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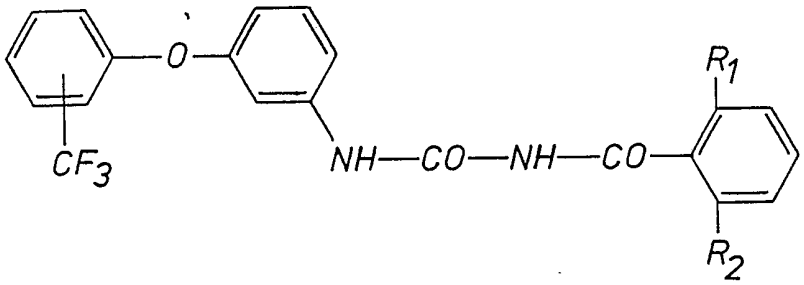
(54) **Phenoxyphenylureas**

(57) Novel halogen-substituted N-3-(trifluoromethylphenoxy)phenyl-N'-benzoylureas of the formula



wherein R_1 is fluorine or chlorine and R_2 is hydrogen, fluorine or chlorine, the production thereof, and compositions containing these compounds for use in pest control, especially for the control of insects which are pests of plants and animals. The novel compounds are especially effective against larval stages of plant-destructive feeding insects.

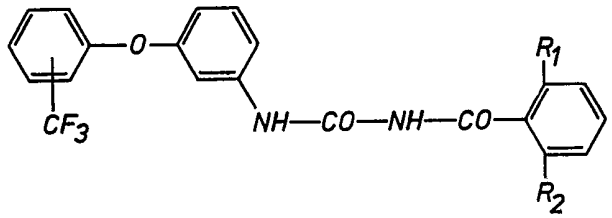
The chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

SPECIFICATION

Phenoxyphenylureas

The present invention relates to novel halogen-substituted N-3-(trifluoromethylphenoxy)phenyl-N'-benzoylureas, to the production thereof and to the use thereof in pest control. The invention is also concerned with novel starting materials and the production thereof.

The halogen-substituted N-3-(trifluoromethylphenoxy)phenyl-N'-benzoylureas have the formula I



(I)

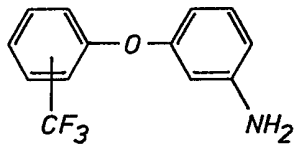
wherein R_1 is fluorine or chlorine and R_2 is hydrogen, fluorine or chlorine.

On account of their pesticidal action, preferred compounds of the formula I are those wherein R_1 and R_2 are fluorine. In the compounds of the formula I, the CF_3 radical is preferably in the meta- or para-position.

The compounds of the formula I can be obtained by methods which are known per se (cf. for example German Offenlegungsschriften 2 123 236 and 2 601 780 and Japanese patent specification 53103447.

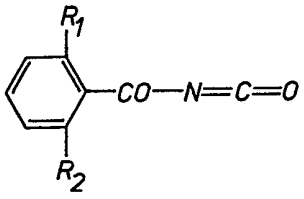
Thus, for example, a compound of the formula I can be obtained by

a) reacting a compound of the formula II



(II)

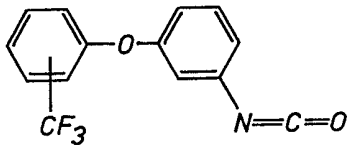
with a compound of the formula III



(III)

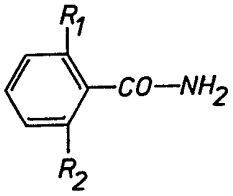
or

b) reacting a compound of the formula IV



(IV)

optionally in the presence of an organic or inorganic base, with a compound of the formula V



(V)

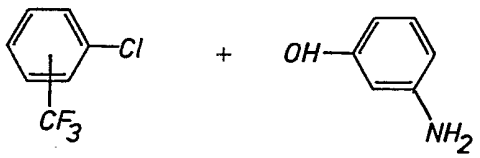
In the formulae III and V above, R_1 and R_2 are as defined for formula I.

Processes a) and b) can preferably be carried out under normal pressure and in the presence of an

organic solvent or diluent. Examples of suitable solvents or diluents are: ethers and ethereal compounds such as diethyl ether, dipropyl ether, dibutyl ether, dioxane, dimethoxyethane and tetrahydrofurane; N,N-dialkylated carboxamides; aliphatic, aromatic and halogenated hydrocarbons, especially benzene, toluene, xylene, chloroform, methylene chloride, carbon tetrachloride and chlorobenzene; nitriles such as acetonitrile or propionitrile; dimethyl sulfoxide; and ketones, e.g. acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone. Process a) is normally carried out in the temperature range between −10° and 100°C, preferably between 0° and 25°C, optionally in the presence of an organic base, e.g. triethylamine. Process b) is carried out in the temperature range between 0° and 150°C, preferably at the boiling point of the solvent employed, and optionally in the presence of an organic base such as pyridine, or with the addition of an alkali metal or alkaline earth metal, preferably sodium.

The starting materials of the formulae III and V are known and can be obtained by methods similar to known ones. The starting materials of the formulae II and IV are novel compounds which can be obtained by methods which are known per se.

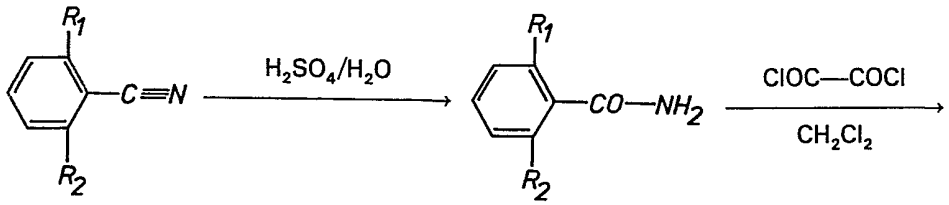
The 3-(trifluoromethylphenoxy)aniline of the formula II can be prepared as follows:



(II)

This reaction is carried out in the temperature range from 20° to 180°C, with the preferred range being from 50° to 160°C, in the presence of an acid acceptor, e.g. a hydroxide or hydride of an alkali metal or alkaline earth metal, preferably potassium hydroxide or sodium hydroxide, and in an inert organic solvent, preferably dimethyl formamide or dimethyl sulfoxide. Further, the aniline of the formula II can also be obtained in analogy to the method described in J. Org. Chem. 29 (1964), 1, by hydrogenation of the corresponding nitro compounds (cf. also the literature cited therein). It is also possible to obtain the aniline of the formula II by chemical reaction (e.g. with Sn(II) chloride/HCl) of the corresponding nitro compound (cf. Houben-Weyl, "Methoden der org. Chemie" 11/2, 422).

The benzylisocyanates of the formula III can be obtained e.g. as follows (cf. J. Agr. Food Chem. *21*, 348 and 993, 1973):



(III)

The 3-(trifluoromethylphenoxy)phenylisocyanate of the formula IV can be obtained e.g. by reacting the aniline of formula II with phosgene by methods commonly employed in the art. The benzamides of the formula V also employed as starting materials are known (cf. for example Beilstein "Handbuch der organischen Chemie", Vol. 9, p. 336).

It is already known that specific substituted N-phenoxyphenyl-N'-benzoylureas possess insecticidal properties. For example, halogen-substituted N-4-(2-chloro-4-trifluoromethylphenoxy)-phenyl-N'-benzoylureas with insecticidal properties are known from German Offenlegungsschrift 2 504 982 and 2 537 413. N-4-(Trifluoromethylphenoxy(phenyl-N'-benzoylureas are also described as insecticidal compounds in Japanese patent specification 53103447.

In contrast to these known compounds, the compounds of the formula I of the present invention are novel N-3-(trifluoromethylphenoxy)phenyl-N'-benzoylureas which, surprisingly, have increased insecticidal activity, especially against insect pests that cause feeding damage, such as Spodoptera littoralis and Heliothis virescens. Unexpected too is the exceedingly pronounced action of the compounds of formula I against eggs and larvae of Musca domestica and of Aedes aegypti. A further advantage of the compounds of the formula I is their very low mammalian toxicity and that they are well tolerated by plants.

In particular, the compounds of the formula I are suitable for controlling insects of the orders: Lepidoptera, Coleoptera, Homoptera, Heteroptera, Diptera, Thysanoptera, Orthoptera, Anoplura, Siphonaptera, Mallophaga, Thysanura, Isoptera, Psocoptera and Hymenoptera.

In addition to their action against flies, e.g. Musca domestica, and mosquito larvae, the compounds of the formula I are also suitable for controlling plant-destructive feeding insects in ornamentals and crops of useful plants, especially in cotton (e.g. against Spodoptera littoralis and

Heliothis virescens) and in vegetables (e.g. against Leptinotarsa decemlineata). The compounds of formula I have a pronounced action against larval stages of insects, especially larval stages of insect pests that cause damage by feeding. When compounds of the formula I are ingested with the feed by adult insect stages, then a reduced oviposition and/or a reduced hatching rate is often observed, especially in Coleoptera, e.g. Anthonomus grandis.

Furthermore, the compounds of the formula I are suitable for controlling ectoparasites, such as Lucilia sericata, in domestic animals and productive livestock, e.g. by treating animals, cowsheds, barns, stables etc., and pastures.

The action of the compounds of the formula I and the compositions containing them can be substantially broadened and adapted to prevailing circumstances by addition of other insecticides and/or acaricides. Examples of suitable additives include: organophosphorus compounds, nitrophenols and derivatives thereof, formamidines, ureas, pyrethroids, carbamates and chlorinated hydrocarbons.

Compounds of formula I can also be combined with particular advantage with substances which exert a pesticidally potentiating effect. Examples of such compounds include: piperonyl butoxide, propynyl ethers, propynyl oximes, propynyl carbamates and propynyl phosphates, 2-(3,4-methylenedioxyphenoxy)-3,6,9-trioxaundecane or S,S,S-tributylphosphorotrithioate.

The compounds of formula I may be used by themselves or together with suitable carriers and/or adjuvants. Suitable carriers and adjuvants can be solid or liquid and correspond to the substances conventionally used in the art of formulation, for example natural or regenerated substances, solvents, dispersants, wetting agents, adhesives, thickeners, binders and/or fertilisers.

For application, the compounds of the formula I may be processed to dusts, emulsifiable concentrates, granules, dispersions, sprays, to solutions, or suspensions, in the conventional formulation which is commonly employed in application technology. In addition, cattle dips and spray races, in which aqueous preparations are used, may also be mentioned. These formulations are particularly suitable for controlling pests which are parasites of animals.

The compositions of the present invention are prepared in known manner by homogeneously mixing and/or grinding compounds of formula I with suitable carriers, with or without the addition of dispersants or solvents which are inert to the active ingredients.

The compounds of formula I may be processed to the following formulations:

Solid formulations:
dusts, tracking powders and granules (coated granules, impregnated granules and homogeneous granules).

Liquid formulations:
a) water-dispersible active ingredient concentrates: wettable powders, pastes and emulsions;
b) solutions.

The content of active ingredient in the above described compositions is between 0.1% and 95%.

The compounds (active ingredients) of formula I can, for example, be formulated as follows (throughout the present specification, all parts and percentages are by weight):

Dusts:

The following substances are used to formulate a) a 5% and b) a 2% dust:

a) 5 parts of active ingredient,
95 parts of talc;

b) 2 parts of active ingredient,
1 part of highly disperse silicic acid,
97 parts of talc.

The active ingredients are mixed and ground with the carriers.

Granules:

The following substances are used to formulate 5% granules:
5.00 parts of active ingredient,
0.25 part of epoxidised vegetable oil,
0.25 part of cetyl polyglycol ether,
3.50 parts of polyethylene glycol,
91.00 parts of kaolin (particle size 0.3—0.8 mm).

The active ingredient is mixed with the epoxidised vegetable oil and the mixture is dissolved in 6 parts of acetone; the polyethylene glycol and cetyl polyglycol ether are then added. The resultant solution is sprayed on kaolin, and the acetone is subsequently evaporated in vacuo.

Wettable powders:

The following constituents are used to formulate a) a 40%, b) and c) a 25%, and d) a 10% wettable powder:

a) 40 parts of active ingredient,

5 parts of sodium lignosulfonate,
1 part of sodium dibutylnaphthalenesulfonate,
54 parts of silicic acid;

b) 25.0 parts of active ingredient,
4.5 parts of calcium lignosulfonate,
1.9 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
1.5 parts of sodium dibutylnaphthalenesulfonate,
19.5 parts of silicic acid,
19.5 parts of Champagne chalk,
28.1 parts of kaolin;

c) 25.0 parts of active ingredient,
2.5 parts of isooctylphenoxy-polyoxyethyleneethanol,
1.7 parts of Champagne chalk/hydroxyethyl cellulose mixture (1:1),
8.3 parts of sodium aluminium silicate,
16.5 parts of kieselgur,
46.0 parts of kaolin;

d) 10 parts of active ingredient,
3 parts of a mixture of the sodium salts of saturated fatty alcohol sulfate,
5 parts of naphthalenesulfonic acid/formaldehyde condensate,
82 parts of kaolin.

The active ingredients are homogeneously mixed with the adjuvants in suitable mixers and the mixture is then ground in appropriate mills and rollers to produce wettable powders which can be diluted with water to give suspensions of any desired concentration.

Emulsifiable concentrates:

The following substances are used to formulate a) a 10%, b) a 25% and c) a 50% emulsifiable concentrate:

a) 10.0 parts of active ingredient,
3.4 parts of epoxidised vegetable oil,
3.4 parts of a combination emulsifier consisting of fatty alcohol polyglycol ether and calcium alkylaralkylsulfonate,
40.0 parts of dimethyl formamide,
43.2 parts of xylene;

b) 25.0 parts of active ingredient,
2.5 parts of epoxidised vegetable oil,
10.0 parts of a mixture of an alkylarylsulfonate and a fatty alcohol polyglycol ether.
5.0 parts of dimethyl formamide,
57.5 parts of xylene;

c) 50.0 parts of active ingredient,
4.2 parts of tributylphenol-polyglycol ether,
5.8 parts of calcium dodecylbenzenesulfonate,
20.0 parts of cyclohexanone,
20.0 parts of xylene.

By diluting these concentrates with water it is possible to obtain emulsions of any required concentration.

Sprays:

The following ingredients are used to formulate a) a 5% spray, and b) a 95% spray:

a) 5 parts of active ingredient,
1 part of epoxidised vegetable oil,
94 parts of ligroin (boiling range 160°—190°C);

b) 95 parts of active ingredient,
5 parts of epoxidised vegetable oil.

The invention is further illustrated by the following Examples.

EXAMPLE 1

To 5.4 g (0.021 mole) of 3-(4-trifluoromethylphenoxy) aniline in 60 ml of anhydrous toluene are added 3.84 g (0.021 mole) of 2,6-difluorobenzoylisocyanate in 20 ml of anhydrous toluene. After the exothermic reaction has subsided, the reaction mixture is stirred for 4 hours at 60°C and then left to stand overnight. The solvent is subsequently distilled off in vacuo and the residue is stirred in hexane. Recrystallisation from acetone/hexane yields N-[3-(4-trifluoromethyl)phenoxy]phenyl-N'-2,6-difluorobenzoylurea with a melting point of 175°—177°C.

The starting compound is obtained as follows:

50 ml of toluene are added to 12 g (0.11 mole) of 3-aminophenol, 7 g of potassium hydroxide and 100 ml of dimethyl sulfoxide and the mixture is heated to c. 150°C, then left to stand for c. 4 hours in order to separate the water. The toluene is then distilled off under normal pressure. The residue is cooled to 120°C and, at this temperature, 14 g of 4-chlorobenzotrifluoride in 20 ml of dimethyl sulfoxide are added dropwise. The reaction mixture is stirred for 8 hours at the same temperature, then cooled, and adjusted to pH 7 with glacial acetic acid. The solvents are then completely distilled off in vacuo and the residue is taken up in toluene, washed repeatedly with water and dried over sodium sulfate. The solvent is evaporated off and the residual oil is distilled in a high vacuum, affording 3-(4-trifluoromethylphenoxy) aniline with a melting point of 98°—100°C/0.1 torr.

EXAMPLES 2 to 16

The following compounds of the formula I are obtained in analogous manner:

Example	Position of the CF_3 group	R_1	R_2	Melting point [°C]
2	4-CF_3	F	F	175—177
3	4-CF_3	F	H	163—164
4	4-CF_3	F	Cl	180—183
5	4-CF_3	Cl	H	182—184
6	4-CF_3	Cl	Cl	162—164
7	3-CF_3	F	F	116—117
8	3-CF_3	F	Cl	128—130
9	3-CF_3	Cl	H	115—116
10	3-CF_3	F	H	127—128
11	3-CF_3	Cl	Cl	
12	2-CF_3	F	F	140—141
13	2-CF_3	F	Cl	
14	2-CF_3	Cl	H	137—138
15	2-CF_3	F	H	116—117.5
16	2-CF_3	Cl	Cl	

EXAMPLE 17

Action against Musca domestica

50 g of freshly prepared CSMA nutrient substrate for maggots are charged into each of a number of beakers. A specific amount of a 1% acetonic solution of the respective active ingredient is pipetted onto the nutrient substrate present in the beakers. The substrate is then thoroughly mixed and the acetone subsequently allowed to evaporate over a period of at least 20 hours.

Then 25 one-day-old maggots of Musca domestica are put into each of the beakers containing the treated nutrient substrate for testing with each active ingredient at one of its given concentrations. After the maggots have pupated, the pupae are separated from the substrate by flushing them out with water and then deposited in containers closed with a perforated top.

Each batch of flushed out pupae is counted to determine the toxic effect of the active ingredient on the maggot development. A count is then made after 10 days of the number of flies which have hatched out of the pupae.

The compounds of Examples 1 to 16 are very effective in this test.

EXAMPLE 18

Action against Lucilia sericata

1 ml of an aqueous solution containing 0.5% of active ingredient is added at 50°C to 9 ml of a culture medium. Then about 30 freshly hatched Lucilia sericata larvae are added to the culture medium, and the insecticidal action is determined after 48 and 96 hours by evaluating the mortality rate. In this

test, compounds of the formula I according to Examples 1 to 16 are very effective against Lucilia sericata.

EXAMPLE 19

Action against Aedes aegypti

Active ingredient concentrations of 10, 5 and 1 ppm respectively are obtained by pipetting a specific amount of a 0.1% solution of the active ingredient in acetone onto the surface of 150 ml of water in each of a number of beakers. After the acetone has evaporated, 30 to 40 three-day-old larvae of Aedes aegypti are put into each of the beakers containing the active ingredient solution. Mortality counts are made after 1, 2 and 5 days.

In this test, compounds of Examples 1 to 16 are very effective against Aedes aegypti.

EXAMPLE 20

Insecticidal action against feeding insects

Cotton plants are sprayed with a 0.05% aqueous emulsion of active ingredient (obtained from a 10% emulsifiable concentrate). After the spray coating has dried, the cotton plants are populated with Spodoptera littoralis and Heliothis virescens larvae in the L_3-stage. The test is carried out at 24°C and 60% relative humidity. At 24 hour intervals, a mortality count is made and the larvae are also examined for inhibition of development and shedding.

In this test, the compounds of Examples 1 to 16 exhibit a good insecticidal action against Spodoptera and Heliothis larvae.

EXAMPLE 21

Action against Epilachna varivestis

Phaseolus vulgaris plants (dwarf beans) about 15—20 cm in height are sprayed with an aqueous emulsion preparation containing the compound to be tested. After the spray coating has dried, each plant is populated with 10 larvae of Epilachna varivestis (Mexican bean beetle) in the L_4-stage. A plastic cylinder is slipped over the treated plants and covered with a copper gauze top. Fatal action (percentage mortality) is assessed after 1 and 2 days. Evaluation of feeding damage (anti-feeding effect), and of exhibition of development and shedding, is made by observing the test organisms for a further 3 days.

The compounds of Examples 1 to 16 are very effective in this test.

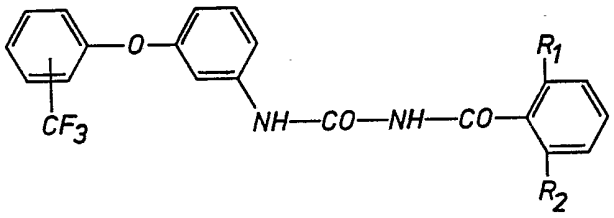
EXAMPLE 22

Action against Leptinotarsa decemlineata (larvae)

Potato plants 15 cm in height in growth containers are sprayed uniformly dripping wet with an aqueous emulsion preparation containing the compound to be tested in a concentration of 500 ppm, using a pressure spray. After the plants have dried, i.e. after about $1\frac{1}{2}$ hours, a plastic cylinder is slipped over them and each plant is then populated with 10 potato beetle larvae in the L_3-stage. The cylinders are sealed with a copper gauze top and left to stand in the dark at 28°C and 60% relative humidity. A mortality count of the test organisms (recumbent position) and an assessment of the percentage feeding damage to the plants is made after 1 and 2 hours as well as after 1, 2 and 8 days. The compounds of Examples 1 to 16 are very effective in this test.

CLAIMS

1. A compound of the formula I



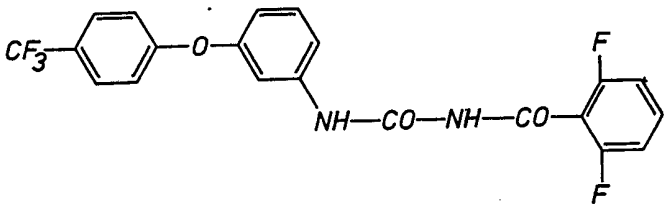
(I)

wherein R_1 is fluorine or chlorine and R_2 is hydrogen, fluorine or chlorine.

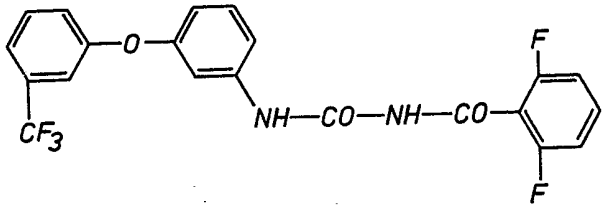
2. A compound according to claim 1, wherein R_1 and R_2 are fluorine.

3. A compound according to either of claims 1 or 2, wherein the CF_3 radical is the 3- or 4-position.

4. A compound according to claim 3 of the formula

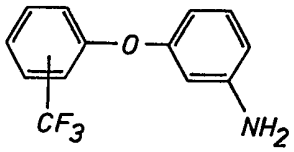


5. A compound according to claim 2 of the formula



6. A compound of formula I substantially as described with reference to any of Examples 1 to 16.

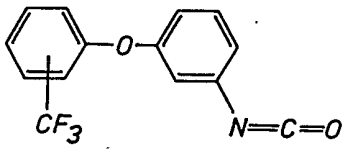
7. A compound of the formula II



(II)

8. A compound of formula II according to Claim 7 substantially as described with reference to Example 1.

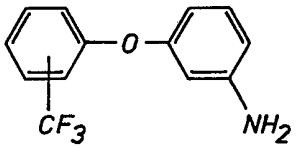
9. A compound of the formula IV



(IV)

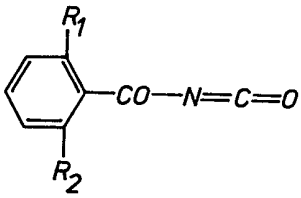
10. A process for the production of a compound of formula I, which process comprises

a) reacting a compound of the formula II



(II)

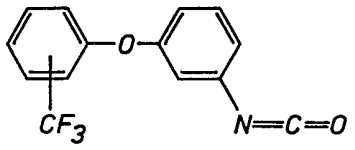
with a compound of the formula III



(III)

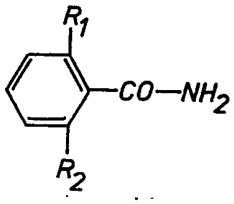
or

b) reacting a compound of the formula



(IV)

with a compound of the formula V



(V)

in which formulae III and V above the symbols R_1 and R_2 are as defined in claim 1.

11. A process according to Claim 10 substantially as described with reference to any of Examples 1 to 16.

12. A compound of formula I when produced by a process claimed in claim 10 or 11.

13. A pesticidal composition which contains, as active component, a compound according to any one of claims 1 to 5, together with suitable carriers and/or other adjuvants.

14. A pesticidal composition according to claim 13 substantially as described with reference to any of Examples 17 to 22.

15. A method of controlling pests, at a locus, which method comprises applying to said locus a compound according to any one of claims 1 to 5.

16. A method according to claim 15 wherein the pests are insects.

17. A method according to claim 15 or 16, wherein the pests to be controlled are larval stages of insects.

18. A method according to claim 15 substantially as described with reference to any of Examples 17 to 22.

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