

PATENT SPECIFICATION

(11) 1298515

NO DRAWINGS

- (21) Application No. 9539/70 (22) Filed 27 Feb. 1970
 (61) Patent of Addition to No. 1 055 603 date 11 May 1965
 (31) Convention Application No. P19 10 588.5
 (32) Filed 1 March 1969 in
 (33) Germany (DT)
 (45) Complete Specification published 6 Dec. 1972
 (51) International Classification C07C 149/32
 (52) Index at acceptance
 C2C 220 227 22Y 30Y 313 316 31Y 339 340 34Y 358
 364 366 36Y 373 37Y 462 464 612 628 658 662
 699 71Y 771 791 79Y QU RA
 (72) Inventors HELLMUT HOFFMANN, INGEBORG HAMMANN
 and GÜNTER UNTERSTENHÖFER



(54) SUBSTITUTED PHENYLCARBAMIC ACID ESTER,
 PROCESS FOR ITS PREPARATION, AND ITS USE AS
 INSECTICIDE

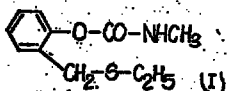
(71) We, BAYER AKTIENGESELLSCHAFT, formerly Farbenfabriken Bayer Aktiengesellschaft, a body corporate organised under the laws of Germany, of Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 The present invention relates to a new substituted phenylcarbamic acid ester, to a process for its production and to its use as an insecticide, especially a systemic-insecticide.

15 Patent 1,055,603 provides N - methyl - O - phenylcarbamic acid esters, such as N - methyl - O - (2 - methylmercaptomethyl - phenyl) - carbamic acid ester, N - methyl - O - (2 - methoxymethyl - phenyl) - carbamic acid ester and N - methyl - O - (2 - ethoxymethyl - phenyl) - carbamic acid ester, which exhibit an insecticidal activity.

The present invention relates to an improvement in or modification of the invention of Patent 1,155,603.

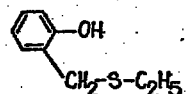
25 The present invention provides N - methyl - O - (2 - ethylmercaptomethyl - phenyl) - carbamic acid ester of the formula



(I)

30 The present invention also provides a process for the production of N - methyl - O - (2 - [Price 25p]

ethylmercaptomethyl - phenyl) - carbamic acid ester of the formula (I) in which
 (a) the phenol of the formula



(II)

is reacted with methylisocyanate or

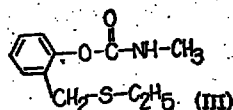
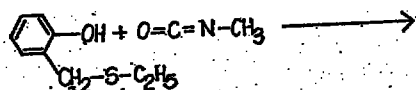
(b) the phenol of the formula (II) is converted with an excess of phosgene into the appropriate chloroformic acid ester, and the latter is reacted with methylamine

or

(c) the phenol of the formula (II) is converted with an approximately equivalent amount of phosgene to give the appropriate bis-(phenyl)-carbonate, and the latter is split by treatment with methylamine.

Surprisingly, N - methyl - O - (2 - ethylmercaptomethyl - phenyl) - carbamic acid ester shows a considerably higher systemic-insecticidal activity than the N - methyl - O - phenylcarbamic acid esters known from the prior art which are the chemically closest substances of the same type of activity. The substance according to the invention therefore represents an enrichment of the art.

If 2-ethylmercaptomethylphenol and methylisocyanate are used as starting materials, the reaction course can be represented by the following formula scheme:



The 2-ethylmercaptomethylphenol used as starting material can be obtained from 2-chloromethylphenol and ethylmercaptan in the presence of sodium methylate.

The three process variants may be carried out in the presence of an inert solvent (this term includes a mere diluent). All inert organic solvents are suitable. Preferred solvents include hydrocarbons, such as benzene, benzine, toluene, xylene; ethers, such as diethyl ether or di-n-butyl ether, dioxan, tetrahydrofuran; low molecular weight aliphatic ketones and nitriles, for example acetone, methylethyl ketone, methylisopropyl ketone, methylisobutyl ketone, acetonitrile and propionitrile.

The process variant (a) can also be carried out in the absence of a solvent.

An acid-binder is normally used in variants (b) and (c). All the usual acid-binding agents can be used. Preferred acid-binders include the alkali metal hydroxides, such as sodium and potassium hydroxide, alkali metal carbonates, such as sodium carbonate, and amines such as triethylamine and pyridine.

The reactions can be carried out within fairly wide temperature ranges. In general, the reaction are carried out at from -10° to $+150^\circ\text{C}$, preferably -10° to $+40^\circ\text{C}$.

The process variants are, in general, carried out under normal pressure.

In the variants of the processes according to the invention, the reactants are generally, used in equivalent amounts, except that the phosgene in process (b) is used in excess.

In the first step of variant (b), the work is preferably carried out at a pH value below 7; in the first step of variant (c), preferably at a pH value of approximately 8.

The working up of the reaction mixture may be carried out in customary manner.

The active compound according to the invention exhibits a strong insecticidal activity, with low phytotoxicity and low toxicity to warm-blooded animals. The active compound can therefore be used with good results for the control of noxious sucking and biting insects and Diptera. The effect sets in rapidly and is long-lasting.

To the sucking insects there belong, in the main aphids, such as the green peach aphid (*Myzus persicae*), the bean aphid (*Vorialis fabae*); scales, such as *Aspidiotus hederae*, *Lecanium hesperidum*, *Pseudococcus maritimus*; Thysanoptera, such as *Hercinotrips*

femoralis; and bugs, such as the beet bug (*Piesma quadrata*) and the bed bug (*Cimex lectularius*).

With the biting insects, there are classed, in the main butterfly caterpillars, such as *Plutella maculipennis*, *Lymantria dispar*; beetles, such as granary weevils (*Sitophilus granarius*), the Colorado beetle (*Leptinotarsa decemlineata*), but also species living in the soil, such as the wireworms (*Agriotes* sp.) and larvae of the cockchafer (*Melolontha melolontha*); cockroaches, such as the German cockroach (*Blattella germanica*); Orthoptera, such as the house cricket (*Gryllus domesticus*); termites such as *Reticulitermes*; Hymenoptera, such as ants.

The Diptera comprise, in particular, the flies, such as the vinegar fly (*Drosophila melanogaster*), the Mediterranean fruit fly (*Ceratitis capitata*), the house fly (*Musca domestica*), and mosquitoes, such as the yellow fever mosquito (*Aedes aegypti*).

The active compound is distinguished particularly by a strong systemic activity.

The active compound according to the present invention can be converted into the usual formulations, such as solutions, emulsions, suspensions, powders, pastes and granulates. These may be produced in known manner, for example by mixing the active compounds with extenders, that is, liquid or solid diluents or carriers, optionally with the use of surface-active agents, that is, emulsifying agents and/or dispersing agents. In the case of the use of water as an extender, organic solvents can, for example, also be used as auxiliary solvents.

As liquid diluents or carriers, there are preferably used aromatic hydrocarbons, such as xylenes or benzene, chlorinated aromatic hydrocarbons, such as chlorobenzenes, paraffins, such as mineral oil fractions, alcohols, such as methanol or butanol, or strongly polar solvents, such as dimethyl formamide or dimethyl sulphoxide, as well as water.

As solid diluents or carriers, there are preferably used ground natural minerals, such as kaolins, clays, talc or chalk; or ground synthetic minerals, such as highly-dispersed silicic acid or silicates.

Preferred examples of emulsifying agents include non-ionic and anionic emulsifiers, such as polyoxyethylene-fatty acid esters, polyoxyethylene-fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkyl sulphonates and aryl sulphonates; and preferred examples of dispersing agents include lignin, sulphite waste liquors and methyl cellulose.

The active compound according to the invention may be present in the formulations in admixture with other active compounds.

The formulations contain, in general, from 0.1 to 95, preferably 0.5 to 90, per cent by weight of active compound.

The active compound may be used as such or in the form of its formulations or of the ap-

60

65

70

75

80

85

90

95

100

105

110

115

120

60 application forms prepared therefrom, such as
ready-to-use solutions, emulsions, suspensions,
powders, pastes and granulates. Application
may take place in the usual manner, for ex-
5 ample by squirting, spraying, dusting, scat-
tering, watering, dressing and incrustation.

65 The concentrations of active compound in
the ready to-use preparations can be varied
within fairly wide ranges. In general, they are
10 from 0.0001 to 5 per cent by weight, prefer-
ably 0.0005 to 1%.

70 In the case of certain methods of application,
very concentrated preparations are used, for
example with contents of active compounds of
15 10 to 80 per cent by weight in the ULV process
(ultra-low-volume process).

75 The active compound according to the inven-
tion also shows an anti-microbial activity, and
can therefore be used in industrial disinfection
20 for the destruction of fungi and bacteria.

80 The invention therefore provides an in-
secticidal composition containing as active in-
gredient the compound according to the inven-
tion in admixture with a solid diluent or car-
25 rier or in admixture with a liquid diluent or
carrier containing a surface-active agent.

85 The invention also provides a method of
combating insect pests which comprises apply-
ing to the pests or a pest habitat the com-
30 pound according to the invention alone or in
the form of a composition containing as active
ingredient the compound according to the inven-
tion in admixture with a solid or liquid
diluent or carrier.

90 35 The invention also provides crops protected

from damage by insects by being grown in
areas in which, immediately prior to and/or
during the time of the growing, the com-
pound according to the invention was applied
40 alone or in admixture with a solid or liquid
diluent or carrier.

The invention is illustrated by the following
Examples.

Example A

Myzus test (contact action) 45

Solvent: 3 parts by weight dimethyl form-
amide

Emulsifier: 1 part by weight alkylaryl poly-
glycol ether

75 To produce a suitable preparation of active
compound, 1 part by weight of the active com-
pound is mixed with the stated amount of sol-
vent containing the stated amount of emulsi-
fier and the concentrate is diluted with water
to the desired concentration. 55

80 Cabbage plants (*Brassica oleraceae*)
which have been heavily infested with peach
aphids (*Myzus persicae*) are sprayed with the
preparation of the active compound until drip-
ping wet. 60

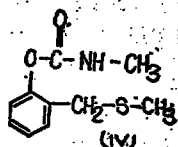
85 After the specified periods of time, the
degree of destruction is determined as a per-
centage: 100% means that all the aphids are
killed whereas 0% means that none of the
aphids are killed. 65

The active compounds, the concentrations of
the active compounds, the evaluation times
and the results can be seen from Table A.

TABLE A
(plant-damaging insects)

Myzus test

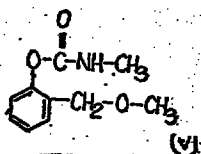
Active compounds Concentration of
active compound in % Degree of destruction
in % after 24 hours



0.2
0.02
0.002
0.0002

100
100
60
0

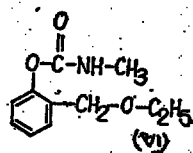
(known)



0.2
0.02

100
60

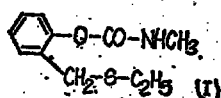
(known)



0.2
0.02

100
0

(known)



0.2
0.02
0.002
0.0002

100
100
90
25

Example B

Doralis test (systemic action)

Solvent: 3 parts by weight dimethyl formamide

- 5 Emulsifier: 1 part by weight alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of the active compound is mixed with the stated amount of solvent containing the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

- 10 Bean plants (*Vicia faba*) which have been heavily infested with the bean aphid (*Doralis fabae*) are water with the preparation of the

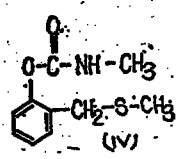
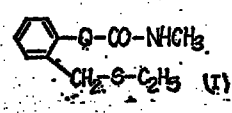
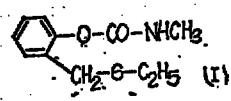
active compound so that the preparation of the active compound penetrates into the soil without wetting the leaves of the bean plants. The active compound is taken up by the bean plants from the soil and so reaches the infested leaves.

After the specified periods of time, the degree of destruction is determined as a percentage. 100% means that all the aphids are killed; 0% means that none of the aphids are killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from Table B.

TABLE B
(plant-damaging insects)

Doralis test (systemic)

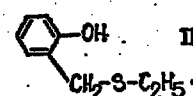
Active compounds	Concentration of active compound in %	Degree of destruction in % after 4 days
 (IV)	0.2	100
	0.02	100
	0.002	0
(known)		
 (I)	0.2	100
	0.02	100
	0.002	100
	0.0002	40
Example 1		
	 (I)	

- 35 30 g of methylisocyanate are added to 0.5 mole of 2-ethylmercaptomethylphenol in 300 ml of benzene and allowed to stand for 12 hours. The solvent is then distilled. There remain behind 72 g (74% of the theory) of the compound of the above formula; refractive index $n_D^{25} = 1.5602$.

- 40 The N-methyl-O-(2-ethylmercaptomethyl-phenyl)-carbamic acid ester is also obtained in 45-55% yield when 2-ethylmercaptomethyl phenol is reacted with an excess of phosgene to give the chloroformic

acid ester or with approximately equimolar amounts of phosgene to give the bis-(phenyl)-carbonate, and then treated with methylamine.

The phenol used as starting material of the formula

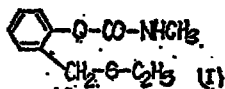


can be prepared as follows:

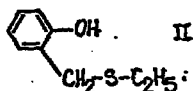
- 71 g of freshly prepared 2-chloromethylphenol in 300 ml of acetonitrile are reacted with 35 g of ethylmercaptan and 0.5 mole of sodium methylate in 100 ml of acetonitrile at 0—10°C. After standing for two hours, pouring into water is effected, followed by taking up with benzene and distillation. b.p. 105°/5 mm Hg. Yield: 50% of the theory.

WHAT WE CLAIM IS:—

1. N - methyl - O - (2 - ethylmercapto-methyl - phenyl - carbamic acid ester of the formula:—



2. A process for the production of the compound of claim 1 in which
(a) the phenol of the formula:—



is reacted with methylisocyanate
or

- (b) the phenol of the formula (II) is converted with an excess of phosgene into the appropriate chloroformic acid ester, and the latter is reacted with methylamine
or
(c) the phenol of the formula (II) is converted with an approximately equivalent amount of phosgene to give the appropriate bis-(phenyl)-carbonate, and the latter is split by treatment with methylamine.
3. A process according to claim 2 (b) in which the first step is carried out at a pH below 7.
4. A process according to claim 2 (c) in which the first step is carried out at a pH of approximately 8.
5. A process according to claim 2 (b) or

(c), 3 or 4 in which an acid-binder is used.

6. A process according to any of claims 2—5 in which the reaction is carried out in the presence of an inert solvent.

7. A process according to any of claims 2—6 in which the reaction is carried out at —10 to +150°C.

8. A process according to claim 7 in which the reaction is carried out at —10 to +40°C.

9. A process for the production of the compound of claim 1 substantially as hereinbefore described in Example 1.

10. The compound of claim 1 whenever prepared by a process according to any of claims 2—9.

11. An insecticidal composition containing as active ingredients a compound according to claim 1 or 10 in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

12. A composition according to claim 11 containing from 0.1 to 95% of the active compound by weight.

13. A method of combating insect pests which comprises applying to the insects or a habitat thereof the compound of claim 1 or 10 alone or in the form of a composition containing as active ingredient a compound of claim 1 or 10 in admixture with a solid or liquid diluent or carrier.

14. A method according to claim 13 in which a composition is used containing from 0.0001 to 5% of the active compound by weight.

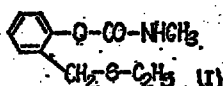
15. Crops protected from damage by insects by being grown in areas in which, immediately prior to and/or during the time of the growing, the compound of claim 1 or 10 was applied alone or in admixture with a solid or liquid diluent or carrier.

For the Applicants
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings,
Chancery Lane,
London, W.C.2.

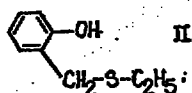
71 g. of freshly prepared 2-chloromethylphenol in 300 ml of acetonitrile are reacted with 35 g of ethylmercaptan and 0.5 mole of sodium methylate in 100 ml of acetonitrile at 0—10°C. After standing for two hours, pouring into water is effected, followed by taking up with benzene and distillation, b.p. 105°/5 mm Hg. Yield: 50% of the theory.

WHAT WE CLAIM IS:—

1. N - methyl - O - (2 - ethylmercapto-methyl - phenyl - carbamic acid ester of the formula:—



2. A process for the production of the compound of claim 1 in which
(a) the phenol of the formula:—



is reacted with methylisocyanate
or

(b) the phenol of the formula (II) is converted with an excess of phosgene into the appropriate chloroformic acid ester, and the latter is reacted with methylamine
or

(c) the phenol of the formula (II) is converted with an approximately equivalent amount of phosgene to give the appropriate bis-(phenyl)-carbonate, and the latter is split by treatment with methylamine.

3. A process according to claim 2 (b) in which the first step is carried out at a pH below 7.

4. A process according to claim 2 (c) in which the first step is carried out at a pH of approximately 8.

5. A process according to claim 2 (b) or

(c), 3 or 4 in which an acid-binder is used.

6. A process according to any of claims 2—5 in which the reaction is carried out in the presence of an inert solvent.

7. A process according to any of claims 2—6 in which the reaction is carried out at —10 to +150°C.

8. A process according to claim 7 in which the reaction is carried out at —10 to +40°C.

9. A process for the production of the compound of claim 1 substantially as hereinbefore described in Example 1.

10. The compound of claim 1 whenever prepared by a process according to any of claims 2—9.

11. An insecticidal composition containing as active ingredients a compound according to claim 1 or 10 in admixture with a solid diluent or carrier or in admixture with a liquid diluent or carrier containing a surface-active agent.

12. A composition according to claim 11 containing from 0.1 to 95% of the active compound by weight.

13. A method of combating insect pests which comprises applying to the insects or a habitat thereof the compound of claim 1 or 10 alone or in the form of a composition containing as active ingredient a compound of claim 1 or 10 in admixture with a solid or liquid diluent or carrier.

14. A method according to claim 13 in which a composition is used containing from 0.0001 to 5% of the active compound by weight.

15. Crops protected from damage by insects by being grown in areas in which, immediately prior to and/or during the time of the growing, the compound of claim 1 or 10 was applied alone or in admixture with a solid or liquid diluent or carrier.

For the Applicants
CARPMAELS & RANSFORD,
Chartered Patent Agents,
24, Southampton Buildings,
Chancery Lane,
London, W.C.2.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

