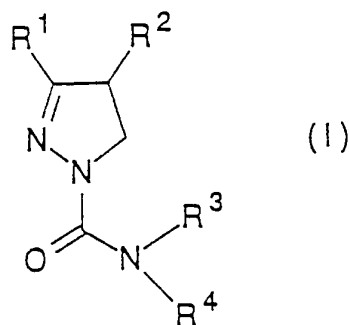




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
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| <b>(21) International Application Number:</b> PCT/EP93/02714<br><br><b>(22) International Filing Date:</b> 4 October 1993 (04.10.93)<br><br><b>(30) Priority data:</b><br>P 42 33 835.2      5 October 1992 (05.10.92)      DE<br><br><b>(71) Applicant (for all designated States except US):</b> SCHERING AKTIENGESELLSCHAFT [DE/DE]; Müllerstrasse 170-178, D-13342 Berlin (DE).<br><br><b>(72) Inventors; and</b><br><b>(75) Inventors/Applicants (for US only) :</b> VAN ALMSICK, Andreas [DE/DE]; Reichssportfeldstrasse 16, D-14055 Berlin (DE). HOFFMANN, Holger [DE/DE]; Gatower Strasse 71, D-13595 Berlin (DE). BOSUM-DYBUS, Annegrit [DE/DE]; Fregestrasse 7A, D-12159 Berlin (DE). WEGMANN, Thomas [DE/DE]; Reißbeckstrasse 11, D-12107 Berlin (DE). JOPPIEN, Hartmut [DE/DE]; Juttastrasse 18, D-14169 Berlin (DE). VON KEYSERLINGK, Harald [DE/DE]; Markgrafenstrasse 38, D-13465 Berlin (DE). |           | <b>(81) Designated States:</b> AU, BG, BR, CA, CZ, FI, HU, JP, KR, NZ, PL, RO, RU, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).<br><br><b>Published</b><br><i>With international search report.</i> |

**(54) Title:** CYANOPHENYLPYRAZOLINES AS PESTICIDES**(57) Abstract**

Pyrazoline derivatives of general formula (I), in which R<sup>1</sup> and R<sup>2</sup> are phenyl, optionally substituted by one or more of the same or different groups selected from cyano, halogen, nitro, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, halo-C<sub>1-6</sub>-alkyl or halo-C<sub>1-6</sub>-alkoxy, in which at least one of the phenyl groups is substituted by cyano; R<sup>3</sup> is phenyl or cyclohexyl, each of which is optionally substituted by one or more of the same or different groups selected from halogen, nitro, cyano, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, halo-C<sub>1-6</sub>-alkyl, halo-C<sub>1-6</sub>-alkoxy, C<sub>1-6</sub>-alkylsulfonyl, halo-C<sub>1-6</sub>-alkylsulfonyl or C<sub>1-6</sub>-alkoxycarbonyl; and R<sup>4</sup> is hydrogen, C<sub>1-6</sub>-alkyl, halo-C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-acyl, C<sub>1-6</sub>-alkoxycarbonyl or halo-C<sub>1-6</sub>-alkoxycarbonyl, have insecticidal and acaricidal activity.

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## CYANOPHENYLPYRAZOLINES AS PESTICIDES

5    Field of the invention

This invention relates to new pyrazoline derivatives, processes for their preparation, as well as their use as pesticides.

10   Prior Art

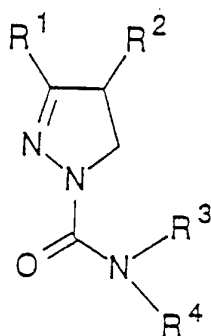
1-Phenylcarbamoypyrazolines with insecticidal activity are already well known. There are a number of patents describing such compounds, for example GB 1,514,285, EP 58 424, EP 113 213, EP 227 055 and EP 300 692. In all  
15 these patents, there are disclosed compounds in which there is a substituted phenyl group in the 3 and 4 positions of the pyrazoline ring. In GB 1,514,285, for instance, these phenyl groups may be substituted by a wide range of substituents including cyano. However no specific  
20 compounds are disclosed in which either phenyl carries a cyano group. In EP 300 692, a few compounds are disclosed in which the phenyl in the 3 position is substituted by 4-cyano. However in EP 300 692, the phenyl in the 4 position must be substituted by a carbonyl-, thiocarbonyl-  
25 or sulfonyl- containing group.

The disadvantage of many of the prior art compounds is the insufficient activity and/or high mammalian toxicity and we have now found that the novel group of compounds of the  
30 present invention overcome these disadvantages.

Description of the Invention

According to the invention there is provided a pyrazoline derivative of general formula I

5



(I),

10

in which

- 15 R<sup>1</sup> and R<sup>2</sup> are phenyl, optionally substituted by one or more of the same or different groups selected from cyano, halogen, nitro, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, halo-C<sub>1-6</sub>-alkyl or halo-C<sub>1-6</sub>-alkoxy, in which at least one of the phenyl groups is substituted by cyano;
- 20 R<sup>3</sup> is phenyl or cyclohexyl, each of which is optionally substituted by one or more of the same or different groups selected from halogen, nitro, cyano, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, halo-C<sub>1-6</sub>-alkyl, halo-C<sub>1-6</sub>-alkoxy, C<sub>1-6</sub>-alkylsulfonyl, halo-C<sub>1-6</sub>-alkylsulfonyl or C<sub>1-6</sub>-alkoxycarbonyl; and
- 25 R<sup>4</sup> is hydrogen, C<sub>1-6</sub>-alkyl, halo-C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-acyl, C<sub>1-6</sub>-alkoxycarbonyl or halo-C<sub>1-6</sub>-alkoxycarbonyl.

By the term "halogen" it is preferably understood to mean  
30 fluorine, chlorine or bromine.

By the term "acyl" are to be understood groups which are derived from acids with up to 6 carbon atoms, especially lower and intermediate aliphatic carboxylic acids. These  
35 acids may be unsaturated and/or branched and/or polybasic

and/or substituted e.g. by hydroxy, amino or halo.  
 Examples are such acids are acetic acid, propionic acid,  
 valeric acid, caproic acid, trimethylacetic acid,  
 haloacetic acid, dialkylaminoacetic acid and succinic  
 5 acid.

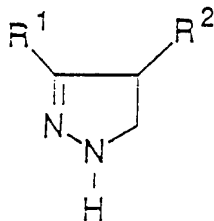
The invention includes isomeric forms and as well as  
 mixtures of isomers.

- 10 Particularly preferred are compounds of formula I in which  
 $R^1$  is 4-cyanophenyl, 4-fluorophenyl or  
 4-(2,2,2-trifluoroethoxy),  
 $R^2$  is phenyl, 4-cyanophenyl, 4-fluorophenyl- or  
 4-difluoromethoxy,  
 15  $R^3$  is 4-difluoromethoxyphenyl, 4-trifluoromethylphenyl-,  
 4-trifluoromethoxyphenyl-,  
 4-(2,2,2-trifluoroethoxy)phenyl-, 4-chlorophenyl-,  
 4-cyanophenyl- or 4-trifluoromethylcyclohexyl, and  
 $R^4$  is hydrogen or methyl, especially hydrogen.

20

The compounds of the invention of general formula I, where  
 R is hydrogen, can be prepared by reacting a pyrazoline of  
 general formula II

25



(II)

30

with an isocyanate of general formula III



- in a solvent and optionally in the presence of a base,  
 35 and if desired treating the resulting carbamoylpyrazoline

in which  $R^4$  is hydrogen, with a compound of general formula IV



in which  $R^4$  is other than hydrogen and X is leaving group,  
5 such as halogen, especially chlorine, bromine or iodine,  
in the presence of an acid-binding agent and a solvent.

The solvent is one which is inert to the reactants, e.g.  
aliphatic, alicyclic or aromatic hydrocarbons, which are  
10 optionally chlorinated, e.g. pentane, hexane, cyclohexane,  
petroleum ether, benzene, toluene, xylene,  
dichloromethane, chloroform, carbon tetrachloride,  
ethylene dichloride, trichloroethylene or chlorobenzene;  
ethers, such as diethyl ether, methyl ethyl ether,  
15 diisopropyl ether, dibutyl ether, methyl tert.-butyl  
ether, dioxane or tetrahydrofuran; nitriles, such as  
acetonitrile, propionitrile or benzonitrile; esters, such  
as ethyl acetate or amyl acetate; amides, such as  
dimethylformamide, N-methylpyrrolidone or  
20 hexamethylphosphoric triamide, as well as sulfones, such  
as dimethyl sulfoxide or sulfolane.

Acid binding agents that can be used include aliphatic,  
aromatic and heterocyclic amine, e.g. triethylamine,  
25 dimethylaniline or pyridine, inorganic bases such as  
sodium or potassium carbonate, magnesium oxide, sodium  
hydroxide, sodium hydrogen carbonate or sodium hydride.

Both reactions can be carried out over a wide temperature  
30 range. In general, the reaction temperature lies between  
-20 and +100°C, preferably at however at room temperature.

The compounds of the invention prepared by these processes  
can be isolated from the reaction mixtures in conventional  
35 manner, for example by distillation of the solvent at

normal or reduced pressure, by precipitation with water or by extraction. A higher level of purity can be achieved as a rule by column chromatography or recrystallisation.

- 5 The pyrazoline derivatives of the invention are colourless and odourless and in most cases are crystalline compounds. They have a low solubility in water and toluene, are more soluble in ethyl acetate and highly soluble in dimethyl-formamide

10

The preparation of the 3,4-dihydro-1H-pyrazoline of general formula II can be carried out in known manner for example as described in J. Agric. Food Chem. Vol. 25, No. 5, (1977) 987, J. Agric. Food Chem. Vol. 27, No. 2, 15 (1979), 406, J. Agric. Food Chem. Vol. 26, No. 4, (1978), 915; USP 4,439,440; EP-A 113 213; EP-A 058 424; USP 4,663,341; DE-A 3 628 647 and EP-A 286 346.

The compounds of the invention have insecticidal and 20 acaricidal activity and are suitable for combating parasites of humans and domestic animals as well as plant pests. Examples are Lepidoptera, such as *Plutella xylostella*, *Spodoptera littoralis*, *Heliothis armigera*, *Heliothis virescens* and *Pieris brassicae*; Diptera, such as 25 *Gasterophilus*, *Cochliomyia*, *Musca domestica*, *Ceratitis capitata*, *Erioischia brassicae*, *Lucilia sericata* and *Aedes aegypti*; Hemiptera, including aphids such as *Megoura viciae* and leafhoppers, such as *Nilaparvata lugens* and *Nephotettix cincticeps*; Coleoptera, such as *Phaedon* 30 *cochleariae*, *Anthonomus grandis* and corn rootworms (*Diabrotica* spp., e.g. *Diabrotica undecimpunctata*); Orthoptera, such as *Blattella germanica*; ticks, such as *Boophilus microplus* and lice, such as *Damalinia bovis* and *Linognathus vituli* as well as mites such as *Tetranychus* 35 *urticae* and *Panonychus ulmi*.

The compounds of the invention can be used either alone or in mixture with each other or another insecticide.

Optionally other plant protection or pesticidal compositions, such as for example insecticides, acaricides  
5 or fungicides can be added depending on the desired result.

An improvement in the intensity and speed of action can be obtained, for example, by addition of suitable adjuvants,  
10 such as organic solvents, wetting agents and oils. Such additives may allow a decrease in the dose.

Suitable mixture partners may also include phospholipids, e.g. such as from the group phosphatidylcholine, hydrated  
15 phosphatidylcholine, phosphatidylethanolamine, N-acyl-phosphatidylethanolamine, phosphatidylinositol, phosphatidylserine, lysolecithin or phosphatidylglycerol.

The designated active ingredients or their mixtures can  
20 suitably be used, for example, as powders, dusts, granules, solutions, emulsions or suspensions, with the addition of liquid and/or solid carriers and/or diluents and, optionally, binding, wetting, emulsifying and/or dispersing adjuvants.

25 Suitable liquid carriers are, for example aliphatic and aromatic hydrocarbons such as benzene, toluene, xylene, cyclohexanone, isophorone, dimethyl sulfoxide, dimethylformamide, other mineral-oil fractions and plant  
30 oils.

Suitable solid carriers include mineral earths, e.g. tonsil, silica gel, talcum, kaolin, attapulgite, limestone, silicic acid and plant products, e.g. flours.

As surface-active agents there can be used for example calcium lignosulfonate, polyoxyethylenealkylphenyl ether, naphthalenesulfonic acids and their salts, phenolsulfonic acids and their salts, formaldehyde condensates, fatty  
5 alcohol sulfates, as well as substituted benzenesulfonic acids and their salts.

The percentage of the active ingredient(s) in the various preparations can vary within wide limits. For example, the  
10 compositions can contain about 10 to 90 percent by weight active ingredients, and about 90 to 10 percent by weight liquid or solid carriers, as well as, optionally up to 20 percent by weight of surfactant.

15 The agents can be applied in customary fashion, for example with water as the carrier in spray mixture volumes of approximately 100 to 1,000 l/ha. The agents can be applied using low-volume or ultra-low-volume techniques or in the form of so-called microgranules.

20 The preparation of these formulations can be carried out in known manner, for example by milling or mixing processes. Optionally, individual components can be mixed just before use for example by the commonly used so-called  
25 tank-mixing method.

Formulations can be prepared, for example, from the following ingredients.

- A1     WETTABLE POWDER
- 5           80 percent by weight active ingredient  
          15 percent by weight kaolin  
          5 percent by weight of surfactant based on  
                  of the sodium salt of N-methyl-N-oleyltaurine  
                  and calcium lignosulfonate
- 10
- A2     WETTABLE POWDER
- 20 percent by weight active ingredient  
          35 percent by weight fuller's earth  
          8 percent by weight calcium lignosulfonate
- 15           2 percent by weight sodium salt of  
                  N-methyl-N-oleyltaurine  
          35 percent by weight silicic acid
- B       PASTE
- 20           45 percent by weight active ingredient  
          5 percent by weight sodium aluminium silicate  
          15 percent by weight cetylpolglycol ether with 8  
                  moles ethylene oxide  
          2 percent by weight spindle oil
- 25           10 percent by weight polyethylene glycol  
          23 parts water
- C       EMULSIFIABLE CONCENTRATE
- 20 percent by weight active ingredient
- 30           75 percent by weight isophorone  
          5 percent by weight of a mixture of  
                  ionic and nonionic surfactants

The following examples illustrate the preparation of compounds according to the invention.

Preparation Example 1

5    4-(4-Cyanophenyl)-N-[4-(1,1-difluoromethoxy)phenyl]-  
     3-[4-(2,2,2-trifluoroethoxy)phenyl]-4,5-dihydropyrazole-  
     1-carboxamide

3.45 g (10 mmol) 4-(4-Cyanophenyl)-3-[4-(2,2,2-trifluoro-  
10    ethoxy)phenyl]-4,5-dihydropyrazole was dissolved in 35 ml  
     methylene chloride and under anhydrous conditions, treated  
     with stirring with 1.85 g (10 mmol) 4-(1,1-difluoro-  
     methoxy)phenyl isocyanate. The mixture was diluted with  
     methylene chloride, washed twice with water and dried over  
15    magnesium sulfate. After removal of the solvent in a  
     rotary evaporator, the residue was purified by silica gel  
     column chromatography (ethyl acetate/hexane, 1:1).

Yield:            1.67 g, 32% of theory  
20                colourless crystals, m.p.: 90-93°C  
                 R<sub>f</sub> = 0.80 (ethyl acetate)

Preparation Example 2

25    N,3-bis-(4-cyanophenyl)-4-(4-fluorophenyl)-N-methyl-  
     4,5-dihydropyrazole-1-carboxamide

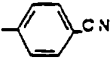
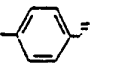
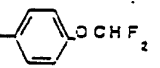
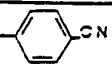
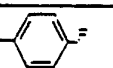
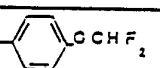
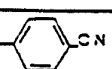
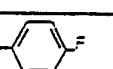
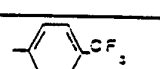
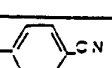
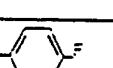
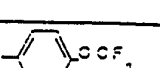
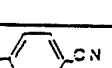
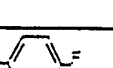
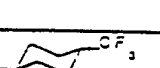
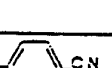
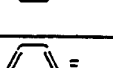
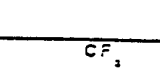
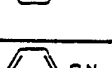
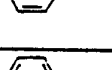
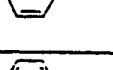
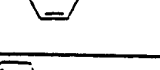
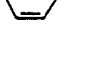
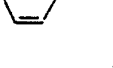
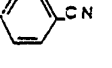
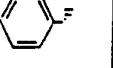
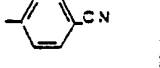
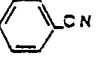
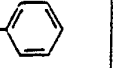
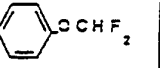
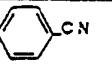
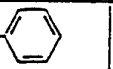
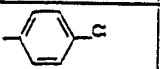
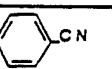
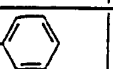
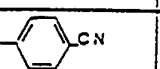
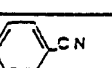
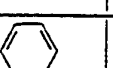
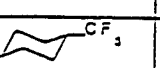
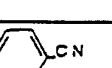
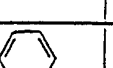
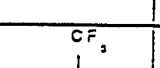
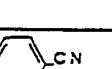
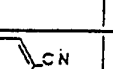
0.78 g (1.9 mmol) of N,3-bis-(4-cyanophenyl)-  
4-(4-fluorophenyl)-4,5-dihydropyrazole-1-carboxamide  
30    (compound 10, prepared in a similar manner to Example 1)  
     was dissolved in 16 ml absolute tetrahydrofuran and  
     treated with 0.07 g (2.33 mmol) 80% sodium hydride  
     under anhydrous conditions. The mixture was stirred for  
     about one hour at room temperature, then 0.15 ml (2.4  
35    mmol) iodomethane added and the mixture heated under

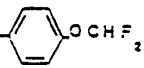
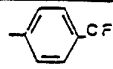
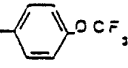
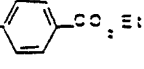
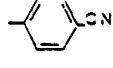
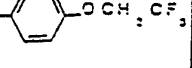
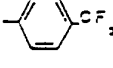
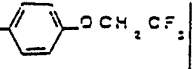
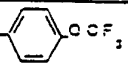
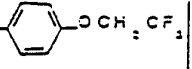
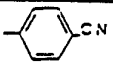
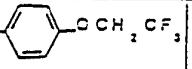
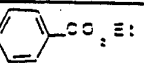
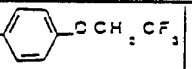
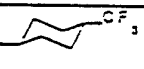
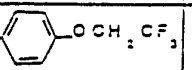
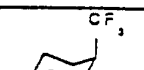
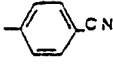
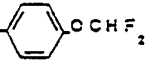
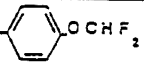
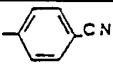
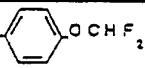
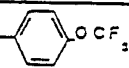
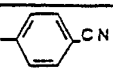
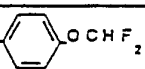
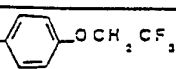
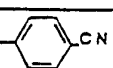
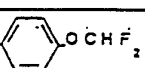
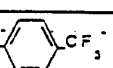
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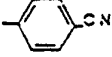
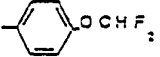
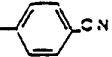
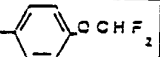
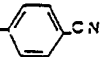
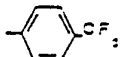
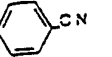
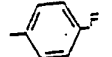
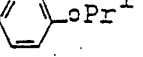
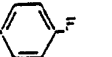
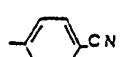
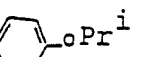
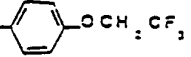
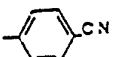
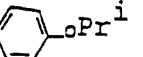
reflux for about one hour. It was then cooled, 10 ml water added and extracted with ethyl acetate. The crude product, obtained by concentration of the organic phases, The organic phase was dried over magnesium sulfate and  
5 concentrated in a rotary evaporator. The product was separated from by-products by silica gel column chromatography (diethyl ether/hexane, 3:1).

Yield: 0.22 g, 27% of theory  
10 colourless crystals, m.p.: >200°C  
R<sub>f</sub> = 0.52 (ethyl acetate)

In a similar manner, the following compounds of formula I were prepared:

| No. | R <sup>1</sup>                                                                      | R <sup>2</sup>                                                                      | R <sup>3</sup>                                                                      | R <sup>4</sup>  | mp. [°C]  |
|-----|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-----------------|-----------|
| 3   |    |    |    | H               | 118 (Dec) |
| 4   |    |    |    | CH <sub>3</sub> | oil       |
| 5   |    |    |    | H               | 188-189   |
| 6   |    |    |    | H               | 196-199   |
| 7   |    |    |    | H               | oil       |
| 8   |    |    |    | H               | oil       |
| 9   |  |  |  | H               | oil       |
| 10  |  |  |  | H               | 193-196   |
| 11  |  |  |  | H               | 224-226   |
| 12  |  |  |  | H               | oil       |
| 13  |  |  |  | H               | 179-182   |
| 14  |  |  |  | H               | 230-232   |
| 15  |  |  |  | H               | 207-209   |
| 16  |  |  |  | H               | oil       |
| 17  |  |  |  | H               | 140-141   |
| 18  |  |  |  | H               | 130-132   |

| No. | R <sup>1</sup>                                                                      | R <sup>2</sup>                                                                      | R <sup>3</sup>                                                                      | R <sup>4</sup> | mp. [°C] |
|-----|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|----------------|----------|
| 19  |    |    |    | H              | 70-73    |
| 20  |    |    |    | H              | 133-135  |
| 21  |    |    |    | H              | 81-82    |
| 22  |    |    |    | H              | 100-101  |
| 23  |    |    |    | H              | 229      |
| 24  |    |    |    | H              | 95-98    |
| 25  |  |  |  | H              | 104-106  |
| 26  |  |  |  | H              | 117-119  |
| 27  |  |  |  | H              | 106-108  |
| 28  |  |  |  | H              | 204-206  |
| 29  |  |  |  | H              | 75-77    |
| 30  |  |  |  | H              | 176-177  |
| 31  |  |  |  | H              | oil      |
| 32  |  |  |  | H              | 171-172  |
| 33  |  |  |  | H              | oil      |

| No. | R <sup>1</sup>                                                                      | R <sup>2</sup>                                                                      | R <sup>3</sup>                                                                      | R <sup>4</sup> | m.p. [°C] |
|-----|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|----------------|-----------|
| 34  |    |    |    | H              | 178-180   |
| 35  |    |    |    | H              | 168-170   |
| 36  |    |    |    | H              | 222-224°C |
| 37  |    |    |    | H              |           |
| 38  |   |   |   | H              |           |
| 39  |  |  |  | H              |           |

The following examples illustrate the possibilities for use of the compounds of the invention.

Test Example A

5 Activity against adult cotton boll-weevil (*Anthonomus grandis*)

The compounds of the invention were made up as aqueous preparations at a concentration of 0.1%. 0.2 ml of this  
10 preparation was pipetted onto feed material, in a polystyrene petri dish and 0.2 ml onto the bottom of the petri dish. After drying, 5 adult (2 day old) cotton boll-weevils (*Anthonomus grandis*) were counted into the dishes. The closed dishes were left for up to 7 days at 25°C under  
15 extended daylight conditions. The % mortality of the weevils at the end of the test indicated the level of activity.

The compounds of Examples 1, 3-9, 11-15, 17-21 and 23-27  
20 showed 80 - 100% activity.

Test Example B

Activity against larvae (L1) of the cotton bollworm (*Heliothis virescens*)

25 The compounds of the invention were made up as aqueous preparations at a concentration of 0.1%. 0.2 ml of this preparation was pipetted onto feed material, in a polystyrene petri dish and 0.2 ml onto the bottom of the  
30 petri dish. After drying, 10 L1 of the cotton bollworm (*Heliothis virescens*) were counted into the dishes. The closed dishes were left for up to 7 days at 25°C under extended daylight conditions. The % mortality of the larvae at the end of the test indicated the level of  
35 activity.

The compounds of Examples 1, 3-9, 11-15 and 17-27 showed 80 - 100% activity.

Use Example C

5 Activity in the prophylactic treatment of feed against the  
against black bean aphids (*Aphis fabae* Scop.)

From the primary leaf of field beans (*Phaseolus vulgaris*  
*nanus* Aschers.), 24 mm diameter discs were cut. Some of  
10 these were treated with a 0.1% aqueous preparations of the  
active ingredient and these alongside untreated discs were  
placed on wet filter papers with the underside of the  
leaves turned upwards. After drying the test pieces, they  
were each infested with wingless stages of *Aphis fabae*  
15 (approx 30 per leaf piece). The leaves were kept on wet  
filter papers for 6 days at 25°C and 16 hours light per  
day. The number of living insects at the end of the test  
was measured. The activity was calculated using Abbott's  
method in comparison with the untreated controls.

20

The compound of Example 14 showed 80 - 100% activity.

Use Example D

25 Activity in prophylactic treatment of leaves against brown  
rice-hoppers (*Nilaparvata lugens* Stål)

In a heated greenhouse, rice seedlings (about 15 per pot)  
were grown until formation of the third leaf and then  
sprayed until dripping wet with an aqueous preparation  
30 containing 0.1% of active material. After drying the spray  
coating, a transparent cylinder was placed over each pot.  
30 Adult brown rice-hoppers (*Nilaparvata lugens*) were  
introduced into each pot. After 6 days at 25-26°C in the  
greenhouse and 16 hours light per day, the amount of dead  
35 hoppers was determined. The activity was calculated

according to Abbott in comparison with several untreated control pots.

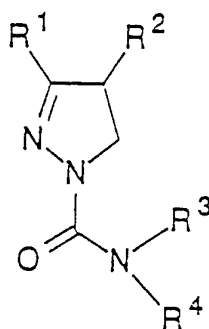
The compounds of Example 3, 5, 6, 7, 13, 14, 20 and 23  
5 showed 80 - 100% activity.

CLAIMS

1. Pyrazolines of general formula I

5

10



(I),

15

in which

20 R<sup>1</sup> and R<sup>2</sup> are phenyl, optionally substituted by one or more of the same or different groups selected from cyano, halogen, nitro, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, halo-C<sub>1-6</sub>-alkyl or halo-C<sub>1-6</sub>-alkoxy, in which at least one of the phenyl groups is substituted by cyano;

25 R<sup>3</sup> is phenyl or cyclohexyl, each of which is optionally substituted by one or more of the same or different groups selected from halogen, nitro, cyano, C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-alkoxy, halo-C<sub>1-6</sub>-alkyl, halo-C<sub>1-6</sub>-alkoxy, C<sub>1-6</sub>-alkylsulfonyl, halo-C<sub>1-6</sub>-alkylsulfonyl or C<sub>1-6</sub>-alkoxycarbonyl; and

30 R<sup>4</sup> is hydrogen, C<sub>1-6</sub>-alkyl, halo-C<sub>1-6</sub>-alkyl, C<sub>1-6</sub>-acyl, C<sub>1-6</sub>-alkoxycarbonyl or halo-C<sub>1-6</sub>-alkoxycarbonyl.

2. Pyrazolines according to claim 1, in which

35 R<sup>1</sup> is 4-cyanophenyl, 4-fluorophenyl or 4-(2,2,2-trifluoroethoxy),

R<sup>2</sup> is phenyl, 4-cyanophenyl, 4-fluorophenyl- or  
4-difluoromethoxy,

R<sup>3</sup> is 4-difluoromethoxyphenyl, 4-trifluoromethylphenyl-,  
4-trifluoromethoxyphenyl-,

5 4-(2,2,2-trifluoroethoxy)phenyl-, 4-chlorophenyl-,  
4-cyanophenyl- or 4-trifluoromethylcyclohexyl, and

R<sup>4</sup> is hydrogen or methyl.

3. An insecticidal and acaricidal composition which  
10 comprises a compound claimed in claim 1 or 2 in admixture  
with an agriculturally acceptable diluent or carrier.

4. Use of a compound claimed in claim 1 or 2 any one of  
the preceding claims, for combating insects or acarids.

15

5. A method of combating insects and acarids which  
comprises applying to the insect or acarid or their locus,  
an effective amount of a compound claimed in claim 1 or 2.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02714

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 5 C07D231/06 A01N43/56

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages               | Relevant to claim No. |
|------------|--------------------------------------------------------------------------------------------------|-----------------------|
| A          | EP,A,0 300 692 (DU PONT) 25 January 1989<br>cited in the application<br>see claims 1,14<br>----- | 1,3                   |

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

10 January 1994

Date of mailing of the international search report

19. 01. 94

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## INTERNATIONAL SEARCH REPORT

Information on patent family members

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| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| EP-A-0300692                              | 25-01-89            | AU-A- 1993988              | 13-02-89            |
|                                           |                     | EP-A- 0367796              | 16-05-90            |
|                                           |                     | JP-T- 2504273              | 06-12-90            |
|                                           |                     | WO-A- 8900562              | 26-01-89            |
|                                           |                     | US-A- 5006524              | 09-04-91            |
| -----                                     |                     |                            |                     |