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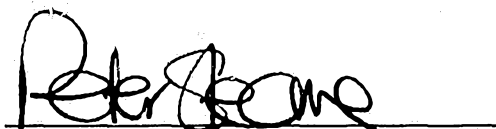
Patents Act 1990

NOTICE OF ENTITLEMENT

We, DOWELANCO, of 9002 Purdue Road, Indianapolis, Indiana, 46268-1189, United States of America, the applicant in respect of Australian Patent Application No 26418/92 state the following:

- 1 DOWELANCO is the Nominated Person in respect of the application.
- 2 The actual inventors of the invention, the subject of the application, are: HACKLER, Ronald E; JOURDAN, Glen P; JOHNSON, Peter L; THOREEN, Brian P; and SAMARITONI, Jack G.
- 3 The Nominated Person, DOWELANCO, is entitled to the grant of the patent in respect of the application because the Nominated Person derived title to the invention from the said inventors by way of assignment.
- 4 The Nominated Person is entitled to claim priority from the application listed in the declaration under Article 8 of the PCT because the Nominated Person is the assignee of the applicant in respect of the application listed in the declaration under Article 8 of the PCT, and because the application was the first application made in a Convention country in respect of the invention.

DATED this 29th day of May 1995.



A member of the firm of
DAVIES COLLISON CAVE
for and on behalf of the applicant.

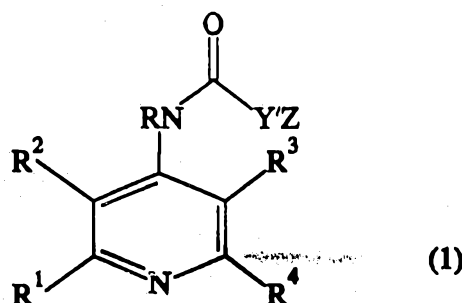


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(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 662017

- (54) Title
N-(4-PYRIDYL OR 4-QUINOLINYL) ARYLACETAMIDE PESTICIDES
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- (56) Prior Art Documents
AU 28748/89 C07D 215/04
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- (57) Claim

1. A compound of the formula (1):



or an N-oxide or a salt thereof; wherein R is H, (C₁-C₄)alkyl, or benzyl; R¹, R², R³, and R⁴ are one of the following:

- (a) R³ and R⁴ are H, and R¹ and R² are independently halo, (C₁-C₄)alkyl, halo(C₁-C₄)alkyl, (C₃-C₄) branched alkyl, (C₃-C₇)cycloalkyl, (C₁-C₄)alkoxy, or halo(C₁-C₄)alkoxy;

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(b) one of R^1 , R^2 , R^3 and R^4 is (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkyl, halo (C_1-C_4) alkoxy, (C_1-C_4) alkylthio, (C_1-C_4) alkylsulfinyl, (C_1-C_4) alkylsulfonyl, aryl or substituted amino, and the rest are H;

(c) R^1 , R^2 , R^3 and R^4 are independently H or halo; or

(d) R^1 and R^2 combine to form a (C_5-C_6) saturated or unsaturated carbocyclic ring that is optionally substituted with one or two groups selected from halo, (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, halo (C_1-C_4) alkyl, (C_3-C_7) cycloalkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy or NO_2 , and R^3 and R^4 are H; R^5 is H, (C_1-C_4) alkyl or (C_1-C_4) acyl; R^6 and R^7 are independently (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, phenyl, or substituted phenyl;

Y' is bond or bivalent hydrocarbon radical one to five carbon atoms long, optionally substituted with (C_1-C_4) alkyl,

Z is

(a) a phenyl group optionally substituted with one or more groups independently selected from:

halo, I, (C_3-C_8) cycloalkyl, (C_3-C_8) cycloalkenyl, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted phenyl, NO_2

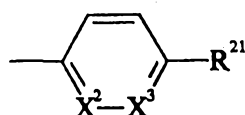
$\begin{array}{c} O \\ || \\ -C-R^8 \end{array}$ where R^8 is (C_1-C_7) alkyl, halo (C_1-C_7) alkyl, (C_3-C_7) branched alkyl, halo (C_3-C_7) branched alkyl, (C_3-C_7) cycloalkyl, halo (C_3-C_7) cycloalkyl, (C_1-C_7) alkoxy, phenyl, or substituted phenyl, acetoxy, OH, CN, $SiR^9R^{10}R^{11}$ or $SiR^9R^{10}R^{11}$, where R^9 , R^{10} , and R^{11} are independently (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, phenyl, or substituted phenyl, $NR^{12}R^{13}$, where R^{12} and R^{13} are independently H, (C_1-C_4) alkyl, or (C_1-C_4) acyl, $S(O)R^{14}$, or SO_2R^{14} , where R^{14} is (C_1-C_{10}) alkyl, phenyl, or substituted phenyl; a (C_1-C_{12}) saturated or unsaturated hydrocarbon chain, straight chain or branched optionally including a hetero atom selected from O, S, SO, SO_2 , NR^5 , or SiR^6R^7 where R^5 , R^6 and

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R⁷ are as defined above, and optionally substituted with halo, halo (C₁-C₄) alkoxy, hydroxy, (C₃-C₈) cycloalkyl or cycloalkenyl, (C₁-C₄) acyl, phenoxy, substituted phenoxy, phenyl, substituted phenyl, phenylthio, or substituted phenylthio; (C₁-C₇) alkoxy optionally substituted with halo, phenyl substituted phenyl, (C₃-C₈) cycloalkyl or cycloalkenyl, phenoxy, or substituted phenoxy; (C₁-C₇) alkylthio optionally substituted with halo, phenyl, substituted phenyl, (C₃-C₈) cycloalkyl or cycloalkenyl, phenoxy or substituted phenoxy;

- (b) a group selected from optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and decahydronaphthyl;
- (c) a group of the formula



one of X² and X³ is N and the other is CH; R²¹ is -Z-R²², phenyl, or substituted phenyl; Z is O or S; and R²² is (C₁-C₄) alkyl, (C₃-C₇) branched alkyl, halo (C₁-C₄) alkyl, halo (C₃-C₇) branched alkyl, (C₁-C₄) alkoxy substituted (C₁-C₄) alkyl, or naphthyl or phenyl, either of which may optionally be substituted with up to three groups selected from halo, (C₁-C₁₀) alkyl, branched (C₃-C₇) alkyl, halo(C₁-C₇) alkyl, hydroxy (C₁-C₇) alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkoxy, phenoxy, substituted phenoxy, phenyl, substituted phenyl, CN, NO₂ OH, (C₁-C₄) alkanoyloxy, or benzyloxy.

- 9. A method of inhibiting an insect or mite population which comprises applying to the locus of the insect or arachnid an effective insect or mite inactivating amount of a compound of claim 1.
- 10. A method of inhibiting a nematode population which comprises applying to the locus of a nematode, a nematode inactivating amount of a compound of claim 1.

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11. A method of inhibiting plant pathogens which comprises applying an effective amount of a compound of claim 1 to a locus of the pathogen.

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(21) International Application Number: PCT/US92/07531 (22) International Filing Date: 2 September 1992 (02.09.92) (30) Priority data: 07/753,519 3 September 1991 (03.09.91) US (71) Applicant: DOWELANCO [US/US]; 9002 Purdue Road, Indianapolis, IN 46268-1189 (US). (72) Inventors: HACKLER, Ronald, E. ; 5234 Hawks Point Road, Indianapolis, IN 46226 (US). JOURDAN, Glen, P. ; Rural Route 1, Box 74B, Morristown, IN 46161 (US). JOHNSON, Peter, L. ; 8016 North Dartmouth, In- dianapolis, IN 46260 (US). THOREEN, Brian, R. ; 7344 Crickwood Place, Indianapolis, IN 46268 (US). SAM- ARITONI, Jack, G. ; 2626 Lynndale Drive, New Castle, IN 46362 (US).		(74) Agent: STUART, Donald, R.; DowElanco Patent Depart- ment, 9002 Purdue Road, Indianapolis, IN 46268-1189 (US). (81) Designated States: AT, AU, BB, BG, BR, CA, CH, CS, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, M'W, NL, NO, PL, RO, RU, SD, SE, European pa- tent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: N-(4-PYRIDYL OR 4-QUINOLINYL) ARYLACETAMIDE PESTICIDES (57) Abstract N-(4-Pyridyl or 4-quinolinyl) arylacetamides, for example N-((3-chloro-2-ethyl)-4-pyridyl)(4-(4-chlorophenoxy)phe- nyl)-acetamide are active against nematodes, insects, mites, and plant pathogens.		

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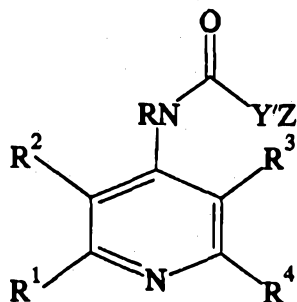
N-(4-PYRIDYL or 4-QUINOLINYL) ARYLACETAMIDE PESTICIDES

5 This invention provides new compounds that are useful as nematicides, insecticides, miticides, and plant fungicides. The invention also provides nematicidal, insecticidal, miticidal, and fungicidal methods.

10 There is an acute need for new nematicides, insecticides, miticides, and plant fungicides. Available nematicides typically have high mammalian toxicity and must be used at high rates. A nematicide that can be applied at lower rates and that has lower mammalian toxicity would represent a significant advance.

15 Mites and insects are developing resistance to the miticides and insecticides in current use. Resistance to insecticides in arthropods is widespread, with at least 400 species resistant to one or more insecticides. The development of resistance to some of the older insecticides, such as DDT, the carbamates, and the organophosphates is well known. But resistance has even developed to some of the newer pyrethroid
20 insecticides and miticides. Similarly, target pathogens are rapidly developing resistance to currently used fungicides. At least 50 species of fungi have developed resistance to the benzimidazole fungicides. Even recently introduced fungicides, like the acylalanines, which initially exhibited excellent control of potato late blight and grape downy mildew in the field, have become less effective because of resistance.
25 Therefore, a need exists for new insecticides, miticides, and fungicides, and particularly for compounds that have new or atypical modes of action.

30 This invention provides compounds of the formula (1):



(1)

and N-oxides and salts thereof, wherein

R is H, (C₁-C₄)alkyl, or benzyl;

R¹, R², R³ and R⁴ are one of the following:

- (a) R³ and R⁴ are H, and R¹ and R² are independently halo, (C₁-C₄)alkyl, halo(C₁-C₄)alkyl, (C₃-C₄) branched alkyl, (C₃-C₇)cycloalkyl, (C₁-C₄)alkoxy, or halo(C₁-C₄)alkoxy;
- (b) one of R¹, R², R³, and R⁴ is (C₁-C₄) alkyl, (C₃-C₄) branched alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkyl, halo(C₁-C₄)alkoxy, (C₁-C₄) alkylthio, (C₁-C₄) alkylsulfinyl, (C₁-C₄) alkylsulfonyl, aryl or substituted amino, and the rest are H;
- (c) R¹, R², R³, and R⁴ are independently H or halo; or
- (d) R¹, and R² combine to form a (C₅-C₆) saturated or unsaturated carbocyclic ring that is optionally substituted with one or two groups selected from halo, (C₁-C₄)alkyl, (C₃-C₄) branched alkyl, halo(C₁-C₄)alkyl, (C₃-C₇)cycloalkyl, (C₁-C₄)alkoxy, halo(C₁-C₄)alkoxy, or NO₂, and R³ and R⁴ are H;

R^5 is H, (C_1-C_4) alkyl or (C_1-C_4) acyl;

R^6 and R^7 are independently (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, phenyl, or substituted phenyl;

5

Y' is bond or bivalent hydrocarbon radical one to five carbon atoms long, optionally substituted with (C_1-C_4) alkyl,

Z is

10

(a) a phenyl group optionally substituted with one or more groups independently selected from:

halo,

I,

15

(C_3-C_8) cycloalkyl,

(C_3-C_8) cycloalkenyl,

phenoxy,

substituted phenoxy,

phenylthio,

20

substituted phenylthio,

phenyl,

substituted phenyl,

NO_2

25

$\begin{array}{c} O \\ || \\ -C-R^8 \end{array}$ where R^8 is (C_1-C_7) alkyl, halo (C_1-C_7) alkyl, (C_3-C_7) branched alkyl, halo (C_3-C_7) branched alkyl, (C_3-C_7) cycloalkyl, halo (C_3-C_7) cycloalkyl, (C_1-C_7) alkoxy, phenyl, or substituted phenyl, acetoxy, OH, CN, $SiR^9R^{10}R^{11}$ or $SiR^9R^{10}R^{11}$, where R^9 , R^{10} and R^{11} are independently (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, phenyl, or substituted phenyl, $NR^{12}R^{13}$, where R^{12} and R^{13} are independently H, (C_1-C_4) alkyl, or (C_1-C_4) acyl, $S(O)R^{14}$, or SO_2R^{14} , where R^{14} is (C_1-C_{10}) alkyl, phenyl, or substituted phenyl; a (C_1-C_{12}) saturated or unsaturated hydrocarbon chain, straight chain or branched optionally including

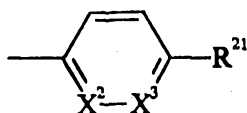
30

5 a hetero atom selected from O, S, SO, SO₂, NR⁵, or SiR⁶R⁷ where R⁵, R⁶ and R⁷ are as defined above, and optionally substituted with halo, halo (C₁-C₄) alkoxy, hydroxy, (C₃-C₈) cycloalkyl or cycloalkenyl, (C₁-C₄) acyl, phenoxy, substituted phenoxy, phenyl, substituted phenyl, phenylthio, or substituted phenylthio; (C₁-C₇) alkoxy optionally substituted with halo, phenyl substituted phenyl, (C₃-C₈) cycloalkyl or cycloalkenyl, phenoxy, or substituted phenoxy; (C₁-C₇) alkylthio optionally substituted with halo, phenyl, substituted phenyl, (C₃-C₈) cycloalkyl or cycloalkenyl, phenoxy or substituted phenoxy;

10 (b) a group selected from optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and decahydronaphthyl;

(c) a group of the formula

15



20

25 one of X² and X³ is N and the other is CH; R²¹ is -Z-R²², phenyl, or substituted phenyl; Z is O or S; and R²² is (C₁-C₄) alkyl, (C₃-C₇) branched alkyl, halo (C₁-C₇) alkyl, halo (C₃-C₇) branched alkyl, (C₁-C₄) alkoxy substituted (C₁-C₄) alkyl, or naphthyl or phenyl, either of which may optionally be substituted with up to three groups selected from halo, (C₁-C₁₀) alkyl, branched (C₃-C₇) alkyl, halo(C₁-C₇) alkyl, hydroxy (C₁-C₇) alkyl, (C₁-C₄) alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkoxy, phenoxy, substituted phenoxy, phenyl, substituted phenyl, CN, NO₂ OH, (C₁-C₄) alkanoyloxy, or benzyloxy.

30

The invention also provides a method of inhibiting a nematode population which comprises applying to the locus of a nematode, a nematode inactivating amount of a compound of the formula (1) as defined above.

35

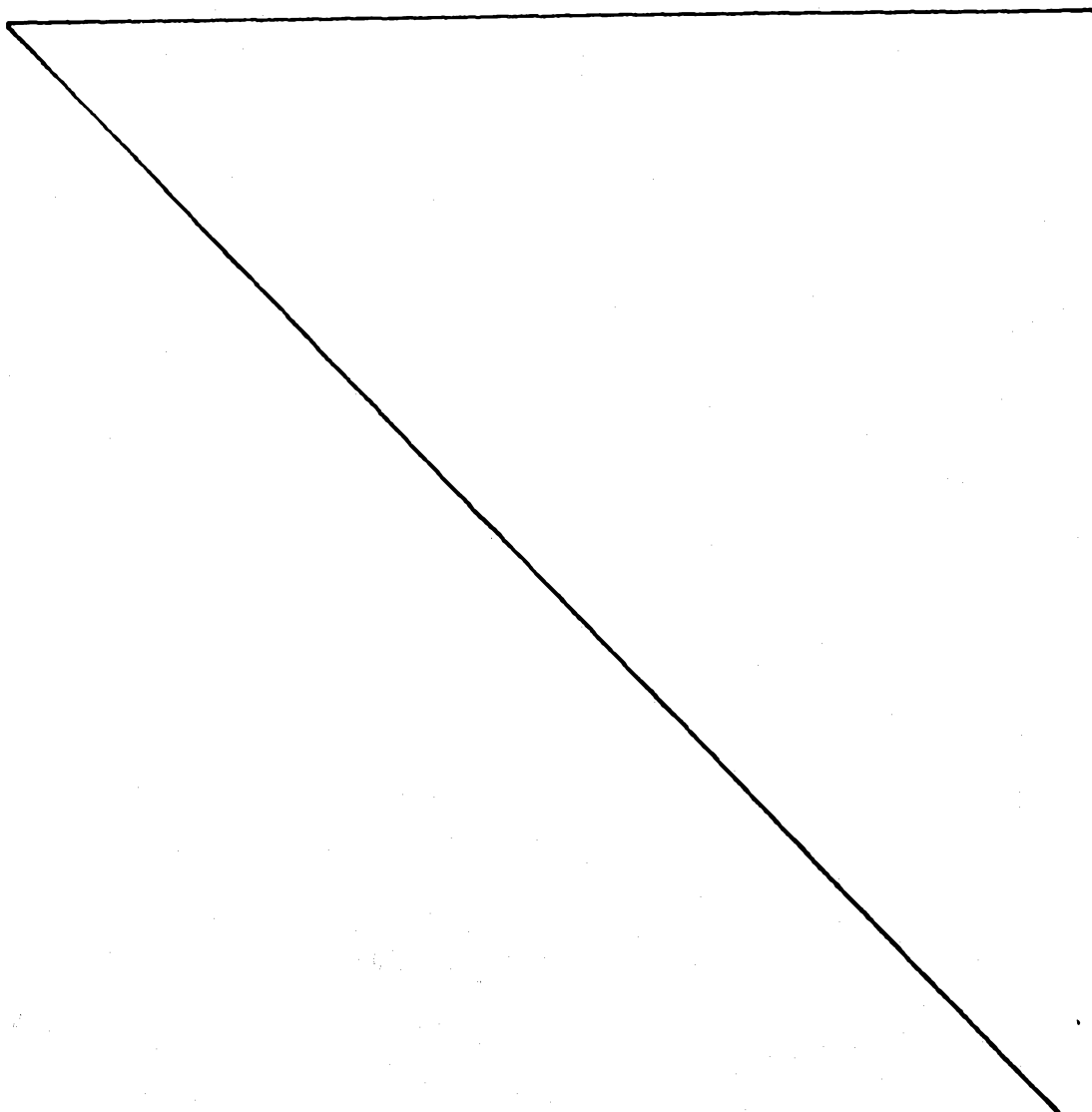
The invention also provides a method of inhibiting an insect or mite population which comprises applying to the locus of the insect or arachnid an effective insect or mite inactivating amount of a compound of formula (1).

- 5 The invention provides a method of inhibiting plant pathogens which comprises applying an effective amount of a compound of formula (1) to a locus of the pathogen.

Throughout this document, all temperatures are given in degrees Celsius, and all percentages are weight percentages unless otherwise stated.

10

The term "halo" refers to a F, Cl, or Br atom.



The terms "alkoxy", "haloalkyl", "alkylsulfinyl", and "alkylsulfonyl" refer to straight chain and branched chain groups.

The terms "substituted phenyl", "substituted phenoxy",
5 "substituted phenylthio", and "substituted phenylsulfonyl",
refer to such groups wherein the phenyl ring is substituted
with up to three groups independently selected from halo, I,
(C₁-C₁₀) alkyl, branched (C₃-C₆) alkyl, halo (C₁-C₇) alkyl,
hydroxy (C₁-C₇) alkyl, (C₁-C₇) alkoxy, halo (C₁-C₇) alkoxy,
10 phenoxy, substituted phenoxy, phenyl, substituted phenyl,
NO₂, OH, CN, (C₁-C₄) alkanoyl, benzoyl, (C₁-C₄) alkanoyloxy,
(C₁-C₄)alkoxycarbonyl, phenoxycarbonyl, or benzoyloxy.

The terms "substituted naphthyl", and "substituted
indolyl" refer to these ring systems substituted with one or
15 more groups independently selected from halo, halo (C₁-C₄)
alkyl, CN, NO₂, (C₁-C₄) alkyl, (C₃-C₄) branched alkyl,
phenyl, (C₁-C₄) alkoxy, or halo (C₁-C₄) alkoxy.

The term "carbocyclic ring" refers to a saturated or
unsaturated carbocyclic ring containing five or six carbon
20 atoms.

The term "unsaturated hydrocarbon chain" refers to a
hydrocarbon chain containing one or more sites of
unsaturation.

The term "HPLC" refers to a high pressure liquid
25 chromatography.

The term "bivalent hydrocarbon radical" refers to
bivalent radicals derived from normal alkanes by removal of
hydrogen atoms from each of the two terminal carbon atoms of
the chain, e.g. methylene, ethylene, trimethylene,
30 tetramethylene, etc.

The term "substituted amino" refers to an amino group
that is substituted with one or two (C₁-C₄) alkyl groups or
one (C₁-C₄) alkanoyl group.

The term "lower alkyl" refers to C₁ to C₆ straight
35 hydrocarbon chains and C₃ to C₆ branched and cyclic
hydrocarbon groups.

The terms "lower alkenyl" and "lower alkynyl" refer to C2 to C6 straight hydrocarbon chains and C3 to C6 branched hydrocarbon groups containing at least one unsaturated bond.

The terms "lower alkoxy" and "lower alkylthio" refer to
5 O-lower alkyl and S-lower alkyl groups.

The term "haloalkyl" refers to lower alkyl groups substituted with one or more halo atoms.

The term "haloalkoxy" refers to lower alkoxy groups substituted with one or more halo atoms.

10 Unless otherwise indicated, when it is stated that a group may be substituted with one or more substituents selected from an identified class, it is intended that the substituents may be independently selected from the class.

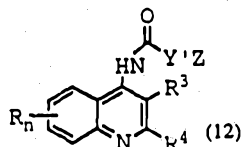
Preferred compounds of formula (1) include the
15 following classes:

- a) compounds of formula (1) wherein Y is -CH₂-;
- b) compounds of formulas (1) wherein Z is phenyl;
- c) compounds of formulas (1) wherein Z is a
20 substituted phenyl group as defined in paragraph (a) of the foregoing definition of "aryl;"
- d) compounds of formulas (1) wherein Z is a phenyl group substituted with a (C₂-C₄) alkoxy group;
- e) compounds of formulas (1) wherein Z is a
25 phenyl group substituted with a (C₃-C₇) branched alkoxy group;
- f) compounds of formulas (1) wherein Z is a phenyl group substituted with a halo(C₂-C₄) alkoxy group;
- g) compounds of formulas (1) wherein Z is a phenyl group substituted with a halo(C₃-C₇) branched alkoxy
30 group;
- h) compounds of formulas (1) wherein Z is a phenyl group substituted with a phenoxy or substituted phenoxy group;
- i) compounds of any of the foregoing groups c) to h) wherein the phenyl group is monosubstituted in the 4-
35 position;

j) compounds of formulas (1) wherein R^1 is (C₁-C₄) alkyl and R^2 is halo;

l) compounds of formulas (1) wherein R^1 is ethyl and R^2 is chloro;

5 m) compounds of formula (1) wherein R^1 and R^2 combine to form , i.e. compounds of the formula (12):

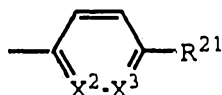


where Y' and Z are as defined above for formula (1), n is 1 or 2, R are independently selected from halo, (C₁-C₄)alkyl, (C₃-C₄) branched alkyl, halo(C₁-C₄)alkyl, (C₃-C₇)cycloalkyl, (C₁-C₄)alkoxy, halo(C₁-C₄)alkoxy, or NO₂, and R^3 and R^4 are H;

n) compounds as defined in foregoing paragraph

m) wherein n is 0 or n is 1 and R is 8-fluoro.

o) compounds of formula (1) wherein Z is a group of the formula

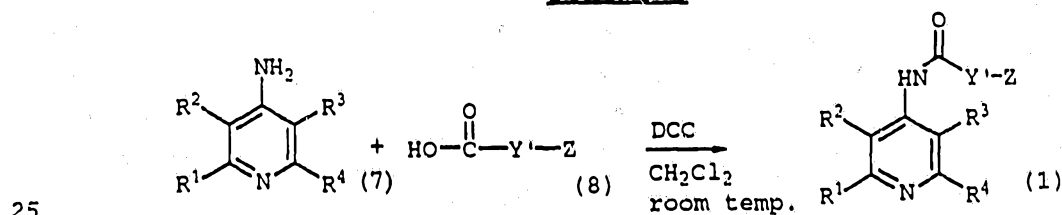


Synthesis

The compounds of this invention are made using well known chemical procedures. The required starting materials are commercially available, or they are readily synthesized using standard procedures.

Compounds of Formula (1) can be prepared using the process illustrated in the following scheme:

Scheme 1

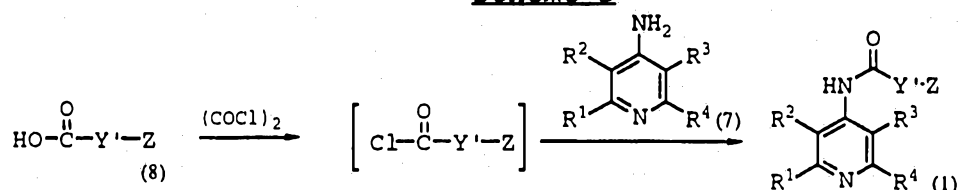


In this procedure, an acid derivative (8) in CH₂Cl₂ is mixed, at room temperature, with an equimolar amount of the 4-aminopyridine derivative (7). To this solution, an equimolar

amount of 1,3-dicyclohexyl-carbodiimide is added. The mixture is stirred about 20 hours, then filtered. The residue is taken up in methylene chloride and filtered again to remove any residual 1,3-dicyclohexyl urea.

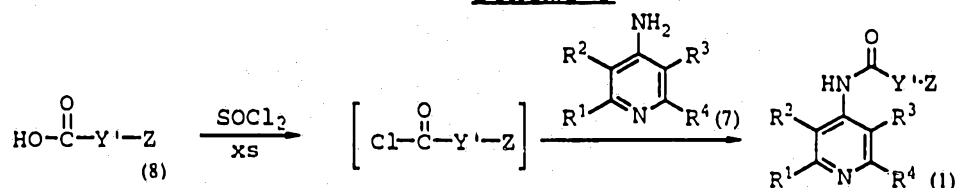
- 5 Compounds of formula (1) can also be prepared using the procedures illustrated in the following schemes 2 and 3.

Scheme 2



- 10 In the procedure illustrated in Scheme 2, a slight excess of oxalyl chloride is added dropwise to a solution of the carboxylic acid (8) in a suitable organic solvent, such as THF, methylene chloride, or xylenes, under nitrogen, at room temperature. The mixture may also include 1-2
- 15 equivalents of pyridine or triethylamine. After stirring the mixture for 30 minutes to 2 hours, the amine, in solution in a suitable organic solvent, such as THF, methylene chloride, or xylene, is added dropwise. The mixture is heated to reflux for 8 to 24 hours, then allowed to cool to room
- 20 temperature and partitioned between 1N sodium hydroxide and ethyl ether. The aqueous phase is extracted with ethyl ether. The combined organics are washed with water and saturated sodium chloride solution, then dried, filtered, and concentrated.

Scheme 3

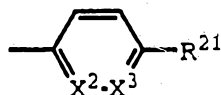


- 25 In the procedure illustrated in Scheme 3, an acid derivative (8) is heated to reflux in excess thionyl chloride for about two hours. The excess thionyl chloride is then
- 30 removed by reducing pressure. To the residue is then added a

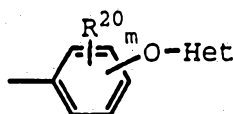
solution of the aminopyridine (7), and optionally about two equivalents of triethylamine, in a suitable organic solvent, such as acetonitrile, toluene, or xylene. The mixture is heated to reflux for 8 to 24 hours, then allowed to cool to room temperature and partitioned between 1N sodium hydroxide and ethyl ether. The aqueous phase is extracted with ethyl ether. The combined organics are washed with water and saturated sodium chloride solution, then dried, filtered, and concentrated.

Compounds of formula (7) can be prepared using known procedures. For example, the preparation of 2-alkyl-4-amino-3-bromopyridine and 2-alkyl-4-amino-3-chloropyridine derivatives is described in J. Med. Chem. vol. 32, pages 1970-77 (1989). J. Prakt. Chem., vol 331, pages 369-374 (1989) describes bromination of aminopicolines, affording other useful starting materials. Compounds of formula (7) can also be made by reduction of the corresponding azides by procedures similar to J. Prakt. Chem., vol 327, pages 521-522 (1985), as illustrated in Preparation 2 hereinafter.

Carboxylic acid derivatives of formula (8) wherein Z is phenyl or substituted phenyl can be prepared using the known procedures illustrated below in Scheme 4. Carboxylic acid derivatives of formula (8) wherein Z is a group of the formula



can be prepared using an analogous procedure. Carboxylic acid derivatives of formula (8) wherein Z is a group of the formula



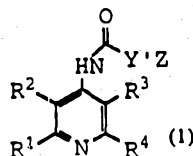
can be prepared by reacting p-hydroxyphenyl acetic acid with the appropriate chloro-substituted heterocyclic compound, as illustrated hereinafter in Preparation 3.

The N-oxides and salts of compounds of formula (1) are obtained in the usual way.

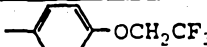
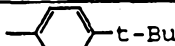
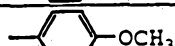
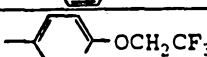
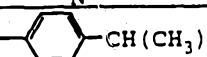
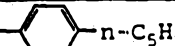
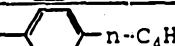
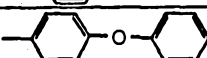
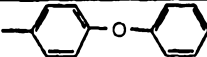
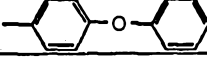
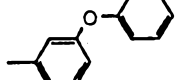
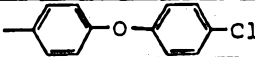
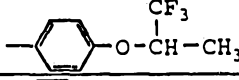
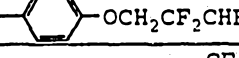
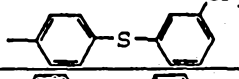
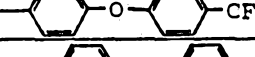
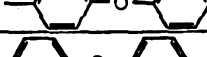
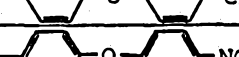
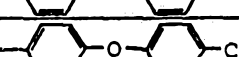
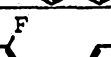
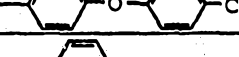
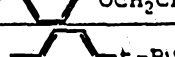
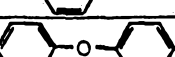
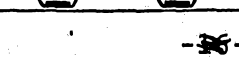
Examples

The following tables identify compounds of formula (1) that were prepared by the processes illustrated in the foregoing schemes. Detailed examples illustrating preparation of exemplary compounds follow the tables.

TABLE I



Compound	Y'	Z	R ¹	R ²	R ³	R ⁴	MP °C
1	CH ₂		H	H	H	H	104-105
2	CH ₂		H	H	H	H	oil
3	CH ₂		H	H	H	H	107
4	CH ₂		H	H	H	H	145
5	CH ₂		H	H	H	H	87
6	CH ₂		H	H	H	H	120
7	CH ₂		H	H	H	H	60
8	CH ₂		H	H	H	H	148
9	CH ₂		H	H	H	H	
10	CH ₂		CH ₃	CH ₃	H	H	92
11	CH ₂		CH ₃	CH ₃	H	H	148
12	CH ₂		CH ₃	CH ₃	H	H	146
13	CH ₂		CH ₃	H	H	H	<50
14	CH ₂		H	H	Cl	CH ₃	152
15	CH ₂		F	F	F	F	138
16	CH ₂		H	H	H	C ₂ H ₅	wax
17	CH ₂		H	Cl	Cl	CH ₃	139
18	CH ₂		H	H	Cl	C ₂ H ₅	oil

Compound	Y'	Z	R ¹	R ²	R ³	R ⁴	MP °C
19	CH ₂		H	H	Cl	C ₂ H ₅	121
20	CH ₂		H	H	Cl	C ₂ H ₅	98
21	CH ₂		H	H	Cl	C ₂ H ₅	107
22	CH ₂		H	H	Cl	C ₂ H ₅	104
23	CH ₂		H	H	Cl	C ₂ H ₅	90
24	CH ₂		H	H	Cl	C ₂ H ₅	102
25	CH ₂		H	H	Cl	C ₂ H ₅	92
26	CH ₂		H	H	Cl	H	88
27	CH ₂		H	H	CH ₃	H	58-61
28	CH ₂		CH ₃	H	CH ₃	H	122
29	CH ₂		H	H	Cl	C ₂ H ₅	63-66
30	CH ₂		H	H	Cl	C ₂ H ₅	72-74
31	CH ₂		H	H	Cl	C ₂ H ₅	75
32	CH ₂		H	H	Cl	C ₂ H ₅	102
33	CH ₂		H	H	Cl	C ₂ H ₅	166
34	CH ₂		H	H	Cl	C ₂ H ₅	101.3
35	CH ₂		CH ₃	H	H	CH ₃	56
36	CH ₂		H	H	Cl	C ₂ H ₅	96
37	CH ₂		H	H	Cl	C ₂ H ₅	120-122
38	CH ₂		H	H	Br	C ₂ H ₅	73-75
39	CH ₂		H	H	Cl	C ₂ H ₅	140-141
40	CH ₂		H	H	Cl	C ₂ H ₅	102-103
41	CH ₂		H	H	H	C ₂ H ₅	132-133
42	CH ₂		H	H	H	C ₂ H ₅	105-106
43	CH ₂		H	H	H	C ₂ H ₅	117-119

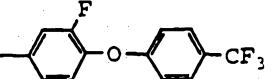
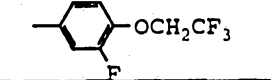
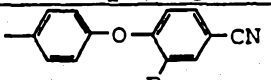
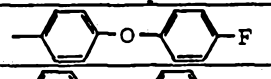
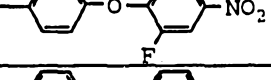
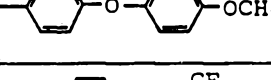
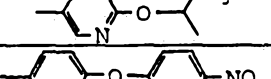
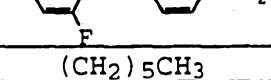
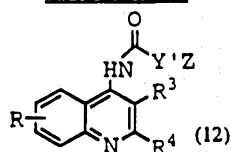
Compound	Y'	Z	R ¹	R ²	R ³	R ⁴	MP °C
44	CH ₂		H	H	Cl	C ₂ H ₅	119-120
45	CH ₂		H	H	Cl	C ₂ H ₅	112-114
46	CHCH ₃	(CH ₂) ₇ CH ₃	H	H	Cl	C ₂ H ₅	52-53
47	CH ₂		H	H	Cl	C ₂ H ₅	117-119
48	CH ₂		H	H	Cl	C ₂ H ₅	84-86
49	CH ₂		H	H	Cl	C ₂ H ₅	139
50	CH ₂		H	H	Cl	C ₂ H ₅	oil
51	CH ₂		H	H	Cl	C ₂ H ₅	oil
52	CH ₂		H	H	Cl	C ₂ H ₅	152-154
53	CH ₂	(CH ₂) ₅ CH ₃	H	H	Cl	C ₂ H ₅	58-60
54	CH ₂	(CH ₂) ₇ CH ₃	H	H	Cl	C ₂ H ₅	63-65
55	CH ₂	(CH ₂) ₉ CH ₃	H	H	Cl	C ₂ H ₅	78-80

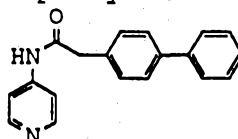
TABLE II



Compound	Y'	Z	R	R ³	R ⁴	MP °C
56	CH ₂		8-F	H	H	167-169
57	CH ₂		8-F	H	H	168-170
58	CH ₂		8-F	H	H	glass
59	CH ₂		8-F	H	H	169
60	CH ₂		H	H	CH ₃	128-130
61	CH ₂		H	H	H	165-167
62	CH ₂		8-F	H	H	123-125
63	CH ₂		8-F	H	H	oil
64	CH ₂		8-F	H	H	145-147
65	CH ₂		8-F	H	H	110-112

Example 1

N-(4-pyridyl)-4-biphenylacetamide (Compound 4)

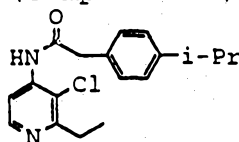


5

To a solution of 0.941 g (10 mmol) of 4-aminopyridine and 2.123 g of 4-biphenylacetic acid in 50 mL of methylene chloride was added 2.063 g of 1,3-dicyclohexylcarbodiimide. After stirring the mixture at room temperature for about 24 hours, the mixture was filtered and concentrated. The residue was taken up in methylene chloride, filtered and concentrated to give 2.997 g of a flaky, light green solid. This was recrystallized from hexane/ethylacetate and vacuum oven dried to give 2.138 g of a light green solid. Yield 74%. M.P. 145.3 °C.

Example 2

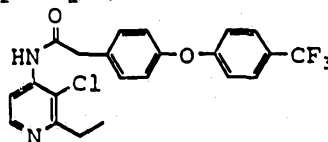
N-(3-chloro-2-ethyl-4-pyridyl)(4-isopropylphenyl)acetamide
(Compound 23)



5 Oxalyl chloride (0.48 mL, 5.50 mmol) was added to
a solution of 4-isopropylphenyl acetic acid (0.935 g, 5.25
mmol) in 20 mL of xylene at room temperature. After the
mixture was stirred for about 15 minutes, 0.8 mL of pyridine
was added. The mixture was stirred for an additional 30
10 minutes, after which 4-amino-3-chloro-2-ethylpyridine (0.783
g., 5.00 mmol) was added, and the resultant mixture was
heated to reflux. After refluxing for about 17 hours, the
mixture was allowed to cool to room temperature and
partitioned between 1 N NaOH (75 mL) and ethyl ether (75 mL).
15 The aqueous phase was extracted with ethyl ether (75 mL).
The combined organics were washed with water (1 x 100 mL),
saturated NaCl (1 x 100 mL), and then dried, filtered, and
concentrated to give 1.71 g. of a brown oil. The oil was
chromatographed on silica gel, eluting with 80% hexane/20%
20 EtOAc. Isolation of the major product gave 0.391 g. of the
desired compound as a solid. M.P. 90°C.

Example 3

N-(3-chloro-2-ethyl-4-pyridyl)(4-((4-(trifluoromethyl)-
phenyl)oxy)phenyl)acetamide (Compound 34)



25

A mixture of (4-((4-(trifluoromethyl)phenyl)oxy)-
phenyl) acetic acid (1.05 g, 3.5 mmol) and 20 mL of thionyl
chloride was heated to reflux. After refluxing two hours,
the excess thionyl chloride was removed by reducing pressure.
30 The residue was then treated with a solution of 4-amino-3-
chloro-2-ethylpyridine and 1 mL of triethylamine in 20 mL of
acetonitrile. The mixture was heated and allowed to reflux

for about 24 hours, then cooled to room temperature and partitioned between 1 N NaOH (75 mL) and ethyl ether (75 mL). The aqueous phase was extracted with ethyl ether (75 mL). The combined organics were washed with water (1 x 75 mL),
5 saturated NaCl (1 x 75 mL), and then dried, filtered, and concentrated to give 1.32 g. of a yellow oil. The was chromatographed on silica gel, eluting with 80% hexane/20% EtOAc. Isolation of the major product gave 0.202 g. of the desired compound as a solid. M.P. 101.3°C.

10

Preparation 1

4-Azido-8-fluoroquinoline

A mixture of 2.08 g (0.0114 mol) of 4-chloro-8-fluoroquinoline, 1.12 g (0.0172 mol) of sodium azide, and 4.10 g ((0.0127 mol) of tetrabutyl ammonium bromide in 70 mL
15 of dichloromethane and 25 mL of water was refluxed overnight. The layers were then separated and the organic layer was washed once with water, passed through phase separating paper, and concentrated to an oil, which was triturated with ether. The solid was filtered and the filtrate was
20 concentrated to give 2.0 g of the title product.

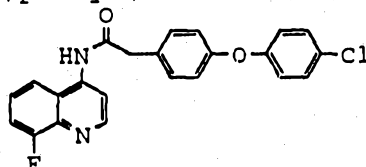
Preparation 2

4-Amino-8-fluoroquinoline

To a solution at 15-20°C of 4-azido-8-fluoroquinoline in 12 mL of absolute ethanol was added a portion of 0.57g
25 (0.015 mol) of sodium borohydride. A powerful exotherm with vigorous evolution of gas was observed. The solution was cooled in ice and the remainder of the hydride was added in small portions within five minutes. The ice bath was then removed. After about two hours, the mixture was poured into
30 about 200 mL of ice water. The precipitate was collected and air dried overnight. Yield 1.35 g. M.P. 184-186°C.

Example 4

N-(8-fluoro-4-quinolinyl)(4-((4-chlorophenyl)oxy)phenyl)acetamide (Compound 59)



5 A mixture of 0.63 g (0.0024 mol) of (4-(4-chlorophenyl)oxy)phenylacetic acid and excess (10 mL) of thionyl chloride was refluxed for two hours. Excess thionyl chloride was then removed by reducing pressure, the residue was taken up in xylene and 0.39 g (0.0024 mol) of 4-amino-8-fluoroquinoline was added. The mixture was refluxed
10 overnight. The xylene was removed by reducing pressure, then the residue was taken up in methylene chloride and the resulting mixture was washed once with water and once with 0.1N sodium hydroxide. The pH of the aqueous layer was
15 adjusted to 7, and product was extracted with ethyl acetate. The methylene chloride and ethyl acetate layers were combined and dried, concentrated to an oil. NMR indicated that the product was a mixture of the starting acid and the desired product. The product was taken up in methylene chloride,
20 washed with base (0.1N sodium hydroxide), dried, and concentrated to an oil. This was chromatographed 100% CH₂Cl₂ → 10% CH₂Cl₂/EtOAc in 2%/liter increments, and 0.14 g of the title product was collected. This was mixed with hexane and filtered, giving a light brown solid. Yield 0.13 g. M.P.
25 169°C.

Preparation 3

4-(3-chloro-6-pyridazinyloxy)phenylacetic acid

To a mixture of 0.54 g (0.013 mol, 2.0 equiv) of 60% sodium hydride/mineral oil dispersion in 10 mL of dry DMF was
30 added dropwise at room temperature a solution 1.02 g (0.0067 mol) of the phenylacetic acid in 2.3 mL of DMF. After 15 - 20 minutes, a solid existed which was difficult to stir. The

pyridazine (1.0 g, .0067 mol) was then added and the mixture was heated at 60 - 65°C for about 2 hours and was allowed to cool. The mixture was poured onto ice water and was adjusted to pH 5 with 2.0 N HCl, and the precipitate was collected.

- 5 This material was triturated under heptane to afford 880 mg of the title product. MP 124-127°C.

Insecticide and Miticide Utility

- The compounds of formula (1) show activity against a number of insects and mites. More specifically, the
- 10 compounds show activity against melon aphid, which is a member of the insect order *Homoptera*. Other members of the *Homoptera* include leafhoppers, planthoppers, pear psylla, apple sucker, scale insects, whiteflies, spittle bugs as well as numerous other host specific aphid species. Activity has
- 15 also been observed against greenhouse thrips, which are members of the order *Thysanoptera*. The compounds also show activity against Southern armyworm, which is a member of the insect order *Lepidoptera*. Other typical members of this order are codling moth, cutworm, clothes moth, Indianmeal
- 20 moth, leaf rollers, corn earworm, European corn borer, cabbage worm, cabbage looper, cotton bollworm, bagworm, eastern tent caterpillar, sod webworm, and fall armyworm.

- The compounds of formula (1) are useful for reducing populations of insects and mites, and are used in a method of
- 25 inhibiting an insect or mite population which comprises applying to a locus of the insect or mite an effective insect- or mite-inactivating amount of a compound of formula (1). The "locus" of insects or mites is a term used herein to refer to the environment in which the insects or mites
- 30 live or where their eggs are present, including the air surrounding them, the food they eat, or objects which they contact. For example, plant-ingesting insects or mites can be controlled by applying the active compound to plant parts, which the insects or mites eat, particularly the foliage. It
- 35 is contemplated that the compounds might also be useful to protect textiles, paper, stored grain, or seeds by applying

an active compound to such substance. The term "inhibiting an insect or mite" refers to a decrease in the numbers of living insects or mites; or a decrease in the number of viable insect or mite eggs. The extent of reduction
5 accomplished by a compound depends, of course, upon the application rate of the compound, the particular compound used, and the target insect or mite species. At least an insect-inactivating or mite-inactivating amount should be used. The terms "insect-inactivating amount" and
10 "mite-inactivating amount" are used to describe the amount, which is sufficient to cause a measurable reduction in the treated insect or mite population. Generally an amount in the range from about 1 to about 1000 ppm active compound is used.

15 Some of the above identified compounds were tested for insecticidal, miticidal and nematicidal activity against eight species. Results are reported in the following table, wherein the following abbreviations are used:

ALH refers to aster leafhopper
BAW refers to beet armyworm
CA refers to cotton aphid
NEM refers to peanut rootknot nematode
SCRW refers to southern corn rootworm
TBW refers to tobacco budworm
TSSM refers to two spotted spider mite
GECR refers to German cockroach

In conducting evaluations of insecticidal activity,
20 each test compound was formulated as a 400 ppm solution, and this solution was then diluted with water to give lesser concentrations. The 400 ppm solution was prepared by combining 19.2 mL of .05% solution of Tween 20 (polyoxyethylene (20) sorbitan monolaurate) in water with a
25 solution of 8 mg of the compound in .8 mL of acetone/EtOH (9/1).

Activity against aster leafhopper (*Macrosteles fascifrons*) was tested as follows. The test was run using

concentrations of 400 ppm and 50 ppm. One ounce plastic cups containing a cotton wick was sprayed with 0.4 mL of formulated material using a flat-fan nozzle. The excess moisture was allowed to evaporate. Then five to ten carbon
5 dioxide anesthetized adult leafhoppers were added to each cup. The cups were capped and held at room temperature for 24 hours. Percent mortality was then determined.

Activity against beet armyworm (*Spodoptera exigua*) was evaluated as follows. The test is run using concentrations of
10 400 ppm and 50 ppm. A general purpose lepidoptera artificial diet was diluted to half strength with a 5% non nutritive agar. 8 mL of this diet material was dispensed into one ounce diet cups. One hour prior to treatment, 35 to 40 eggs were dispensed onto the diet surface. The cups were then
15 sprayed with formulated material through a flat-fan nozzle. Treated cups were air dried prior to sealing with plastic caps. The cups were held for 6 days at room temperature. Activity was then rated based on the total number of live and dead larvae, and on the size of live larvae.

20 Activity against cotton aphid (*Aphis gossypii*) and two spotted spider mite (*Tetranychus urticae*) was evaluated as follows. Golden crookneck squash plants were grown to the expanded cotyledon stage (about 6 to 8 days). The plants were infested with cotton aphids and two spotted spider mites
25 16 to 24 hours before application of the test material by transfer of infested foliage cut from a stock colony. Immediately prior to spray application of the test material the transfer foliage is removed from the squash plants. The test is run using concentrations of 400 ppm and 50 ppm. The
30 plants are sprayed with test solution using an atomizing sprayer at 17 psi. Both surfaces of the leaves are covered until runoff, and then allowed to dry. Activity of each compound was determined three days after treatment. Activity was rated as a percent based on the mites/aphids present in
35 plants sprayed with solvent alone.

Activity against peanut root knot nematode (*Meloidogyne arenaria*) was evaluated as follows. Five untreated cucumber seeds are placed into the bottom of a clear one ounce cup, 20 g of clean white sand is added, and the cups were sprayed while rotating on a pedestal allowing 1.0 mL of a 400 ppm solution to be deposited on the sand. To each cup was dispensed 2.5 to 3.0 mL of deionized water containing 300 to 500 nematodes. The cups were held for 10 to 12 days in an environmental growth chamber at a temperature of 76 to 85 °F and ambient humidity of 50 to 60%. After 10 to 12 days the cups were evaluated by inverting the cup and observing nematode mortality and feeding damage to the cucumber plants.

Activity on Southern corn rootworm (*Diabrotica undecimpunctata howardi* Barber) was evaluated by adding one mL of test solution containing a predetermined concentration of test compound to a cup containing a kernel of corn in 16 g of sterile soil. This produces a soil concentration of 24 ppm. After 1.5 to 2 hours of drying, five 4th instar corn rootworm larvae were added to the individual cups. Mortality was measured at 3-4 days by emptying the cup onto a pan and inspecting the soil for live rootworms.

Activity against tobacco budworm (*Heliothis virescens*) was evaluated as follows. A general purpose lepidoptera artificial diet was diluted to half strength with a 5% non nutritive agar. 8 mL of this diet material was dispensed into each one ounce diet cup. One hour prior to treatment 18 to 20 eggs were dispensed onto the diet surface. The cups were then sprayed with formulated material through a flat-fan nozzle. The test was run using concentrations of 400 ppm and 50 ppm. Treated cups were air dried prior to sealing with plastic caps. The cups were held for 6 days at room temperature. Activity was then rated based on the total number of live and dead larvae, and on the size of live larvae.

Activity against German cockroach (*Blattella germanicus*) was evaluated as follows. 8 mL of alfalfa based

green insect diet material was dispensed into a one ounce diet cup. The cups were then sprayed with formulated material through a flat-fan nozzle. The test was run using concentrations of 400 ppm and 50 ppm. Treated cups were air dried for 24 hours and infested with five late third or early fourth instar German cockroaches. The cups were capped and held for ten days in an environmental growth chamber at a temperature of 76-85°C. Activity was then rated based on the total number of live and dead insects.

INSECTICIDE, MITICIDE, AND NEMATICIDE DATA								
Compound	ALH 400 ppm 50 ppm	BAW 400 ppm 50 ppm	CA 400 ppm 50 ppm	NEM 400 ppm 50 ppm	SCRW 400 ppm 50 ppm	TBW 400 ppm 50 ppm	TSSM 400 ppm 50 ppm	GEGR 400 ppm 50 ppm
1	100 -	0 -	0 -		0 -	0 -	0 -	0 -
2								
3								
4	0 -	0 -	0 -		0 -	70 -	0 -	0 -
5		0 -	0 -		0 -	0 -	0 -	0 -
6		0 -	0 -		0 -	0 -	0 -	0 -
7	0 -	0 -	0 -		0 -	0 -	0 -	0 -
8	0 -	0 -	0 -		0 -	0 -	0 -	0 -
9	0 -	0 -	0 -		0 -	60 -	0 -	20 -
10	100 100	100 0	100 100	100 100	0 -	0 0	100 100	60 0
11	100 100	100 100	100 100	0 0	0 -	100 100	100 100	100 0
12	100 100	80 0	0 0	0 0	0 -	60 0	0 J	0 0
13	100 100	0 0	60 0	0 0	0 -	50 0	100 100	0 0
14	100 100	100 100	100 100	100 0	0 -	100 100	100 100	20 40
15	0 0	0 0	0 0	60 0	0 -	0 0	0 0	0 0
16	100 100	100 0	0 0	40 -	0 -	100 0	0 0	0 0
17	0 60	0 0	0 0	0 0	0 -	0 0	0 0	0 0
18	80 80	100 100	100 100	100 -	100 -	100 100	100 100	100 40
19	100 100	100 100	100 100	100 -	100 -	100 100	100 100	40 40

Compound	ALH 400 ppm 50 ppm	BAW 400 ppm 50 ppm	CA 400 ppm 50 ppm	NEM 400 ppm 50 ppm	SCRW 400 ppm 50 ppm	TBW 400 ppm 50 ppm	TSSM 400 ppm 50 ppm	GEGR 400 ppm 50 ppm
20	100 100	100 100	100 100	100 -	0 -	100 100	100 100	80 0
21	100 40	100 100	100 70	100 -	0 -	100 100	100 100	0 0
22	100 100	100 100	100 100	100 -	100 -	100 80	0 0	60 0
23	100 100	100 100	100 90	0 -	0 -	100 100	100 100	20 0
24	100 100	100 100	100 100	0 -	0 -	100 100	100 100	80 40
25	100 100	100 100	100 100	0 -	100 -	100 100	100 100	80 20
26	100 100	100 100	100 90	100 -	0 -	80 0	0 0	0 0
27	100 100	100 0	100 100	30 -	0 -	0 0	0 0	0 0
28	100 100	0 0	0 0	0 0	0 -	0 0	0 0	0 0
29	100 100	100 100	100 100	0 -	0 -	100 100	100 100	0 0
30	100 100	100 100	100 100	100 -	100 -	100 100	100 100	100 60
31	100 100	100 100	100 100	0 -	100 -	100 100	100 100	40 0
32	80 60	100 100	0 0	0 -	100 -	100 100	0 0	0 0
33	100 100	100 100	100 0	0 -	0 -	80 40	100 0	0 20
34	100 100	100 100	100 100	100 -	100 -	100 100	100 100	100 60
35	80 80	0 0	0 0	0 -	0 -	0 0	0 0	20 0
36	100 100	100 100	100 100	100 -	100 -	100 100	100 100	100 100
37	100 100	100 100	100 100	100 -	100 -	100 100	100 100	100 100
38	100 100	100 100	100 100	100 -	100 -	100 100	100 100	100 100
39	100 100	100 100	100 100	100 -	100 -	100 100	100 100	0 0
40	100 100	100 100	100 100	0 -	100 -	100 100	100 100	100 80
41	- -	- -	- -	- -	- -	- -	- -	- -
42	100 100	0 0	100 100	0 -	0 -	0 0	100 100	- -
43	100 100	100 100	0 0	0 -	0 -	100 100	0 0	- -
44	100 100	100 100	100 100	0 -	100 -	100 100	100 100	- -

Compound	ALH 400 ppm 50 ppm	BAW 400 ppm 50 ppm	CA 400 ppm 50 ppm	NEM 400 ppm 50 ppm	SCRW 400 ppm 50 ppm	TBW 400 ppm 50 ppm	TSSM 400 ppm 50 ppm	GEGR 400 ppm 50 ppm
45	100 100	100 100	100 100	0 -	100 -	100 100	100 0	- -
46	100 100	100 100	100 100	0 -	0 -	100 0	100 100	- -
47	100 100	100 100	100 100	0 -	0 -	100 100	100 100	- -
48	100 100	100 100	100 100	0 -	0 -	100 100	100 100	- -
49	100 100	100 10	100 100	0 -	0 -	100 100	0 0	- -
50	100 100	100 100	100 100	0 -	100 -	100 100	100 100	- -
51	100 100	100 100	100 100	0 -	100 -	100 100	100 100	- -
52	100 100	100 100	0 0	0 -	0 -	100 100	0 0	- -
53								
54								
55								
56	100 100	100 100	100 100	0 0	0 0	100 100	100 100	60 0
57	100 60	100 100	100 100	0 -	0 -	100 100	100 90	0 0
58	60 80	100 100	0 0	100 -	0 -	100 100	0 0	0 0
59	100 100	100 100	100 100	100 -	100 -	100 100	100 100	0 0
60	100 80	100 100	100 100	0 -	0 -	60 0	0 0	- -
61	100 100	100 100	100 100			100 0	100 100	
62	100 100	100 100	100 100	100 0		100 100	100 100	
63	100 100	100 70	100 100	0 0	0 0	100 100	90 80	
64	100 100	100 100	100 100	0 0	100 0	100 100	100 100	

Nematicide Utility

The compounds of the present invention are useful for reducing populations of nematodes. Accordingly, a significant aspect of the invention is a method of inhibiting a nematode population which comprises applying to a locus of a nematode an effective nematode inactivating amount of a compound of formula (1). The term "inhibiting a nematode" refers to a decrease in the numbers of living nematodes. The

extent of reduction accomplished by a compound depends upon the application rate of the compound, the particular compound used, and the target species. At least a nematode-inactivating amount should be used. The term "nematode-inactivating amount" is used to describe the amount, which is sufficient to cause a measurable reduction in the treated nematode population.

The method is practiced in accordance with standard techniques for the application of nematicides. In general, good nematicidal activity can be expected at rates of 1-10 lbs/acre. The compound can be formulated as described below in the Compositions section. When formulated as dispersions, nematicides are typically applied as aqueous drenches around growing plants or applied incrementally via irrigation systems. When applied as granules, nematicides may be incorporated into the soil before planting, or applied in a band on top of a seed row, or broadcast and then incorporated into the soil, or used as a side dressing to an established crop.

Fungicide Utility

The compounds of the present invention have been found to control fungi, particularly plant pathogens. When employed in the treatment of plant fungal diseases, the compounds are applied to the plants in a disease inhibiting and phytologically acceptable amount. The term "disease inhibiting and phytologically acceptable amount," as used herein, refers to an amount of a compound of the invention which kills or inhibits the plant disease for which control is desired, but is not significantly toxic to the plant. This amount will generally be from about 1 to 1000 ppm, with 10 to 500 ppm being preferred. The exact concentration of compound required varies with the fungal disease to be controlled, the type formulation employed, the method of application, the particular plant species, climate conditions and the like. A suitable application rate is typically in the range from .25 to 4 lb/A. The compounds of the invention

may also be used to protect stored grain and other non-plant loci from fungal infestation.

Greenhouse Tests

The following experiments were performed in the laboratory to determine the fungicidal efficacy of the compounds of the invention.

The test compounds were formulated for application by dissolving 50 mg of the compound into 1.25 ml of solvent. The solvent was prepared by mixing 50 ml of "Tween 20" (polyoxyethylene (20) sorbitan monolaurate emulsifier) with 475 ml of acetone and 475 ml of ethanol. The solvent/compound solution was diluted to 125 ml with deionized water. The resulting formulation contains 400 ppm test chemical. Lower concentrations were obtained by serial dilution with the solvent-surfactant mixture.

The formulated test compounds were applied by foliar spray. The following plant pathogens and their corresponding plants were employed.

Pathogen	Designation in following Table	Host
<i>Erysiphe graminis tritici</i> (powdery mildew)	ERYSGT	wheat
<i>Pyricularia oryzae</i> (rice blast)	PYRIOR	rice
<i>Puccinia recondita</i> <i>tritici</i> (leaf rust)	PUCCRT	wheat
<i>Leptosphaeria nodorum</i> (glume blotch)	LEPTNO	wheat
<i>Plasmopara viticola</i> (downy mildew)	PLASVI	grape

The formulated technical compounds were sprayed on all foliar surfaces of the host plants (or cut berry) to past run-off. Single pots of each host plant were placed on raised, revolving pedestals in a fume hood. Test solutions were sprayed on all foliar surfaces. All treatments were allowed to dry and the plants were inoculated with the appropriate pathogens within 2-4 hours.

The following table presents the activity of typical compounds of the present invention when evaluated in this

experiment. The effectiveness of test compounds in controlling disease was rated using the following scale.

0 = not tested against specific organism
 - = 0-19% control at 400 ppm
 + = 20-89% control at 400 ppm
 ++ = 90-100% control at 400 ppm
 +++ = 90-100% control at 100 ppm

COMPOUND NUMBER	ERYSGT	PYRIOR	PUCCRT	LEPTNO	PLASVI
1	-	-	-	-	+
2	++	-	-	0	0
3	-	-	+++	-	++
4	+	+	+	-	+++
5	-	-	++	-	-
6	+	+	+	-	+
7	-	-	+	-	-
8	+	-	+	-	+
9	+	+	++	0	0
10	++	+	+++	++	+++
11	+++	++	+++	++	++
12	++	+	++	-	+
13	++	++	+++	-	++
14	+++	+++	+++	++	+++
15	-	+	+	+	++
16	+++	++	+++	++	+++
17	-	-	-	-	-
18	+++	+++	+++	++	+++
19	+++	+++	+++	++	+++
20	+++	+++	+++	-	+++
21	++	++	++	++	++
22	++	+	++	+	+++
23	++	+	++	+	+++
24	++	+	++	+	+++
25	+	+	++	+	+++
26	++	++	++	+	++
27	++	+	+	++	++
28	++	-	++	+++	++
29	+++	+++	++	+	+++
30	+++	+++	++	+++	+++
31	+++	++	++	++	++
32	+++	+	++	++	++
33	+++	+	++	+	++
34	+++	++	++	+++	+++
35	++	+	++	++	++
36	++	+	++	+	++
37	++	+	++	++	+
38	++	+	++	++	+
39	-	-	++	+	-
40	++	+	++	++	++

COMPOUND NUMBER	ERYSGT	PYRIOR	PUCCRT	LEPTNO	PLASVI
41	+++	+++	++	++	++
42	++	++	++	++	++
43	+++	++	-	+++	+++
44	++	++	++	++	-
45	++	+	++	++	++
46	++	+	++	++	+
47	++	-	++	-	++
48	++	++	++	-	++
49	+	-	++	+	-
50	++	++	++	++	++
51	++	++	++	++	++
52	+	+	++	+	-
53					
54					
55					
56	+++	++	0	++	+++
57	+++	-	0	-	+++
58	+++	+	0	+	+
59	+++	++	0	+	+++
60	+	-	0	-	+
61	-	-	0	-	+++
62	+	-	0	+	+++
63	+	+++	0	++	+++
64	+++	+	0	++	+++

Compositions

The compounds of formula (1) are applied in the form of compositions which are important embodiments of the invention, and which comprise a compound of formula (1) and a phytologically-acceptable inert carrier. The compositions are either concentrated formulations which are dispersed in water for application, or are dust or granular formulations which are applied without further treatment. The compositions are prepared according to procedures and formulae which are conventional in the agricultural chemical art, but which are novel and important because of the presence therein of the compounds of this invention. Some description of the formulation of the compositions will be given, however, to assure that agricultural chemists can readily prepare any desired composition.

The dispersions in which the compounds are applied are most often aqueous suspensions or emulsions prepared from concentrated formulations of the compounds. Such water-soluble, water-suspendable or emulsifiable formulations are either solids usually known as wettable powders, or liquids usually known as emulsifiable concentrates or aqueous suspensions. Wettable powders, which may be compacted to form water dispersible granules, comprise an intimate mixture of the active compound, an inert carrier and surfactants. The concentration of the active compound is usually from about 10% to about 90% by weight. The inert carrier is usually chosen from among the attapulgite clays, the montmorillonite clays, the diatomaceous earths, or the purified silicates. Effective surfactants, comprising from about 0.5% to about 10% of the wettable powder, are found among the sulfonated lignins, the condensed naphthalenesulfonates, the naphthalenesulfonates, the alkylbenzenesulfonates, the alkyl sulfates, and non-ionic surfactants such as ethylene oxide adducts of alkyl phenols.

Emulsifiable concentrates of the compounds comprise a convenient concentration of a compound, such as from about 50 to about 500 grams per liter of liquid, equivalent to about

10% to about 50%, dissolved in an inert carrier which is either a water miscible solvent or a mixture of water-immiscible organic solvent and emulsifiers. Useful organic solvents include aromatics, especially the xylenes, and the petroleum fractions, especially the high-boiling naphthalenic and olefinic portions of petroleum such as heavy aromatic naphtha. Other organic solvents may also be used, such as the terpenic solvents including rosin derivatives, aliphatic ketones such as cyclohexanone, and complex alcohols such as 2-ethoxyethanol. Suitable emulsifiers for emulsifiable concentrates are chosen from conventional nonionic surfactants, such as those discussed above.

Aqueous suspensions comprise suspensions of water-insoluble compounds of this invention, dispersed in an aqueous vehicle at a concentration in the range from about 5% to about 50% by weight. Suspensions are prepared by finely grinding the compound, and vigorously mixing it into a vehicle comprised of water and surfactants chosen from the same types discussed above. Inert ingredients, such as inorganic salts and synthetic or natural gums, may also be added, to increase the density and viscosity of the aqueous vehicle. It is often most effective to grind and mix the compound at the same time by preparing the aqueous mixture, and homogenizing it in an implement such as a sand mill, ball mill, or piston-type homogenizer.

The compounds may also be applied as granular compositions, which are particularly useful for applications to the soil. Granular compositions usually contain from about 0.5% to about 10% by weight of the compound, dispersed in an inert carrier which consists entirely or in large part of clay or a similar inexpensive substance. Such compositions are usually prepared by dissolving the compound in a suitable solvent, and applying it to a granular carrier which has been pre-formed to the appropriate particle size, in the range of from about 0.5 to 3 mm. Such compositions may also be formulated by making a dough or paste of the

carrier and compound, and crushing and drying to obtain the desired granular particle size.

Dusts containing the compounds are prepared simply by intimately mixing the compound in powdered form with a suitable dusty agricultural carrier, such as kaolin clay, ground volcanic rock and the like. Dusts can suitably contain from about 1% to about 10% of the compound.

It is equally practical, when desirable for any reason, to apply the compound in the form of a solution in an appropriate organic solvent, usually a bland petroleum oil, such as the spray oils, which are widely used in agricultural chemistry.

Insecticides and miticides are generally applied in the form of a dispersion of the active ingredient in a liquid carrier. It is conventional to refer to application rates in terms of the concentration of active ingredient in the carrier. The most widely used carrier is water.

The compounds of formula (1) can also be applied in the form of an aerosol composition. In such compositions the active compound is dissolved or dispersed in an inert carrier, which is a pressure-generating propellant mixture. The aerosol composition is packaged in a container from which the mixture is dispensed through an atomizing valve. Propellant mixtures comprise either low-boiling halocarbons, which may be mixed with organic solvents, or aqueous suspensions pressurized with inert gases or gaseous hydrocarbons.

The actual amount of compound to be applied to loci of insects and mites is not critical and can readily be determined by those skilled in the art in view of the examples above. In general, concentrations of from 10 ppm to 5000 ppm of compound are expected to provide good control. With many of the compounds, concentrations of from 100 to 1500 ppm will suffice. For field crops, such as soybeans and cotton, a suitable application rate for the compounds is about 0.5 to 1.5 lb/A, typically applied in 50 gal/A of spray formulation containing 1200 to 3600 ppm of compound. For citrus crops, a suitable application rate is from about 100

to 1500 gal/A spray formulation, which is a rate of 100 to 1000 ppm.

The locus to which a compound is applied can be any locus inhabited by an insect or arachnid, for example, vegetable crops, fruit and nut trees, grape vines, and ornamental plants. Inasmuch as many mite species are specific to a particular host, the foregoing list of mite species provides exemplification of the wide range of settings in which the present compounds can be used.

Because of the unique ability of mite eggs to resist toxicant action, repeated applications may be desirable to control newly emerged larvae, as is true of other known acaricides.

The following formulations of compounds of the invention are typical of compositions useful in the practice of the present invention.

A. 0.75 Emulsifiable Concentrate

Compound of formula (1)	9.38%
"TOXIMUL D"	2.50%
(nonionic/anionic surfactant blend)	
"TOXIMUL H"	2.50%
(nonionic/anionic surfactant blend)	
"EXXON 200"	85.62%
(naphthalenic solvent)	

B. 1.5 Emulsifiable Concentrate

Compound of formula (1)	18.50%
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	76.50%

C. 1.0 Emulsifiable Concentrate

Compound of formula (1)	12.50%
N-methylpyrrolidone	25.00%
"TOXIMUL D"	2.50%
"TOXIMUL H"	2.50%
"EXXON 200"	57.50%

D. 1.0 Aqueous Suspension

	Compound of formula (1)	12.00%
	"PLURONIC P-103"	1.50%
5	(block copolymer of propylene oxide and ethylene oxide, surfactant)	
	"PROXEL GXL"	.05%
	(biocide/preservative)	
	"AF-100"	.20%
10	(silicon based antifoam agent)	
	"REAX 88B"	1.00%
	(lignosulfonate dispersing agent)	
	propylene glycol	10.00%
	veegum	.75%
15	xanthan	.25%
	water	74.25%

E. 1.0 Aqueous Suspension

	Compound of formula (1)	12.50%
20	"MAKON 10" (10 moles ethyleneoxide nonylphenol surfactant)	1.00%
	"ZEOSYL 200" (silica)	1.00%
	"AF-100"	0.20%
	"AGRIWET FR" (surfactant)	3.00%
25	2% xanthan hydrate	10.00%
	water	72.30%

F. 1.0 Aqueous Suspension

	Compound of formula (1)	12.50%
30	"MAKON 10"	1.50%
	"ZEOSYL 200" (silica)	1.00%
	"AF-100"	0.20%
	"POLYFON H"	0.20%
	(lignosulfonate dispersing agent)	
35	2% xanthan hydrate	10.00%
	water	74.60%



G. Wettable Powder

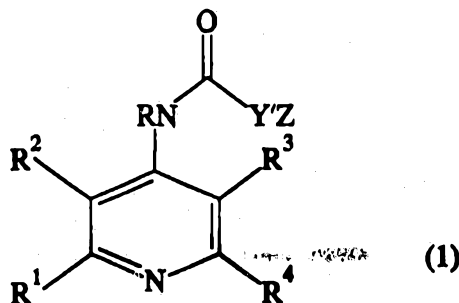
	Compound of formula (1)	25.80%
	"POLYFON H"	3.50%
	"SELLOGEN HR"	5.00%
5	"STEPANOL ME DRY"	1.00%
	gum arabic	0.50%
	"HISIL 233"	2.50%
	Barden clay	61.70%

H. Granules

10	Compound of formula (1)	5.0%
	propylene glycol	5.0%
	Exxon 200	5.0%
	Florex 30/60 granular clay	85.0%

The claims defining the invention are as follows:

1. A compound of the formula (1):



or an N-oxide or a salt thereof; wherein R is H, (C₁-C₄)alkyl, or benzyl; R¹, R², R³, and R⁴ are one of the following:

- 20
- 25
- 30
- 35
- (a) R³ and R⁴ are H, and R¹ and R² are independently halo, (C₁-C₄)alkyl, halo(C₁-C₄)alkyl, (C₃-C₄) branched alkyl, (C₃-C₇)cycloalkyl, (C₁-C₄)alkoxy, or halo(C₁-C₄)alkoxy;
- (b) one of R¹, R², R³ and R⁴ is (C₁-C₄) alkyl, (C₃-C₄) branched alkyl, (C₁-C₄) alkoxy, halo (C₁-C₄) alkyl, halo(C₁-C₄)alkoxy, (C₁-C₄) alkylthio, (C₁-C₄) alkylsulfinyl, (C₁-C₄) alkylsulfonyl, aryl or substituted amino, and the rest are H;
- (c) R¹, R², R³ and R⁴ are independently H or halo; or
- (d) R¹, and R² combine to form a (C₃-C₆) saturated or unsaturated carbocyclic ring that is optionally substituted with one or two groups selected from halo, (C₁-C₄)alkyl, (C₃-C₄) branched alkyl, halo(C₁-C₄)alkyl, (C₃-C₇)cycloalkyl, (C₁-C₄)alkoxy, halo(C₁-C₄)alkoxy or NO₂, and R³ and R⁴ are H; R⁵ is H, (C₁-C₄) alkyl or (C₁-C₄) acyl; R⁶

and R^7 are independently (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, phenyl, or substituted phenyl;

Y' is bond or bivalent hydrocarbon radical one to five carbon atoms long, optionally substituted with (C_1-C_4) alkyl,

Z is

(a) a phenyl group optionally substituted with one or more groups independently selected from:

halo, I, (C_3-C_8) cycloalkyl, (C_3-C_8) cycloalkenyl, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted phenyl, NO_2

$\begin{array}{c} O \\ || \\ -C-R^8 \end{array}$ where R^8 is (C_1-C_7) alkyl, halo (C_1-C_7) alkyl, (C_3-C_7)

branched alkyl, halo (C_3-C_7) branched alkyl, (C_3-C_7) cycloalkyl,

halo (C_3-C_7) cycloalkyl, (C_1-C_7) alkoxy, phenyl, or substituted

phenyl, acetoxy, OH, CN, $SiR^9R^{10}R^{11}$ or $SiR^9R^{10}R^{11}$, where R^9 ,

R^{10} , and R^{11} are independently (C_1-C_4) alkyl, (C_3-C_4) branched

alkyl, phenyl, or substituted phenyl, $NR^{12}R^{13}$, where R^{12} and R^{13}

are independently H, (C_1-C_4) alkyl, or (C_1-C_4) acyl, $S(O)R^{14}$,

or SO_2R^{14} , where R^{14} is (C_1-C_{10}) alkyl, phenyl, or substituted

phenyl; a (C_1-C_{12}) saturated or unsaturated hydrocarbon chain,

straight chain or branched optionally including a hetero atom

selected from O, S, SO, SO_2 , NR^5 , or SiR^6R^7 where R^5 , R^6 and

R^7 are as defined above, and optionally substituted with halo,

halo (C_1-C_4) alkoxy, hydroxy, (C_3-C_8) cycloalkyl or cycloalkenyl,

(C_1-C_4) acyl, phenoxy, substituted phenoxy, phenyl, substituted

phenyl, phenylthio, or substituted phenylthio; (C_1-C_7) alkoxy

optionally substituted with halo, phenyl substituted phenyl,

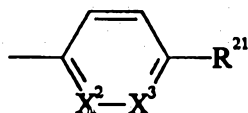
(C_3-C_8) cycloalkyl or cycloalkenyl, phenoxy, or substituted

phenoxy; (C_1-C_7) alkylthio optionally substituted with halo,

phenyl, substituted phenyl, (C_3-C_8) cycloalkyl or cycloalkenyl,

phenoxy or substituted phenoxy;

- (b) a group selected from optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and decahydronaphthyl;
- (c) a group of the formula



one of X^2 and X^3 is N and the other is CH; R^{21} is $-Z-R^{22}$, phenyl, or substituted phenyl; Z is O or S; and R^{22} is (C_1-C_4) alkyl, (C_3-C_7) branched alkyl, halo (C_1-C_4) alkyl, halo (C_3-C_7) branched alkyl, (C_1-C_4) alkoxy substituted (C_1-C_4) alkyl, or naphthyl or phenyl, either of which may optionally be substituted with up to three groups selected from halo, (C_1-C_{10}) alkyl, branched (C_3-C_7) alkyl, halo (C_1-C_7) alkyl, hydroxy (C_1-C_7) alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkoxy, phenoxy, substituted phenoxy, phenyl, substituted phenyl, CN, NO_2 , OH, (C_1-C_4) alkanoyloxy, or benzyloxy.

2. A compound of claim 1 wherein R is H; R^1 , R^2 , R^3 , and R^4 are one of the following:

- (a) R^1 and R^2 are independently halo, (C_1-C_4) alkyl, (C_1-C_4) alkoxy, or halo (C_1-C_4) alkoxy, and R^3 and R^4 are H;
- (b) one of R^1 , R^2 , R^3 , and R^4 is (C_1-C_4) alkyl, (C_3-C_4) branched alkyl, (C_1-C_4) alkoxy, halo (C_1-C_4) alkyl, halo (C_1-C_4) alkoxy, (C_1-C_4) alkylthio, (C_1-C_4) alkylsulfinyl, (C_1-C_4) alkylsulfonyl, aryl, or substituted amino, and the rest are H; or
- (c) R^1 , R^2 , R^3 , and R^4 are independently halo or H;

Y' is bond or bivalent hydrocarbon radical one to five carbon atoms long, optionally substituted with (C_1-C_4) alkyl;

Z is

- (a) a phenyl group optionally substituted with one or more groups independently selected from:

halo, I, (C₃-C₈) cycloalkyl, (C₃-C₈) cycloalkenyl, phenoxy, substituted phenoxy, phenylthio, substituted phenylthio, phenyl, substituted phenyl, NO₂



where R⁸ is (C₁-C₇) alkyl, halo (C₁-C₇) alkyl, (C₃-C₇) branched alkyl, halo (C₃-C₇) branched alkyl, (C₃-C₇) cycloalkyl, halo (C₃-C₇) cycloalkyl, phenyl or substituted phenyl, acetoxy, OH, CN, SiR⁹R¹⁰R¹¹, or OSiR⁹R¹⁰R¹¹, where R⁹, R¹⁰, and R¹¹ are independently (C₁-C₄) alkyl, (C₃-C₄) branched alkyl, phenyl, or substituted phenyl, NR¹²R¹³, where R¹² and R¹³ are independently H, (C₁-C₄) alkyl, or (C₁-C₄) acyl, S(O)R¹⁴, or SO₂R¹⁴, where R¹⁴ is (C₁-C₁₀) alkyl, phenyl, or substituted phenyl; a C₁-C₁₂ saturated or unsaturated hydrocarbon chain, straight chain or branched optionally including a hetero atom selected from O, S, SO, SO₂, NR⁵, or SiR⁶R⁷, where R⁵, R⁶ and R⁷ are as defined above, and optionally substituted with halo, halo (C₁-C₄) alkoxy, hydroxy, (C₃-C₈) cycloalkyl or cycloalkenyl, (C₁-C₄) acyl, phenoxy, substituted phenoxy, phenyl, substituted phenyl, phenylthio, or substituted phenylthio; (C₁-C₇) alkoxy optionally substituted with halo, phenyl, substituted phenyl, (C₃-C₈) cycloalkyl or cycloalkenyl, phenoxy, or substituted phenoxy; or (C₁-C₇) alkylthio optionally substituted with halo, phenyl, substituted phenyl, (C₃-C₈) cycloalkyl or cycloalkenyl, phenoxy or substituted phenoxy;

- (b) a group selected from optionally substituted naphthyl, dihydronaphthyl, tetrahydronaphthyl, and decahydronaphthyl; and optionally substituted pyridyl.

3. A compound of claim 1 wherein R¹ is (C₁-C₄) alkyl and R² is halo or I.

4. A compound of claim 3 wherein R¹ is ethyl and R² is chloro.
5. A compound of claim 1 wherein Y' is -CH₂-.
- 5 6. A compound of claim 1 wherein Z is a substituted phenyl group as defined in paragraph (a) of the definition of Z.
7. The compound of claim 1 which is N-(3-chloro-2-ethyl-4-pyridyl) (4-chlorophenyl)oxy)phenyl)acetamide.
- 10 8. A compound of claim 1 wherein R¹ and R² combine to form a (C₅-C₆) saturated or unsaturated carbocyclic ring that is optionally substituted with one or two groups selected from halo, (C₁-C₄)alkyl, (C₃-C₄) branched alkyl, halo(C₁-C₄)alkyl, (C₃-C₄)cycloalkyl, (C₁-C₄)alkoxy, halo(C₁-C₄)alkoxy, or NO₂.
- 15 9. A method of inhibiting an insect or mite population which comprises applying to the locus of the insect or arachnid an effective insect or mite inactivating amount of a compound of claim 1.
- 20 10. A method of inhibiting a nematode population which comprises applying to the locus of a nematode, a nematode inactivating amount of a compound of claim 1.
- 25 11. A method of inhibiting plant pathogens which comprises applying an effective amount of a compound of claim 1 to a locus of the pathogen.

Dated this 29th day of May 1995.

DOWELANCO

30 By their Patent Attorneys
DAVIES COLLISON CAVE



INTERNATIONAL SEARCH REPORT

PCT/US92/07531

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) : Please See Extra Sheet.

US CL : 544/128,546/159,270,283,284,309,312, 546/14

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)

U.S. : 544/128,546/159,270,283,284,309,312, 546/14

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 practicable, 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.
X	US,A, 5,114,939 (DREIKORN ET AL) 19 MAY 1992 See entire document	1-6 and 8-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*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
A document defining the general state of the art which is not considered to be part of particular relevance	*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
E earlier document published on or after the international filing date	*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
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)	*G* document member of the same patent family
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	

Date of the actual completion of the international search

24 DECEMBER 1992

Date of mailing of the international search report

06 JAN 1993

Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/07531

A. CLASSIFICATION OF SUBJECT MATTER: IPC (5):

A01N 43/40, 43/42; C07F 7/02; C07D 413/12, 401/12, 409/12, 213/68, 213/74, 215/38