
1.6.3 Mixed organotins

X=	Comments	Reference
$R_nR'_{(3-n)}SnX$ e.g. $BuMe_2SnCl$(B)	B controlled *E. polygoni* on beans at 100 $\mu g\,g^{-1}$, *U. phaseoli* on pinto beans at 200 $\mu g\,g^{-1}$, and *Helminthosporium* on rice at 200 $\mu g\,g^{-1}$	117
$Me(C_6H_3Cl_2\text{-}3,4)_2SnOAc$ (and analogues)	At 19 $\mu g\,g^{-1}$ gave 93% control of downy mildew (*P. viticola*) on grape seedlings	118

1.6.4 Miscellaneous compounds

X=	Comments	Reference
Cy_3SnX X = halogen, pseudohalogen	Fungi: *C. albicans, C. neoformans, M. canis, A. niger, A. fumigatus* and *T. mentagrophites* Bacteria: *S. aureus, S. faecalis, K. pneumoniae, S. typhi* and *E. coli* Excellent activity was shown towards gram-positive bacteria, but gram-negative bacteria (latter two) are resistant. Was most active against the fungus *C. neoformans*	119

Table 1.6 (continued)

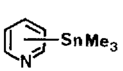
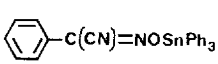
X=	Comments	Reference
Tricyclopentyltin hydroxide 	Behaved as a simultaneous fungicide and miticide. Controlled downy mildew (*P. viticola*) on grape and 2-spotted spider mite (*T. urticae*) on bean	120
	Was sprayed on wheat plants which were then innoculated with rust (*P. recondita*). After 14 days no treated plants were infected whereas all controls were	121
$Bu_2Sn(OCH_2CH_2)_2NH$ (and others)	At 0.5% was extremely active against *B. subtilis*, *B. mesentericus* and *C. globosum* in vitro	122
 adduct	Showed excellent levels of control against coffee berry disease (*C. coffeeanum*), coffee leaf rust (*H. vasatrix*) and coffee bacterial blight (*P. syringae*)	111
Tin(IV) derivative of 2-hydroxy-1-naphthalene carbaldehyde semicarbazone 	Showed complete inhibition of spore germination at 500 $\mu g\,g^{-1}$ of *C. capsi*, *A. brassicicola* and *H. graminium*, and at 250 $\mu g\,g^{-1}$ of *C. gloeosporides* and *A. brassicae*	123

SECTION 2 HERBICIDAL PROPERTIES

This appears to be a little explored area. During the period 1958–1974 it was variously discovered that triphenyl compounds, in particular the acetate, were suitable for the control of algae in rice fields or in water cultures of celery.[40] It was found that triphenyltin acetate present in the water at a level of 0.7 $\mu g\,g^{-1}$ caused all algae to die within 48 hours and that this effect lasted for about 7–10 days. In addition no phytotoxic effects to the young rice plants were seen, nor were fish living in the rice fields harmed. The extent to which triphenyltins are used in this application are not known, but it is likely to be small, if they are used at all.

During the 1980's two studies, involving novel organotin compounds have been reported, these are summarised in Table 2.1.

Table 2.1 Novel organotin herbicides

X=	Comments	Reference
	Controlled *Echinochla cru-galli, Digitaria sanguinalis, Amaranthus blitum, Abutilon theophasti* and *Cyperus rotundus* in corn and soybean at 80 g/acre	124
	Was a herbicide safening agent. Thus rice seeds were soaked in 100 $\mu g\,g^{-1}$ for 24 hours and drip dried. Treated seed was sown in moist soil and a herbicide was applied. No phytotoxic effects were observed on treated group, whereas controls showed severe symptoms in 7 days	125

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