

PATENT SPECIFICATION

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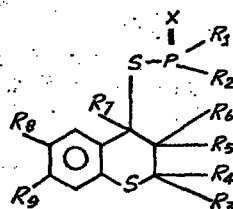


(54) 4-THIOCHROMANYL-(DI)-THIOPHOSPHORIC AND PHOSPHONIC ACID ESTERS AND ESTER AMIDES, PROCESS FOR THEIR PREPARATION AND PESTICIDAL COMPOSITIONS CONTAINING THEM

(71) We, HOECHST AKTIENGESSELLSCHAFT, formerly known as Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, a company recognised under German Law of, 6230 Frankfurt (Main) 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to 4-thiochromanyl-(di)-thiophosphoric and phosphonic acid esters and ester amides, to a process for their preparation and to pesticidal compositions containing them.

The present invention provides compounds of the formula



(I)

in which

R₁ is an alkyl group having from 1 to 4 carbon atoms, an alkoxy group having from 1 to 6 carbon atoms, or a phenyl group;

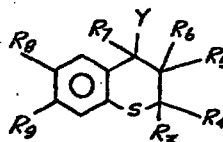
R₂ is an alkoxy group having from 1 to 6 carbon atoms, an amino group, an alkyl-amino group having from 1 to 6 carbon atoms, a dialkylamino group having from 1 to 6 carbon atoms per alkyl group or an alkenylamino group having from 3 to 6 carbon atoms;

R₃, R₄, R₅, R₆, and R₇, which may be the same or different, is each a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms, at least three of R₃, R₄, R₅, R₆, and R₇ being hydrogen atoms;

R₈ and R₉, which may be the same or different, is each a hydrogen or halogen atom, an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms; and

X is oxygen or sulfur.

The present invention also provides a process for the preparation of compounds of formula I, which comprises reacting 4-halogeno-thiochromanyl compounds of the formula



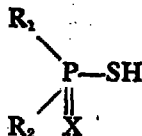
(II)

[Price 33p]

Price 75p

in which $R_3, R_4, R_5, R_6, R_7, R_8$ and R_9 have the meanings given above and Y is a halogen atom, preferably a chlorine or bromine atom, with phosphorus compounds of the formula

(111)



in which R_1, R_2 , and X have the meanings given above, or the salts thereof, optionally in the presence of an acid binding agent.

The reaction is generally carried out using approximately stoichiometric amounts of the reactants; a slight excess of the compound of formula 111 being advantageous. It is recommended to operate in the presence of a solvent which is inert under the reaction conditions. Such solvents are, for example, benzene or alkyl-benzenes, for example toluene or xylene; halogeno-benzenes, for example, chlorobenzene or dichlorobenzene; halogenated aliphatic compounds, for example methylene chloride, chloroform, carbon tetrachloride, dichloroethane; ethers, for example diethyl ether, diisopropyl ether, glycol-dimethyl ether, tetrahydrofuran, dioxan; and ketones and nitriles, for example acetone, methyl-ethylketone, methyl-isopropylketone, methyl-butylketone, benzonitrile and propionitrile. Polar solvents are preferred.

The reaction temperatures are not critical and may be widely varied, for example in a range of from -20° to $+140^\circ\text{C}$. Generally, room temperature or temperatures establishing themselves by the exothermic reaction are preferred.

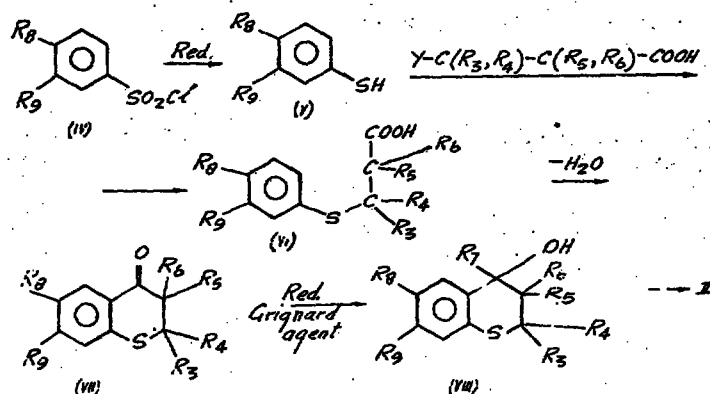
The reaction proceeds by exchange of the halogen atom Y . Therefore, it is carried out either with addition of acid binding agents, or using salts, especially alkali metal or ammonium salts of the phosphorus compounds of formula 111. Preferred acid binding agents are alkali metal hydroxides and alkali metal carbonates; but tertiary nitrogen bases, for example pyridine or triethylamine, may also be employed.

According to the process of the invention, the compounds of formula 1 are obtained in a very high yield and with a high degree of purity.

The starting compounds of formula 111 are known and can be easily prepared according to usual methods on a large scale.

The 4-halogeno-thiochromanyl compounds of formula 11 and their preparation are partly described in French Patent Specification No. 1,584,755; partly they are novel compounds, also their preliminary products are new in part. They are prepared according to known processes by first reducing benzene sulfochlorides to the corresponding thiophenols. In a second reaction step, the thiophenols are reacted with corresponding substituted halogeno-propionic acids or 1,2-unsaturated acids, and the phenylmercapto-propionic acids which are formed are cyclized to thiochromanones in the presence of dehydrating agents, for example concentrated sulfuric acid, polyphosphoric acid or phosphorus pentoxide.

By reduction of the thiochromanones according to known processes, for example by means of sodium borohydride or by Grignard reduction, 4 hydroxy-thiochroman compounds are obtained which, also in known manner, are converted to the 4-halogeno-thiochromanyl compounds of formula 11 with the aid of a halogenating agent, for example phosphorus trichloride, phosphorus tribromide, thionyl chloride, sulfur chloride or halogen hydracids. The reaction proceeds for example according to the following scheme:



As substituents R_1 and R_2 , the following are advantageously used:

R_1 = methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, secondary butyl, tertiary butyl, phenyl;

R_1, R_2 = methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, secondary butoxy, tertiary butoxy;

R_2 = methylamino, ethylamino, diethylamino, n-propylamino, n-butylamino, di-n-butylamino, n-hexylamino, allylamino.

Preferred substituents R_1 to R_7 are hydrogen atoms and methyl or ethyl groups. Examples of substituents R_1 and R_2 are: fluorine, chlorine and bromine atoms, methyl, ethyl, isopropyl, tertiary butyl, methoxy, ethoxy, propoxy, and tertiary butoxy groups.

The alkyl and alkoxy groups preferably contain 1 or 2 carbon atoms. Those compounds are preferred in which R_1 and R_2 are hydrogen atoms, or one of R_1 and R_2 at least is a chlorine or bromine atom.

Two preferred groups of compounds of the formula I are those in which R_1 is an alkoxy group having from 1 to 6 carbon atoms and R_2 is an alkoxy group having 1 or 2 carbon atoms, an alkylamino or dialkylamino group having from 1 to 6 carbon atoms per alkyl group or an alkenylamino group having from 3 to 6 carbon atoms, and those in which R_1 is an alkyl group having from 1 to 4 carbon atoms and R_2 is an alkoxy group having from 1 to 6 carbon atoms.

The compounds of formula I are suitable for the destruction of numerous pests in their various development stages of different crop plants and they have an insecticidal as well as an acaricidal activity. Thus, different spider mite species, for example the European red mite (*Metatetranychus ulmi*), or mites like *Panonychus citri* or *Tetranychus urticae*, as well as strains resistant to phosphoric esters, can be controlled with good results.

In addition numerous biting and sucking insects noxious to crop plants can be destroyed by the compounds of the present invention, for example beetles, such as the Mexican bean beetle (*Epilachna varivestis*), the Colorado beetle (*Leptinotarsa decemlineata*), the flower beetle (*Epicometis hirta*), the flea (*Phyllotreta* spp.), the strawberry borer (*Coenorrhinus germanicus*), or the boll weevil (*Anthonomus grandis*); butterflies and their larvae, such as the Egyptian and the Old World boll worm (*Earias insulana* and *Heliothis armigera*); leaf rollers, especially the codling moth (*Carpocapsa pomonella*), the green oak roller (*Tortrix viridana*), the tortrix moth (*Capua reticulana*), the corn borer (*Ostrinia nubilalis*) or the winter moth (*Cheimatobia brumata*); aphids, such as the bean aphid (*Doralis fabae*), the green peach aphid (*Myzodes persicae*), the cotton aphid (*Aphis gossypii*); or bugs, such as milkweed bugs and cotton stainers (*Oncopeltus fasciatus* and *Dysdercus* spp., especially *fasciatus*).

The compounds of the present invention are also suitable for combating ectoparasites living on productive livestock. Thus, mallophaga, lice (*Anoplura*), fleas (*Aphaniptera*), mites and ticks (*Acarina*, such as ixodides (*Ixodidae*), argasides (*Argasidae*), dermanyssides (*Dermanyssidae*); sarcoptides (*Sarcoptidae*)), as well as those resistant to phosphoric esters, are destroyed. Additionally, the compounds have a proved systemic action in animals.

Finally, the compounds are also suitable for combating certain nematode species noxious to plants.

The compounds of the present invention are remarkably non-toxic to warmblooded animals and partly have a very low toxicity to fish, so that they may be used, for example, for combating infection-carrying mosquitoes (yellow fever mosquitoes, anophles) in their larval stage. Their activity is also seen in the control of those strains of organisms which are resistant to other biocides.

The present invention therefore also provides pesticidal compositions, for example insecticidal, acaricidal and/or nematocidal compositions, which contain compounds of formula I as active ingredients, together with carrier materials.

The present invention further provides a method of combating insects, members of the order acarina, nematodes and animal ectoparasites, which comprises applying to their habitat a compound of the formula I.

The phosphoric acid esters in accordance with the present invention may be formulated in admixture with solid or liquid inert carrier substances, adhesives, wetting and dispersing agents, or grinding auxiliaries in the form of wettable powders, emulsions, suspensions, dusting powders, granules, fly-bands, and products for spreading and washing. They may be mixed with other insecticides, fungicides, nematocides and herbicides.

As carrier material, mineral substances, for example aluminium silicates, argillaceous earths, kaolin, chalks, siliceous chalks, talcum, kieselguhr or hydrated silicic acids can be used, or preparations of these mineral substances with special additives, for example chalk with sodium stearate. As carrier material for liquid preparations, all usual

and suitable organic solvents may be employed, for example toluene, xylene, diacetone alcohol, isophorone, gasolines, paraffin oils, dioxan, dimethyl formamide, dimethyl sulfide, ethyl acetate, butyl acetate, tetrahydrofuran and chlorobenzene.

Suitable adhesives are glue-like cellulose products or polyvinyl alcohols.

As wetting agents, all suitable emulsifiers may be used, for example ethoxylated alkylphenols, salts of aryl- or alkylaryl-sulfonic acids, salts of ethoxylated benzenesulfonic acids, or soaps.

Suitable dispersing agents are cellulose pitch (salts of sulfite cellulose waste liquor), salts of naphthalenesulfonic acid or, in certain cases, hydrated silicic acids or kieselguhr.

As grinding auxiliaries, suitable inorganic or organic salts, for example sodium sulfate, ammonium sulfate, sodium carbonate and sodium bicarbonate, sodium thiosulfate, sodium stearate, or sodium acetate may be used.

The content of the active ingredients in accordance with this invention in the ready-for-use products is generally from 2 to 95% by weight.

The active substances to be used in accordance with the present invention in the veterinary field are applied normally by spraying, dusting or dipping methods, as well as, in the special case of the anti-tick agents, in the so-called dip or spray equipment.

Simple compositions suitable for testing the activity of the components may be obtained in the following manner:

Wettable powder:

6 g of active substances are ground with 6 g of finely dispersed silicic acid, and subsequently mixed in a mixer with 48 g of a mixture containing 13.3% by weight of dried cellulose waste liquor, 65.3% by weight of quartz and aluminium silicate; 15.3% by weight of finely dispersed silicic acid, 4.7% by weight of polypropylene-glycol and 1.3% by weight of the sodium salt of oleylmethyltauride. Thus, 60 g of a 10% by weight wettable powder are obtained.

Emulsifiable concentrate:

2 g of active substance, 16 g of cyclohexanone and 2 g of alkylaryl-polyglycol ether alcohol are mixed with each other. 20 g of a 10% by weight emulsifiable concentrate are obtained.

The following Examples illustrate the invention.

General preparation:

0.1 Mole of halothiochroman of formula 11 is added, at room temperature and with agitation, to a solution or suspension of 0.10 to 0.11 mole of a salt of a phosphorus compound of formula 111 in 200 ml of glycol-dimethyl ether. Stirring is continued for about 3 to 5 hours at 50°C, the precipitated salt is separated by suction-filtration, the filtrate is diluted with about 400 ml of benzene, the organic phase is thoroughly washed with water and dried over Na_2SO_4 . After having distilled off the solvent, the products of the process are obtained as oils which, in part, crystallize on trituration.

According to the process described above, the following compounds are obtained:

TABLE I

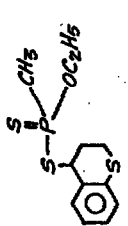
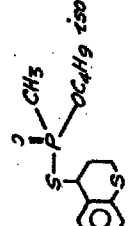
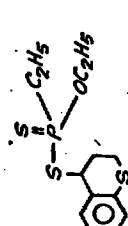
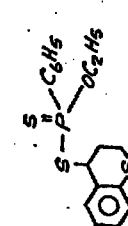
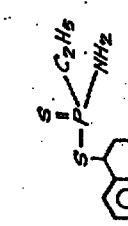
Example	Formula	n_D or melting point ($^{\circ}C$)	Yield % of theoretical yield	Analysis	
				Calc.	Found
1		$n_D^{34.5}$ 1.6329	80	47.3 5.6 10.2 31.6	C 48.4 H 5.6 P 10.4 S 31.6
2		n_D^{24} 1.5767	60	53.2 6.6 9.8 20.2	C 53.0 H 6.7 P 9.5 S 20.2
3		n_D^{24} 1.6227	74	49.1 6.0 9.7 30.2	C 49.4 H 5.8 P 9.3 S 30.0
4		n_D^{24} 1.6385	75	55.8 5.2 8.5 26.2	C 55.5 H 5.3 P 7.5 S 25.7
5		Oil	40	33.2	S 33.1

TABLE I (Continued)

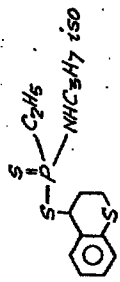
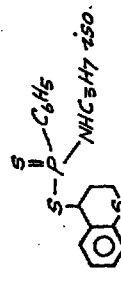
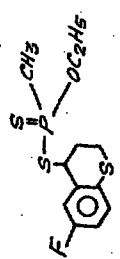
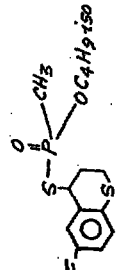
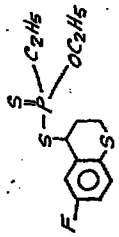
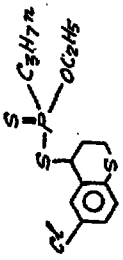
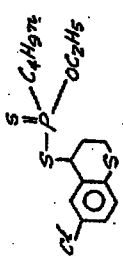
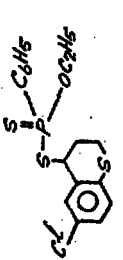
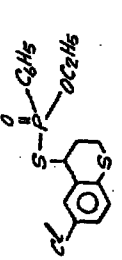
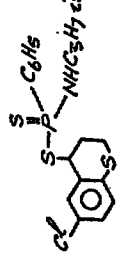
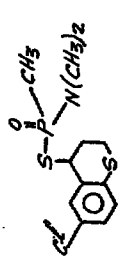
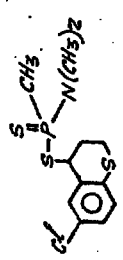
Example	Formula	n_D or melting point (°C)	Yield % of theoretical yield	Calc.	Analysis	Found
6		Oil	55	50.7 6.6 9.3	C H P	50.4 6.4 8.3
7		oil	40	57.0 5.7 25.3	C H S	57.8 5.6 24.7
8		n_D^{34} 1.6132	90	44.7 5.0 9.6 29.8	C H P S	44.5 5.0 9.6 30.0
9		$n_D^{23.5}$ 1.5588	81	50.3 6.0 9.3 19.2	C H P S	50.0 6.1 8.3 18.9
10		oil	91	46.5 5.4 9.2 28.6	C H P S	46.0 5.4 8.4 29.2

TABLE I (Continued)

TABLE I (Continued)

Example	Formula	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis	Found
11		oil	95	8.1 25.0	P S	8.4 24.4
12		oil	60	48.2 6.0 27.5	C H S	48.7 5.8 28.0
13		n_D^{39} 1.6329	96	42.6 4.7 9.1 28.3	C H P S	42.6 4.8 8.9 28.4
14		Melting point 64-69	91	9.6 29.6	P S	9.0 29.6
15		n_D^{24} 1.5785	96	8.8 18.2	P S	8.5 18.0
16		n_D^{24} 1.6123	61	45.8 5.5 26.2	C H S	46.2 5.5 25.0
17		n_D^{24} 1.6233	93	44.3 5.1 8.8 27.2	C H P S	44.6 5.2 8.6 27.5

TABLE I (Continued)

Example	Formula	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis	Found
18		n_D 24.5 1.6076	86	45.8 5.5 8.4 26.2	C H P S	46.8 5.5 8.0 25.0
19		n_D 24.5 1.617	91	8.2 25.2	P S	8.3 25.5
20		n_D 24 1.6412	96	7.7 24.0	P S	7.3 23.6
21		n_D 24 1.6229	71	8.1 16.6	P S	8.4 16.0
22		n_D 24 1.66	68	7.5 3.4 23.2	P N S	6.9 3.0 23.0
23		n_D 23.2 1.6118	40	44.8 5.3 19.9	C H S	44.5 5.2 19.4
24		oil	70	42.7 5.0 9.2 28.4	C H P S	43.1 4.9 8.9 28.8



9.2
28.4

P
S

8.9
28.8

9

9

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TABLE I (Continued)

Example	Formula	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis	Found
25		n_D^{24} 1.5786	60	47.9 5.7 8.8 18.2	C H P S	48.0 6.2 8.5 18.0
26		n_D^{28} 1.6569	86	37.6 4.2 8.3	C H P	37.6 4.2 8.0
27		n_D^{24} 1.6094	86	7.9 16.2	P S	8.2 16.6
28		n_D^{25} 1.5745	72	9.4 19.4	P S	10.0 20.3
29		n_D^{25} 1.5646	75	8.3 17.2	P S	8.4 17.6
30		n_D^{39} 1.62	72	28.9	S	28.5

TABLE I (Continued)

Example	Formula	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis Found
31		n_D^{23} 1.591	85	4.2 9.4 19.5	N 4.0 P 8.6 S 20.2
32		melting point 85-87	88	4.2 9.4 19.3	N 4.1 P 8.8 S 19.1
33		n_D^{24} 1.5788	88	4.0 8.9 18.5	N 3.8 P 8.5 S 18.8
34		melting point 91-92	59	5.5 4.0 8.9 18.3	F 5.4 N 3.6 P 8.6 S 18.2
35		n_D^{24} 1.6022	90	3.8 8.5 17.6	N 3.4 P 7.9 S 18.4
36		$n_D^{26.5}$ 1.5808	83	9.7 3.8 8.5 17.5	Cl 9.7 N 3.8 P 8.3 S 17.1

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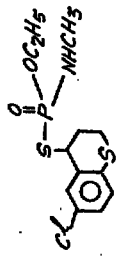
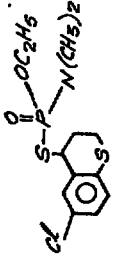
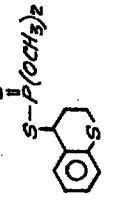
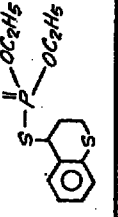
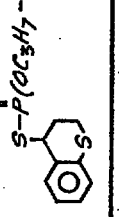
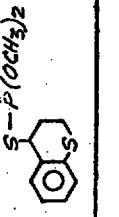
Example	Formula'	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis	Found
37		n_D^{26} 1.5969	99	4.15 9.2 19.0	N P S	4.0 8.5 18.5
38		n_D^{24} 1.5934	89	4.0 8.8 18.2	N P S	4.0 8.0 18.4
39		$n_D^{29.5}$ 1.6226	91.5	43.14 4.9 10.13 31.37	C H P S	43.3 4.9 10.0 31.4
40		melting point 49-50	90	46.7 5.7 9.3 28.7	C H P S	46.9 5.6 9.2 29.7
41		n_D^{31} 1.5809	96	49.72 6.35 8.56 26.52	C H P S	50.4 6.4 8.6 27.1
42		n_D^{24} 1.5818	86	45.5 5.2 10.7 22.0	C H P S	45.8 5.3 10.2 21.7

TABLE I (Continued)

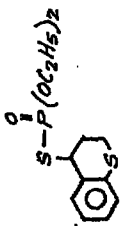
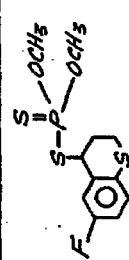
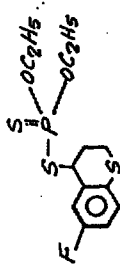
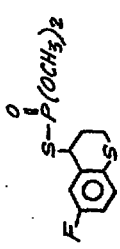
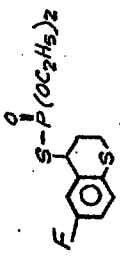
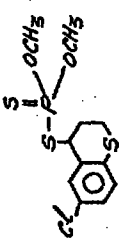
Example	Formula	n _D or melting point (°C)	Yield % of theoretical yield	Calc.	Analysis	Found
43		n _D ²⁴ 1.5701	81	49.1 6.0 9.7	C H P	48.9 6.3 9.3
44		n _D ^{29.5} 1.6056	90	9.6 29.6	P S	9.8 30.0
45		n _D ^{31.5} 1.5879	91	8.8 27.2	P S	8.6 27.6
46		n _D ^{23.5} 1.566	86	10.1 20.8	P S	10.6 20.9
47		n _D ^{21.5} 1.5558	89	9.2 19.0	P S	9.5 19.1
48		melting point 52-54	92	38.77 4.11 9.1 28.19	C H P S	38.6 4.1 8.8 28.4

TABLE I (Continued)

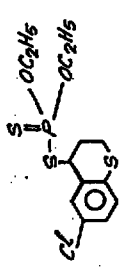
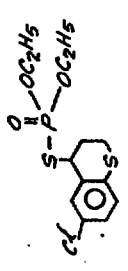
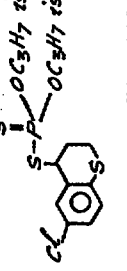
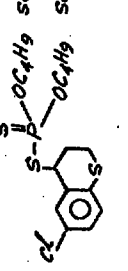
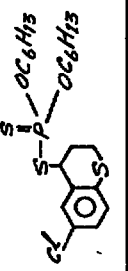
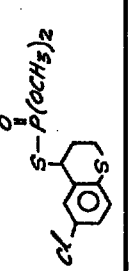
Example	Formula	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis	Found
49		$n_D^{31.5}$ 1.611	97	42.34 4.88 8.41 26.06	C H P S	42.4 4.9 8.2 26.3
50		$n_D^{29.5}$ 1.5794	96.5	8.8 18.2	P S	8.5 18.4
51		n_D^{24} 1.5979	90	45.40 5.55 7.83 24.21	C H P S	46.0 5.4 7.5 23.7
52		n_D^{24} 1.5929	89	48.06 6.13 7.30 22.85	C H P S	48.8 5.8 7.0 22.4
53		n_D^{24} 1.574	98	52.65 7.08 6.45 19.98	C H P S	52.9 7.0 6.1 20.3
54		n_D^{24} 1.5789	76	9.5 19.7	P S	9.4 19.7

TABLE I (Continued)

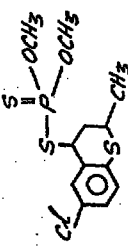
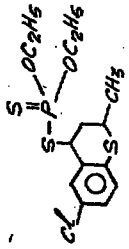
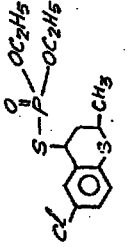
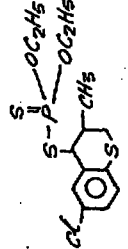
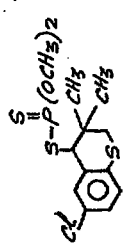
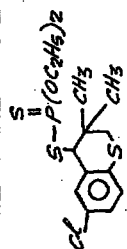
Example	Formula	n_D or melting point (°C)	Yield % of theoretical yield	Analysis	
				Calc.	Found
55		melting point 67-70	94.5	8.75 27.10	P S 8.5 26.8
56		n_D^{28} 1.5958	96.5	8.1 25.1	P S 8.0 26.0
57		n_D^{33} 1.5633	88.5	8.5 17.4	P S 8.5 17.0
58		n_D^{34} 1.602	78	44.0 5.24 25.1	C H S 44.2 5.2 24.7
59		n_D^{24} 1.583	60	8.4 26.6	P S 8.0 26.0
60		n_D^{24} 1.591	81	45.4 5.5 7.8 24.2	C H P S 45.4 5.5 7.4 23.3

TABLE I (Continued)

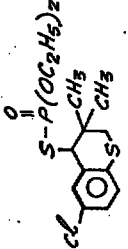
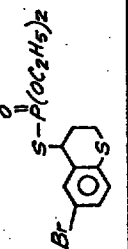
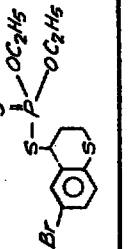
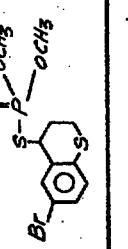
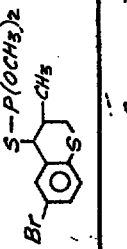
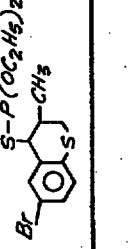
Example	Formula	n_D or melting point (°C)	Yield % of theoretical yield	Calc.	Analysis Found
61		n_D^{24} 1.5691	86	8.1 16.8	P 7.8 S 16.4
62		n_D^{22} 1.5901	87	39.3 4.5 7.8 16.1	C 39.3 H 4.8 P 7.9 S 16.1
63		n_D^{28} 1.633	93	37.77 4.36 7.51 23.24	C 37.6 H 4.2 P 7.0 S 22.9
64		n_D^{28} 1.637	81	34.28 3.64 8.05 24.93	C 34.8 H 3.7 P 8.2 S 26.0
65		n_D^{24} 1.6072	68	36.2 4.0 7.7	C 35.8 H 4.3 P 7.6
66		n_D^{24} 1.615	67	7.2 22.5	P 7.0 S 22.2

TABLE I (Continued)

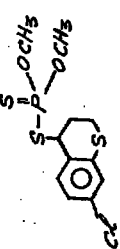
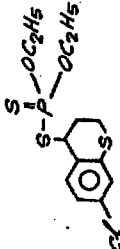
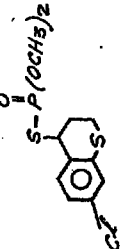
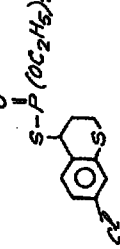
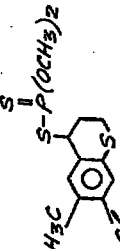
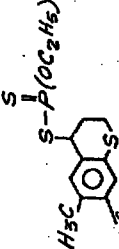
Example	Formula	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis	Found
67		melting point 65-67	91.5	38.77 4.11 9.1 28.19	C H P S	39.3 4.1 8.8 28.0
68		n_D^{34} 1.6061	85	42.34 4.88 8.41 26.06	C H P S	42.1 5.2 8.4 26.1
69		n_D^{24} 1.5928	75	9.5 19.7	P S	9.5 19.3
70		n_D^{24} 1.5798	87	8.8 18.2	P S	8.6 17.9
71		n_D^{22} 1.6156	97	40.7 4.5 8.7 27.0	C H P S	40.4 4.8 8.4 26.6
72		n_D^{22} 1.6102	91	43.9 5.2 8.1 25.0	C H P S	44.2 5.4 7.1 24.1

TABLE I (Continued)

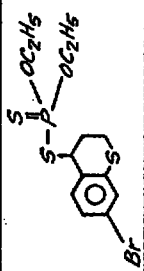
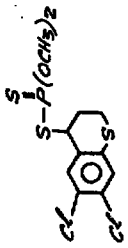
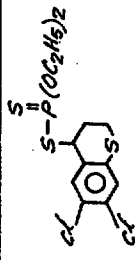
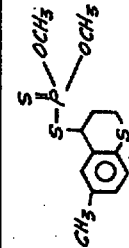
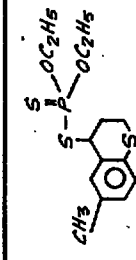
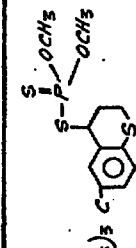
Example	Formula	n_D or melting point ($^{\circ}\text{C}$)	Yield % of theoretical yield	Calc.	Analysis	Found
73		n_D^{34} 1.6154	99	37.8 4.4 7.5 23.2	C H P S	37.5 4.6 7.5 22.6
74		$n_D^{23.2}$ 1.635	65	8.2 25.6	P S	7.7 25.8
75		$n_D^{23.2}$ 1.6221	92	38.8 4.2 7.7 23.8	C H P S	38.6 4.2 7.3 24.2
76		$n_D^{31.5}$ 1.6283	97	9.7 30.0	P S	9.0 29.0
77		n_D^{32} 1.606	98	48.3 6.04 27.6	C K S	49.3 6.0 27.1
78		n_D^{32} 1.5919	96	8.5 26.6	P S	8.0 26.0

TABLE I (Continued)

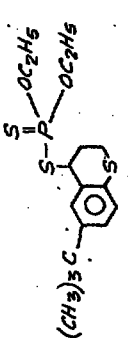
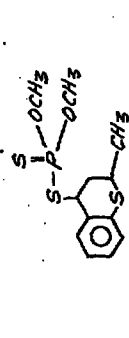
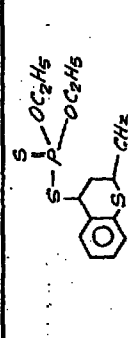
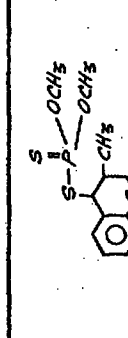
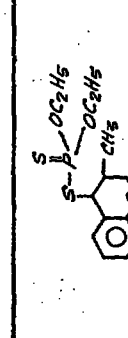
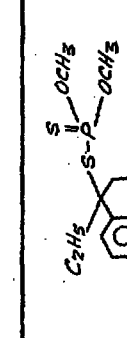
Example	Formula	n_D or melting point (°C)	Yield % of theoretical yield	Analysis	
				Calc.	Found
79		n_D 29.5 1.5815	99	24.6	S 24.0
80		melting point 67-68	82.5	45.0 5.31 9.69 30.0	C 45.2 H 5.3 P 9.4 S 30.0
81		melting point 49-50	85	48.28 6.03 8.91 27.6	C 48.2 H 6.2 P 8.9 S 28.2
82		n_D 29.5 1.6112	95	9.69 30.0	P 9.0 S 29.8
83		n_D 29.5 1.595	91	48.28 6.03 8.91 27.6	C 49.0 H 6.1 P 8.5 S 27.5
84		n_D 34 1.6028	90	28.7	S 28.7

TABLE I (Continued)

Example	Formula	n_D or melting point (°C)	Yield % of theoretical yield	Calc.	Analysis	Found
85		n_D^{34} 1.6128	88	26.5	S	26.8
86		$n_D^{31.5}$ 1.601	84	28.6	S	28.2
87		$n_D^{29.5}$ 1.6262	90	46.2 5.78 8.52 26.4	C H P S	46.5 5.8 8.0 26.4

EXAMPLE 88.

Bean plants (*Phaseolus vulgaris*) heavily infested with a phosphoric acid ester resistant spider mite strain (*Tetranychus urticae*) were sprayed, until rip-off began, with an aqueous dilution of an emulsifiable concentrate containing 0.003 weight % of 4-thiochromanyl-O,O-dimethyl-dithiophosphate as active substance. Subsequently, the sprayed plants were placed in a greenhouse at 20°C. Examination under the microscope after 8 days proved that all mobile and immobile stages of the mites were killed.

The phosphoric acid esters tested comparatively showed none or only insufficient activity despite high concentration of active substances (AS = active substance).

diazinone 0.1 weight % of AS	40% killing rate of mite population
azinphos-ethyl 0.1 weight % of AS	60% killing rate of mite population
dimethoate 0.1 weight % of AS	no effect
demeton-S-methyl 0.1 weight % of AS	no effect

5

10

EXAMPLE 89.

Caterpillars (3rd stage) of the white cabbage butterfly (*Pieris brassicae*) and leaves of white cabbage (*Brassica oleracea* var. *capitata*) or Savoy cabbage (*Brassica oleracea* var. *sabauda*) were sprayed with an aqueous dilution of an emulsifiable concentrate of 3-methyl-4-thiochromanyl-O,O-dimethyl-dithiophosphate, and subsequently placed in open vessels in the laboratory at about 22°C.

A concentration of active substance of 0.005 weight % or 0.003 mg/cm² was sufficient to obtain a 100% killing rate of the caterpillars after 48 hours.

EXAMPLE 90.

About 7 weeks old larvae of the mealworm (*Tenebrio molitor*) on a substrate (filter paper) were sprayed with a dosed amount of an aqueous suspension of a wettable powder of the compounds of Examples 45 and 76, and subsequently placed in the laboratory on Petri dishes at about 22°C.

A concentration of 0.005 weight % or 0.003 mg/cm² of active substance was sufficient to kill all larvae within 48 hours.

EXAMPLE 91.

Larvae of the yellow fever mosquito, stage IV (*Aedes aegypti*) and other mosquito larvae, stage IV (*Culex pipiens*) were placed in beakers containing 100 ml of an aqueous dilution of a wettable powder concentrate, the concentration of 6-fluoro-4-thiochromanyl-O,O-dimethyl-dithiophosphate being 0.0006 ppm by weight. This concentration was sufficient to kill all larvae within 24 hours.

This concentration amounts to only 1/2000 of that killing fishes (for example *Lebistes reticulatus* and *Xiphophorus helleri*), and 1/100000 of that killing fish nutrition organisms (*Daphnia magna*) within the same period of time.

Phosphoric esters applied also as agents for combating mosquito larvae, for example fenitrothion, Dursban (registered Trade Mark), or dichlorvos, showed a higher degree of toxicity in the above fishes (1/500 ratio). Therefore, 6-fluoro-4-thiochromanyl-O,O-dimethyl-dithiophosphate can be employed with considerably reduced risks for fishes in waters infested with fever mosquitoes.

EXAMPLE 92.

3 to 4 Weeks old grain weevils (*Calandra granaria*) were treated, as described in Example 90, with an aqueous suspension of a wettable powder of 6-fluoro-4-thiochromanyl-O,O-dimethyl-dithiophosphate. 0.003 mg of active substance per cm² resulted in a 100% mortality rate after 48 hours.

EXAMPLE 93.

In the manner described in Example 92, the compound 6-methoxy-4-thiochromanyl-O,O-di-ethyl-dithiophosphate was tested on the American milkweed bug (*Onco-peltus fasciatus*), in which test all bugs were killed using a concentration of 0.006 weight % of active substance in the spray liquor.

EXAMPLE 94.

1 ml each of a suspension of nematodes comprising all development stages (*Meloidogyne incognita*), which had been dyed in a 0.1% acridine orange solution, was introduced into an aqueous medium containing different concentration amounts of 4-thiochromanyl-O,O-dimethyl-dithiophosphate as active substance.

Evaluation was carried out after 72 hours by means of the fluorescence microscope with determination of the percental mortality. The cited compound at a concentration of 0.3 weight % of active substance showed an activity three times as intense as that of the active substance carbofuran applied in a comparative test.

EXAMPLE 95.

Young apple trees planted in pots and heavily infested with a phosphoric ester resistant strain of the European red mite (*Metatetranychus ulmi*) were sprayed, until beginning drip-off, with the aqueous dilution of an emulsifiable concentrate containing 0.003 weight % of the preparation of Example 13, and subsequently placed in a greenhouse at 20°C.

A microscopic control after 8 days showed that all mobile and immobile stages were killed.

Tested in the same manner, the compounds of Examples 1, 9, 15, 17, 19, 28 and 33 proved to be of equal activity. In the case of the compound of Example 49, a 100%

kill was attained at a concentration of 0.006 weight %, in the case of the compound of Example 81, at a concentration of 0.025 weight %.

The following commercial phosphoric acid esters used in comparative tests showed no activity even at higher concentration:

5	phenkapton	0.025 weight %	no effect	5
	demeton-S-methyl	0.05 " "	" "	
	dimethoate	0.05 " "	" "	

EXAMPLE 96.

Horse beans (*Vicia faba*) heavily infested with bean aphids (*Doralis fabae*) were sprayed, until beginning drip-off, with the aqueous dilution of an emulsifiable concentrate containing 0.000375 weight % of the preparation of Example 3. The sprayed plants were then placed at 20°C in a greenhouse; evaluation was carried out 24 hours after the spraying. All aphids were killed.

Tested in the same manner, the compounds of Examples 1, 2, 8, 10, 13, 15, 23, 25 and 30 showed equal activity. In the case of the compound of Example 40, a concentration of 0.00075 weight % was sufficient to kill all aphids.

EXAMPLE 97.

Young cotton plants (*Gossypium spec.*) in pots, infested with African cotton stainers (*Dysdercus fasciatus*), were sprayed, until drip-off, with the aqueous dilution of a wettable powder concentrate containing 0.006 weight % of the preparation of Example 23. Subsequently, the plants containing the bugs were put into cylindrical gauze cages and placed in a greenhouse at 20°C. A control after 48 hours showed that all cotton stainers were killed.

Tested in the same manner, the compounds of Examples 1, 3, 28, 33, 76 and 82 showed the same good activity; a 100% kill was attained in the case of the compound of Example 55 at a concentration of 0.003 weight %. The following phosphoric acid esters tested comparatively showed their activity only at a considerably higher concentration:

		lethal concentr.	
30	diazinone	0.025 % of AS	30
	dimethoate	0.025 % of AS	
		(AS = active substance)	
		(% = weight %)	
35	azinphos-ethyl	0.05 % of AS	

EXAMPLE 98.

Larvae (4th stage) of the Mexican bean beetle (*Epilachna varivestis*) and leaves of the dwarf-bush bean (*Phaseolus vulgaris*) were sprayed, by means of a spraying apparatus, with a dosed amount (corresponding to an application amount of 600 liters of spray liquor/ha in the open fields) of the aqueous dilution of an emulsifiable concentrate containing the preparation of Example 10 in a concentration of 0.002 weight %. The leaves and beetle larvae were placed in open vessels at 22°C. The control 47 hours after spraying proved that all larvae were killed.

Tested in the same manner, the compounds of Examples 1, 3, 15, 17, 21, 23 and 25 had equal activity. In the case of the compounds of Examples 39 and 50, a 100% kill was attained at a concentration of 0.0012 weight %, in the case of the compound of Example 49 even at only 0.0006 weight %.

The activity of the compounds of the invention against strains of ticks having different sensitivity degrees to phosphoric acid esters, as well as the systemic activity in animals were proved by the following Examples:

EXAMPLE 99.

In vitro test on ticks of the *Boophilus* species

1. *Boophilus microplus*
 - a) strain of normal sensitivity
 - b) Biarra strain, resistant
 - c) Mackay strain, "

2. *Boophilus decoloratus*, resistant strain

For the preparation of a suitable formulation, 10 parts by weight of active substance were dissolved in 100 parts by volume of a mixture of cyclohexanone and nonyl-

phenol (10 EO, 8:1), and the emulsifiable concentrate so obtained was diluted with water to attain the desired concentration.

5 10 Adult female ticks of the cited species and different sensitivity to phosphoric esters, which had sucked themselves full of blood, were dipped for 5 minutes into these dilutions. Subsequently, the ticks were stuck with their dorsal side onto an adhesive tape and kept in a warming closet (28°C, about 80% of relative air moisture) for the oviposition.

10 Two weeks after the treatment, the activity of the formulations was determined by evaluating the inhibition of oviposition, which is expressed in percent; 100% meaning that all ticks treated with one active substance concentration did not oviposit, 0% meaning that all ticks did oviposit.

10

TABLE II
In vitro test on ticks of different phosphoric ester sensitivity

Compound of Example	Concentration of active substance in % by weight	Inhibition of oviposition in %			
		Boophilus microplus			Boophilus decoloratus (resistant)
		strain of normal sensitivity	Biarra strain (resistant)	Mackay strain (resistant)	
1	0,2	100	90		
	0,05	100	70		
	0,0125	100	50		
	0,0031	100	0		
2	0,2	100	100	100	100
	0,05	100	90	100	100
	0,0125	100	80	90	90
	0,0031	90	0	30	10
3	0,2	100	100	90	100
	0,05	90	70	20	100
	0,0125	100	0	0	0
	0,0031	80	20	0	0
9	0,2	100	80		
	0,05	100	90		
	0,0125	100	90		
	0,0031	100	20		
10	0,2	100	100	100	100
	0,05	90	70	100	100
	0,0125	90	60	0	10
	0,0031	70	0	0	0
13	0,21	100	100		
	0,05	100	70		
	0,0125	90	0		
	0,0031	30	0		

TABLE II (Continued)
In vitro test on ticks of different phosphoric ester sensitivity

Compound of Example	Concentration of active substance in % by weight	Inhibition of oviposition in %			
		Boophilus microplus			Boophilus decoloratus (resistant)
		strain of normal sensitivity	Biara strain (resistant)	Wackay strain (resistant)	
15	0.2	100	100	100	100
	0.05	90	100	100	100
	0.0125	90	70	100	100
	0.0031	90	70	100	100
17	0.2	100	90	90	100
	0.05	90	60	70	90
	0.0125	90	40	0	10
	0.0031	50	10	0	0
23	0.2	100	70		
	0.05	100	60		
	0.0125	90	50		
	0.0031	100	10		
25	0.2	100	100	100	100
	0.05	100	90	100	100
	0.0125	100	100	100	100
	0.0031	100	90	100	90
39	0.2	70	90	90	20
	0.05	60	90	90	10
	0.012	50	90	80	0
	0.006	30	90	60	0
40	0.2	90	10	10	80
	0.05	90	0	0	20
	0.012	90	0	10	20
	0.006	30	0	0	0

TABLE II (Continued)
In vitro test on ticks of different phosphoric ester sensitivity

Compound of Example	Concentration of active substance in % by weight	Inhibition of oviposition in %			
		Boophilus microplus			Boophilus decoloratus (resistant)
		strain of normal sensitivity	Biarra strain (resistant)	Mackay strain (resistant)	
43	0,2	100	100	80	100
	0,05	100	30	20	100
	0,012	100	10	0	100
	0,006	100	0	0	0
45	0,2	100	40	70	90
	0,05	100	10	20	60
	0,012	90	0	0	10
	0,006	70	0	0	0
47	0,2	90	100	100	100
	0,05	90	90	90	90
	0,012	90	90	20	90
	0,006	90	0	10	30
49	0,2	100	10	90	100
	0,05	100	0	10	40
	0,012	100	0	10	0
	0,006	40	0	20	0
50	0,2	100	100	90	100
	0,05	100	90	90	100
	0,012	100	70	90	100
	0,006	70	40	30	100
63	0,2	100	10	0	100
	0,05	90	0	10	90
	0,012	90	0	0	10
	0,006	50	10	10	10

TABLE II (Continued)
In vitro test on ticks of different phosphoric ester sensitivity

Compound of Example	Concentration of active substance in % by weight	Inhibition of oviposition in %				
		Boophilus microplus				Boophilus decoloratus (resistant)
		strain of normal sensitivity	Biarra strain (resistant)	Mackay strain (resistant)		
62	0.2	100	90	100	100	
	0.05	90	80	90	100	
	0.012	90	70	70	100	
	0.006	90	60	30	60	
58	0.2	100	80	100	90	
	0.05	100	40	70	40	
	0.012	90	0	0	10	
	0.006	30	0	10	0	
77	0.2	100				
	0.05	100				
	0.012	100				
	0.006	0				
81	0.2	100				
	0.05	70				
	0.012	0				
	0.006	0				
85	0.2	100				
	0.05	90				
	0.012	80				
	0.006	0				
Dursban	0.2	100	100	100	90	
	0.05	90	50	0	10	
	0.012	100	40	0	0	
	0.006	90	20	0	0	
coumaphos	0.2	100	80			
	0.05	90	60			
	0.012	60	10			
	0.006	20	0			

EXAMPLE 100.

Systemic activity in animals; model test on guinea pigs

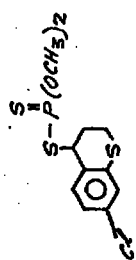
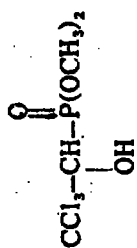
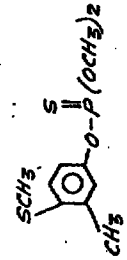
For the preparation of an administrable formulation, 2 parts by weight of active substance were dissolved in 100 parts by volume of olive oil and administered as oily solution orally in the desired doses to guinea pigs by means of a probang.

Before the treatment, as a comparison, as well as in determined time intervals after the treatment, 10 adult, unfed bedbugs (*Cimex lectularius*) each were placed for blood-sucking on the shaved abdominal skin of the guinea pigs.

The mortality rate of the test insect groups fed on the treated guinea pigs was evaluated until up to 24 hours after the absorption of blood. There was a 100% activity degree when all test insects had been killed within a certain time after the absorption of blood; it was zero, when all test insects of a group were still living.

10
060
200.012
0.006

TABLE III (Continued)
Systemic activity in animals/guinea pigs

Active substance	Dose mg/kg	hrs. after treatment put on for bloodsucking comparison	% mortality after hrs.											
			1	2	3	4	5	6	7	8	24			
	100	comparison 1 3 7 24	0	0	0	0	0	0	0	0	0			
			100											
			100											
			0								100			
	50	comparison 1 3 7 24	0	0	0	0	0	0	0	0	0			
			0	0	0	0	0	0	0	0	0			
			100											
			20								100			
	50	comparison 1 3 7	0	0	0	0	0	0	0	0	0			
			100											
			0											
			0											
 known	25	comparison 1 3 7	0	0	0	0	0	0	0	0	0			
			90	100										
			0	0	0	0	0	0	0	0	0			
			0	0	0	0	0	0	0	0	0			
	50	comparison 1 3 7	0	0	0	0	0	0	0	0	0			
			40	100										
			0	100										
			0								100			
	25	comparison 1 3 7	0	0	0	0	0	0	0	0	0			
			0	0	0	0	0	0	0	0	0			
			0	100							30			
			0								100			

Toxicological data

Thiochromanyl-phosphoric acid esters

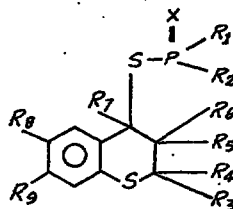
4-thiochromanyl-O,O-dimethyl-dithiophosphate LD 50 5—10 mg/kg rat orally

5-chloro-4-thiochromanyl-O,O-diethyl-dithiophosphate LD 50 63/200 mg/kg rat orally

6-chloro-4-thiochromanyl-O,O-dimethyl-dithiophosphate LD 50 200—630 mg/kg rat orally

WHAT WE CLAIM IS:—

1. A compound of the general formula



in which

R₁ is an alkyl group having from 1 to 4 carbon atoms, an alkoxy group having from 1 to 6 carbon atoms, or a phenyl group;R₂ is an alkoxy group having from 1 to 6 carbon atoms, an amino group, an alkyl-amino group having from 1 to 6 carbon atoms, a dialkylamino group having from 1 to 6 carbon atoms per alkyl group or an alkenylamino group having from 3 to 6 carbon atoms;R₃, R₄, R₅, R₆ and R₇, which may be the same or different, is each a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms at least three of R₃, R₄, R₅, R₆ and R₇ being hydrogen atoms;R₈ and R₉ which may be the same or different, is each a hydrogen or halogen atom, an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms;

and

X is oxygen or sulfur.

2. A compound according to claim 1 in which R₁ is an alkoxy group having from 1 to 6 carbon atoms and R₂ is an alkoxy group having 1 or 2 carbon atoms, an alkyl-amino or dialkylamino group having from 1 to 6 carbon atoms per alkyl group or an alkenylamino group having from 3 to 6 carbon atoms, or in which R₁ is an alkyl group having from 1 to 4 carbon atoms and R₂ is an alkoxy group having from 1 to 6 carbon atoms.

3. 6-Chloro-4-thiochromanyl-O,O-dimethyl-dithiophosphate.

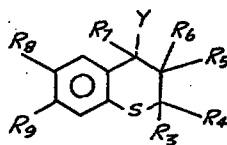
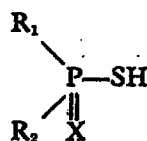
4. 6-Chloro-4-thiochromanyl-O,O-diethyl-dithiophosphate.

5. S-(6-Chloro-4-thiochromanyl)-dimethyl-thiophosphate.

6. S-(6-Chloro-4-thiochromanyl)-diethyl-thiophosphate.

7. 7-Chloro-4-thiochromanyl-O,O-dimethyl-dithiophosphate.

8. A process for the preparation of a compound according to claim 1 which comprises reacting a 4-halogeno-thiochromanyl compound of the formula

in which R₃, R₄, R₅, R₆, R₇, R₈ and R₉ have the meanings specified in claim 1 and Y is a halogen atom, with a phosphorus compound of the formula

Toxicological data

Thiochromanyl-phosphoric acid esters

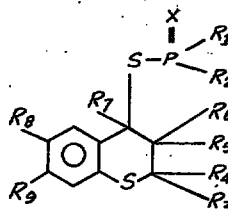
4-thiochromanyl-O,O-dimethyl-dithiophosphate LD 50 5—10 mg/kg rat orally

5 5-chloro-4-thiochromanyl-O,O-diethyl-dithiophosphate LD 50 63/200 mg/kg rat orally 5 5

6-chloro-4-thiochromanyl-O,O-dimethyl-dithiophosphate LD 50 200—630 mg/kg rat orally

WHAT WE CLAIM IS:—

1. A compound of the general formula



in which

R₁ is an alkyl group having from 1 to 4 carbon atoms, an alkoxy group having from 1 to 6 carbon atoms, or a phenyl group;15 R₂ is an alkoxy group having from 1 to 6 carbon atoms, an amino group, an alkyl-amino group having from 1 to 6 carbon atoms, a dialkylamino group having from 1 to 6 carbon atoms per alkyl group or an alkenylamino group having from 3 to 6 carbon atoms;20 R₃, R₄, R₅, R₆, and R₇, which may be the same or different, is each a hydrogen atom or an alkyl group having from 1 to 4 carbon atoms at least three of R₃, R₄, R₅, R₆ and R₇ being hydrogen atoms;25 R₈ and R₉, which may be the same or different, is each a hydrogen or halogen atom, an alkyl group having from 1 to 4 carbon atoms or an alkoxy group having from 1 to 4 carbon atoms; and

X is oxygen or sulfur.

30 2. A compound according to claim 1 in which R₁ is an alkoxy group having from 1 to 6 carbon atoms and R₂ is an alkoxy group having 1 or 2 carbon atoms, an alkyl-amino or dialkylamino group having from 1 to 6 carbon atoms per alkyl group or an alkenylamino group having from 3 to 6 carbon atoms, or in which R₁ is an alkyl group having from 1 to 4 carbon atoms and R₂ is an alkoxy group having from 1 to 6 carbon atoms.

35 3. 6-Chloro-4-thiochromanyl-O,O-dimethyl-dithiophosphate.

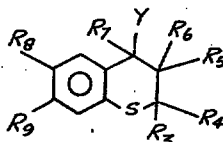
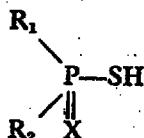
4. 6-Chloro-4-thiochromanyl-O,O-diethyl-dithiophosphate.

5. S-(6-Chloro-4-thiochromanyl)-dimethyl-thiophosphate.

6. S-(6-Chloro-4-thiochromanyl)-diethyl-thiophosphate.

7. 7-Chloro-4-thiochromanyl-O,O-dimethyl-dithiophosphate.

8. A process for the preparation of a compound according to claim 1 which comprises reacting a 4-halogeno-thiochromanyl compound of the formula

40 in which R₃, R₄, R₅, R₆, R₇, R₈ and R₉ have the meanings specified in claim 1 and Y is a halogen atom, with a phosphorus compound of the formula

in which R_1 and R_2 have the meanings specified in claim 1, or a salt thereof, optionally in the presence of an acid binding agent.

9. A process according to claim 8, wherein Y is a chlorine or bromine atom.

10. A process according to claim 8 carried out substantially as described in Examples 1 to 87 herein.

11. A compound according to claim 1 whenever prepared by a process according to any one of claims 8 to 10.

12. A pesticidal composition which comprises, as active ingredient, a compound according to claim 1 together with a carrier material.

13. A method of combating insect, members of the order acarina, nematodes and animal ectoparasites, which comprises applying to their habitat a compound according to claim 1.

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