PESTICIDAL 1-ARYLPYRAZOLES

CROSS-REFERENCE TO RELATED APPLICATION

This application claims the priority of United States Provisional Patent Application No. 60/033,888, filed December 24, 1996, incorporated by reference herein in its entirety and relied upon.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to novel 1-arylpyrazolecarboxaldehyde oximes, compositions, and derivatives thereof. It relates to their unexpected and useful systemic insecticidal activity. The invention particularly pertains to compositions of said compounds and methods, using said compounds, for the control of arthropod, nematode, helminth or protozoan pests. In particular to the application of said compounds or compositions in agricultural methods of use, particularly as pesticides, for controlling arthropods, especially insects by systemic action. The invention also relates to 1-arylpyrazole hydrazones.

2. Description of the Related Art

The control of insects, nematodes or helminths by means of active material having a 1-arylpyrazole group therein has been described by many patents or patent application such as International Patent Publication No. WO 93/06089 (and the equivalent U.S. Patent No. 5,451,598), WO 94/21606 and WO 87/03781 as well as in European Patent Publication Numbers 0295117, 659745, 679650, 201852 and 412849, German Patent No. DE19511269 and U.S. Patent No. 5,232,940.

Other compounds are disclosed in WO 92/13451, 20 August 1992, to Schering Agrochemicals Ltd., which describes 5-chloro-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(4,5-dicyano-1H-imadazol-2-yl)-3-hydroxyiminomethyl-1H-pyrazole as an intermediate, also with activity against a single species Lucilia sericata, sleep blow fly.

This Schering reference appears to be the only reference describing 1-arylpyrazole-oxime compounds as insecticides.

It is an object of the present invention to provide new pesticidal compounds of the 1-arylpyrazole family together with processes for their preparation.

A second object of the present invention is to provide pesticidal compositions and pesticidal methods of use of the pesticidal pyrazole compounds against arthropods, especially insects, plant nematodes, or helminth or protozoan pests,

particularly in agricultural or horticultural crops, forestry, veterinary medicine or livestock husbandry, or in public health.

A third object of the present invention is to provide very active compounds, with broad spectrum pesticidal activity, as well as compounds with selective special activity, e.g., aphicidal, miticidal, foliar insecticidal, soil insecticidal and nematicidal, systemic, antifeeding or pesticidal activity via seed treatment.

A fourth object of the present invention is to provide compounds with substantially enhanced and more rapid activity, especially against insects and more particularly insects in their larval stages.

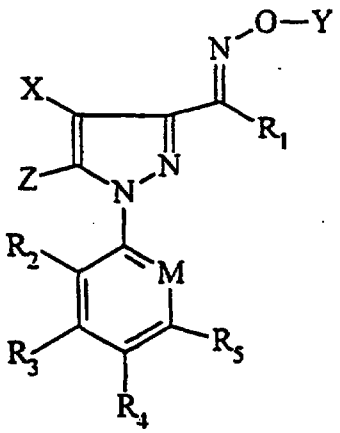
A fifth object of the present invention is to provide compounds with greatly improved (greater and faster) penetration into pest species when topically applied and thus provide enhanced movement of the compounds to the pesticidal site(s) of action within the pest.

Another object of the present invention is to provide compounds with high activity and improved safety to the user and the environment.

These and other objects of the invention shall become readily apparent from the detailed description of the present invention. These objects are met in whole or in part by the instant invention.

SUMMARY OF THE INVENTION

This invention describes novel systemic chemical compositions and methods for treating plants with the compositions having insecticidal or nematocidal systemic activity of the following formula (I):



(I)

wherein:

X is $-S(O)_mR_6$ or R_7,

Y is hydrogen, C-3 to C-6 alkenyl, alkynyl, formyl, alkylcarbonyl, cycloalkylcarbonyl, halocycloalkyl carbonyl, aroyl, arylalkylcarbonyl, alkylsulfonyl, arylsulfonyl, haloalkylcarbonyl, aminoalkylcarbonyl, alkylaminoalkylcarbonyl, dialkylaminoalkylcarbonyl, alkoxyalkylcarbonyl, aryloxyalkylcarbonyl, alkylthioalkylcarbonyl, alkylsulfonylalkylcarbonyl, arylthioalkylcarbonyl, N-alkylcarbamoyl, N-arylcarbamoyl, N-alkylthiocarbamoyl, N-arylthiocarbamoyl, alpha-hydroxyarylalkylcarbonyl, hydroxyalkylcarbonyl, carboxyalkylcarbonyl, alkoxycarbonylalkylcarbonyl, -P(=O)(O-Alkyl)$_2$, -P(=S)(O-alkyl)$_2$, -P(=O)(S-alkyl)$_2$, -P(=S)(S-alkyl)$_2$, trialkylsilyl, alkylcarbonylaminoalkylcarbonyl, alkylcarbonyloxyalkylcarbonyl, aryl, pyridinyl, pyrimidinyl, -C(=O)S-alkyl, -C(=O)S-aryl, -C(=O)S-alkylaryl, alkoxyalkoxycarbonyl, alkylthioalkoxycarbonyl, alkylsulfonylalkoxycarbonyl, arylthioalkoxycarbonyl, alkoxycarbonyl, aryloxycarbonyl and aryloxycarbonylalkylcarbonyl; or alkyl or haloalkyl, optionally substituted by alkoxy, alkoxycarbonyl, carboxy, cyano, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthio, nitro, alkylsulfinyl, alkylsulfonyl, alkylcarbonyl, amino, alkylamino, dialkylamino, hydroxy, alkylcarbonylamino or alkylcarbonyloxy;

Z is hydrogen, halogen, -C(O)R_7-,-S(O)$_n$$R_8$, -C(O)O$R_9$, alkyl, haloalkyl, -O$R_9$, -N=C($R_{10}$)($R_{11}$), alkenyl, hydrazino, alkylthiocarbonyl, 1H-pyrrol-1-yl or 1H-pyrazol-1-yl,

-CHO, -CH=NOH, amino, R_{12}NH-or $R_{13}R_{14}$N-;

R_1 is hydrogen, alkyl or-N$R_{15}R_{16}$;

R_2 is hydrogen or halogen;

R_3 and R_5 are hydrogen, halogen or alkyl;

R_4 is halogen, haloalkyl, haloalkoxy, R_{17}S(O)$_p$-or SF_5;

R_6 is alkyl or haloalkyl, alkenyl or haloalkenyl, alkynyl or haloalkynyl or cycloalkyl having 3 to 5 carbon atoms;

R_7 is alkyl or haloalkyl;

R_8 is R_7 or phenyl;

R_9 and R_{10} are hydrogen, alkyl or haloalkyl;

R_{11} is alkyl, haloalkyl, alkoxy, or a phenyl group which is optionally substituted by one or more groups selected from hydroxy, halogen, alkoxy, cyano, R_7 or -S(O)$_q$$R_7$;

R_{12}, R_{13} and R_{14}, which are identical or different, are R_7S(O)$_r$-, formyl, alkynyl, alkoxycarbonyl, alkylthiocarbonyl or aroyl; or alkyl, C-3 to C-6 alkenyl or

-C(O)alkyl wherein the alkyl and alkenyl portions are optionally substituted by one or more R_{18}; or R_{13} and R_{14} are joined so as together form a divalent radical having 4 to 6 atoms in the chain, this divalent radical being alkylene, alkyleneoxyalkylene or alkyleneaminoalkylene, preferably to form a morpholine, pyrrolidine, piperidine or piperazine ring;

R_{15} and R_{16} are independently hydrogen or alkyl;

R_{17} represents haloalkyl;

R_{18} is cyano, nitro, alkoxy, haloalkoxy, -C(O)R_7, $R_8S(O)_s$-, -C(O)OR_9, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, halogen, hydroxy, aminosulfonyl, alkylaminosulfonyl or dialkylaminosulfonyl;

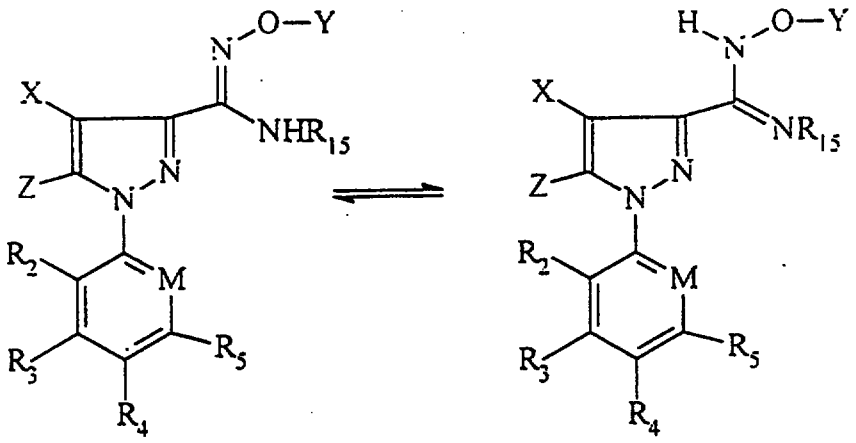
m, n, p, q, r and s represent zero, one or two;

M is C-halo, C-CH_3, C-CH_2F, C-CH_2Cl, C-NO_2, or N;

geometric isomers, tautomeric forms and pesticidally active salts thereof.

By the term "pesticidally acceptable salts" is meant salts the anions and cations of which are known and accepted in the art for the formation of pesticidally acceptable salts. Preferably such salts are water soluble. Suitable acid addition salts formed from compounds of formula (I) containing an amine group, include salts with inorganic acids for example hydrochlorides, phosphates, sulfates and nitrates, and salts with organic acids for example acetates. Suitable base addition salts formed from compounds of formula (I) containing a carboxylic acid group, include alkali metal (for example sodium or potassium) salts, ammonium salts and organic amine (for example diethanolamine or morpholine) salts.

Compounds of formula (I) wherein R_1 represents -$NR_{15}R_{16}$ in which R_{16} represents hydrogen and R_{15} represents hydrogen or alkyl may exist in tautomeric forms as shown in formulae (Ia) and (Ib). Such tautomerism is well known as is described in S.Patai (The Chemistry of Functional Groups: Amidines and Imidates, Vol 2, 1991, pages 276-277). It will be understood that all such tautomeric forms are embraced by the present invention.



(Ia) (Ib)

Unless otherwise specified alkyl, alkoxy and alkylthio groups have from one to six (preferably one to four) carbon atoms, alkenyl groups have from two to six (preferably two to four) carbon atoms and alkynyl groups have from three to six (preferably three or four) carbon atoms. Cycloalkyl groups have from 3 to 8 carbon atoms, preferably 5 to 7 carbon atoms. By the term "aryl" is meant mono or polycyclic aromatic moieties. preferably including phenyl, pyridyl, pyrimidinyl, furyl and naphthyl groups. It shall be understood that the rings formed by the divalent alkylene radicals which include the nitrogen atoms to which they are attached are generally 5, 6 and 7 membered rings. In the instant invention, some words are used in a specific sense:
The term "aminocarbonyl" means a carbamoyl radical. that is, a radical of the formula $-C(O)NH_2$. Similarly, the term "alkylaminocarbonyl" means an alkylcarbamoyl radical. that is, a radical of the formula -C(O)-NH-alkyl; and the term "dialkylaminocarbonyl" means a dialkylcarbamoyl radical, that is, a radical of the formula $-C(O)-N(alkyl)_2$ in which the alkyl moieties can be the same or different. The term "aminosulfonyl" means a sulfamoyl radical, that is, $-SO_2NH_2$. Similarly, the term "alkylaminosulfonyl" means an alkylsulfamoyl radical, that is, a radical of the formula $-SO_2NH$-alkyl; while the term "dialkylaminosulfonyl" means a dialkylsulfamoyl radical, which has the formula $-SO_2N(alkyl)_2$ wherein the alkyl moieties can be the same or different.

The term "halo" before the name of a radical means that this radical is partially or completely halogenated, that is to say, substituted by F, Cl, Br, or I, in any combination, preferably by F or Cl. The term "halogen" means F, Cl, Br or I. When the name of any substituent is repeated, it keeps the same meaning unless otherwise specified. The term "aroyl" designates a carbonyl aromatic radical, that is, aryl-C(O)-, which is preferably a benzoyl optionally substituted by one or more alkyl, alkoxy or halogen groups.

Compounds in which Z is amino, $R_{12}NH$-or $R_{13}R_{14}N$-are preferred.

Compounds in which X is $-S(O)_mR_6$ are preferred.

R_1 is preferably amino or hydrogen;

R_6 is preferably alkyl; especially preferred are methyl and ethyl;

R_3 and R_5 are preferably hydrogen;

R_4 is preferably haloalkyl, haloalkoxy or SF_5; especially preferred is trifluoromethyl.

M is preferably C-halo, or N.

Y is preferably hydrogen or alkoxycarbonyl.

Preferred phenyl groups or pyridyl groups comprising the R_2 to R_5 and M radicals in formula (I) are: 2,6-dichloro-4-trifluoromethylphenyl; 2,6-dichloro-4-trifluoromethoxyphenyl; 2-bromo-6-chloro-4-trifluoromethylphenyl; 2-bromo-6-chloro-4-trifluoromethoxyphenyl; 2,6-difluoro-4-trifluoromethylphenyl; 2-chloro-4-trifluoromethylphenyl; 3-chloro-5-trifluoromethyl-2-pyridinyl; 3-chloro-5-trifluoromethoxy-2-pyridinyl; 2-bromo-6-fluoro-4-difluoromethylphenyl; 2-chloro-6-fluoro-4-trifluoromethylphenyl; 2,6-dibromo-4-trifluoromethylphenyl; 2,6-dibromo-4-trifluoromethoxyphenyl; and 2.6-dichloro-4-pentafluorothiophenyl.

A preferred class of compounds of formula (I) are those wherein:

X is $-S(O)_mR_6$;

Y is hydrogen; alkyl having 1 to 4 carbon atoms (including linear, branched and cyclic) optionally substituted by aminocarbonyl, alkylsulfonyl, alkoxy, alkoxycarbonyl, alkylcarbonyl, cyano or nitro; C-3 to C-4 alkenyl; C-3 to C-5 alkynyl; alkylcarbonyl; optionally substituted aroyl; arylalkylcarbonyl; alkylsulfonyl; alkoxycarbonylalkylcarbonyl; haloalkylcarbonyl; N-alkylcarbamoyl; alkoxycarbonyl; aryloxycarbonyl; alkoxyalkylcarbonyl; alpha-hydroxyarylalkylcarbonyl; hydroxyalkylcarbonyl; aminoalkylcarbonyl; -C(=O)S-alkyl and trialkylsilyl;

Z is amino, $R_{12}NH$-, $R_{13}R_{14}N$-, halogen or methyl;

R_1 is hydrogen, methyl, amino or methylamino;

R_2 is F, Cl, Br or H;

R_3 and R_5 are hydrogen;

R_4 is CF_3, CF_3O, CHF_2, $CF_3S(O)_p$, CF_2Cl, $CFCl_2$, CF_2ClO, $CFCl_2O$, Cl, Br, or F;

R_6 is methyl or ethyl optionally substituted by F, Cl or Br;

M is CCl, CF, CBr, or N;

R_{12}, R_{13} and R_{14} are $CF_3S(O)_r$-, alkynyl or alkoxycarbonyl;

or alkyl, C-3 to C-6 alkenyl or -C(O)alkyl wherein the alkyl and alkenyl portions are optionally substituted by one or more R_{18}; and

R_{18} is cyano, nitro, alkoxy, haloalkoxy, $-C(O)R_7$, $R_8S(O)_5$-, $-C(O)OR_9$, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, halogen, hydroxy, aminosulfonyl, alkylaminosulfonyl or dialkylaminosulfonyl.

A further preferred class of compounds of formula (I) are those wherein:

Y represents hydrogen; a C_1 to C_3 alkyl group optionally substituted by cyano, carbamoyl, carboxy, alkoxycarbonyl, alkylthio, alkylsulfinyl or alkylsulfonyl; trialkylsilyl; acetyl; propionyl substituted by alkoxycarbonyl; benzoyl optionally substituted by alkyl; alkoxycarbonyl; or N-alkylcarbamoyl;

Z represents amino, $R_{12}NH$-, $R_{13}R_{14}N$-, -CHO, -CH=NOH, halogen or methyl;

R_1 represents hydrogen, methyl, amino or methylamino;

R_2 represents chlorine, bromine or hydrogen;

R_3 and R_5 represent hydrogen;

R_4 represents CF_3 or OCF_3;

R_6 represents optionally halogenated methyl or ethyl;

R_7 represents CF_3;

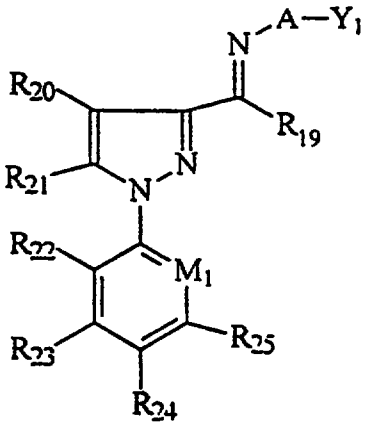
R_{12}, R_{13} and R_{14} represent alkynyl; or methyl or ethyl optionally substituted by $R_8S(O)_5$-, cyano or aminocarbonyl;

R_8 represents alkyl or phenyl; and

M represents C-Cl, C-Br or N.

According to another aspect of the invention, Y may be a sugar moiety, preferably Y is a ring containing 4, 5, or 6 carbon atoms and which is interrupted by one oxygen atom, the carbon atoms substituted by one or more hydroxy groups, one or more CH_2OH groups or one or more OC(O)alkyl groups

The instant invention also provides arylpyrazoles of the following formula (I bis):



(I bis)

wherein:

A is $-NR_{26}-$;

Y_1 is hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aryl, $-S(O)_aR_{28}$, $-P(O)R_{29}R_{30}$, $-P(S)R_{29}R_{30}$, $-Si(R_{31})(R_{32})(R_{33})$, $-C(O)R_{27}$, $-C(S)R_{27}$, cyano or nitro;

R_{19} is hydrogen, alkyl, haloalkyl, or $-NR_{34}R_{35}$;

R_{20} is $-S(O)_bR_{36}$ or R_{37};

R_{21} is hydrogen, halogen, $-C(O)R_{38}$, $-S(O)_cR_{39}$, alkyl, haloalkyl, $-OR_{40}$, $-N=C(R_{41})(R_{42})$, alkenyl, $-NR_{43}R_{44}$, 1H-pyrrol-1-yl, 1H-pyrazol-1-yl, or $-CH=NOH$;

R_{22}, R_{23} and R_{25} are independently selected from hydrogen, halogen or alkyl;

R_{24} is halogen, haloalkyl, haloalkoxy, $-S(O)_dR_{45}$ or SF_5;

R_{26} is hydrogen or substituted or unsubstituted alkyl;

R_{27} is hydrogen, substituted or unsubstituted alkyl of C_1 to C_{20}, substituted or unsubstituted aryl, $-OR_{46}$, $-NR_{47}R_{48}$, or $-SR_{49}$;

R_{28} is substituted or unsubstituted alkyl or substituted or unsubstituted aryl;

R_{29} and R_{30} are independently selected from alkoxy and thioalkoxy;

R_{31}, R_{32} and R_{33} are independently selected from alkyl, haloalkyl and aryl;

R_{34} and R_{35} are independently selected from hydrogen or substituted or unsubstituted alkyl;

R_{36} is alkyl, alkenyl, alkynyl, or C_3-C_6 cycloalkyl each of which is optionally substituted by one or more halogens;

R_{37} is alkyl or haloalkyl;

R_{38} is hydrogen, alkyl, haloalkyl, alkoxy or thioalkoxy;

R_{39} is alkyl haloalkyl or aryl;

R_{40} and R_{41} are independently selected from hydrogen, alkyl and haloalkyl;

R_{42} is alkyl, haloalkyl, alkoxy or phenyl each of which is optionally substituted by one or more groups selected from hydroxy, halogen, alkoxy, -CN, alkyl, $-S(O)_e$alkyl;

R_{43} and R_{44} are independently selected from hydrogen, NH_2, $-S(O)_fR_{50}$, $-C(O)R_{51}$, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl and alkynyl; or R_{43} and R_{44} may form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_{45} is haloalkyl;

R_{46} and R_{49} are independently selected from substituted or unsubstituted alkyl and substituted or unsubstituted aryl;

R_{47} and R_{48} are independently selected from hydrogen, substituted or unsubstituted alkyl and substituted or unsubstituted aryl; or R_{47} and R_{48} may form together a divalent alkylene radical which may be interrupted by one or more heteroatoms preferably selected from oxygen, nitrogen and sulfur;

R_{50} is substituted or unsubstituted alkyl;

R_{51} is hydrogen, alkyl, haloalkyl, aryl, alkenyl, $-OR_{52}$, $-SR_{53}$, or $-NR_{54}R_{55}$;

R_{52} and R_{53} are independently selected from alkyl and haloalkyl;

R_{54} and R_{55} are independently selected from hydrogen, alkyl, haloalkyl and aryl;

a, b, c, d, e and f independently represent zero, one or two;

M_1 is C-halo, $C\text{-}CH_3$, $C\text{-}CH_2F$, $C\text{-}CH_2Cl$, $C\text{-}NO_2$, or N;

or a pesticidally acceptable salt thereof.

A preferred group of compounds of formula (I bis) are those with one or more of the following features wherein:

A is $-NR_{26}-$;

Y_1 is hydrogen, alkyl, or $-C(O)R_{27}$;

R_{19} is hydrogen or NH_2;

R_{20} is $-S(O)_bR_{36}$;

R_{21} is $-NR_{43}R_{44}$;

R_{22} is halogen;

R_{23} and R_{25} are hydrogen;

R_{24} is haloalkyl;

R_{27} is alkyl or O-alkyl; or

M is C-halo.

Another preferred group of compounds of formula (I bis) are those wherein:

A is $-NR_{26}-$;

Y_1 is hydrogen, alkyl, or $-C(O)R_{27}$;

R_{19} is hydrogen or NH_2;

R_{20} is $-S(O)_bR_{36}$;

R_{21} is $-NR_{43}R_{44}$;

R_{22} is halogen;

R_{23} and R_{25} are hydrogen;

R_{24} is haloalkyl;

R_{27} is alkyl or O-alkyl; and

M is C-halo.

In the compounds of formula (I bis), preferably by the term "substituted" is meant by one or more of the following substituents: halogen, hydroxy, alkylthio, cyano, carboxy, -C(O)alkyl, -C(O)Oalkyl, $-C(O)NH_2$, -C(O)NHalkyl, $-C(O)N(alkyl)_2$, aryl, nitro, azido, amino,alkylamino, dialkylamino, alkylsulfenyl, alkylsulfinyl, alkylsulfonyl, aryloxy, arylthio, alkylcarbonylamino, alkylcarbonyloxy, or aryloxycarbonyl.

Among the compounds of general formula (I) or (I bis) are the following particularly preferred compounds, which provide particularly useful control of insect species by systemic action. The compound numbers are for reference purposes only.

1) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

2) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-ethylamino-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

3) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methylamino-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

4) 5-Amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

5) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

6) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylthio-1H-pyrazole-3-carboxaldehyde oxime

7) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-difluoromethylthio-1H-pyrazole-3-carboxaldehyde oxime

8) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carboxaldehyde oxime

9) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylthio-1H-pyrazole-3-carboxaldehyde O-(methyl)oxime

10) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(acetyl)oxime

11) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(2-methylbenzoyl)oxime

12) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(methoxycarbonyl)oxime

13) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-[2-(ethoxycarbonyl)propionyl]oxime

14) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carboxaldehyde O-(acetyl)oxime

15) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carboxaldehyde O-(methoxycarbonyl)oxime

16) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfonyl-1H-pyrazole-3-carboxaldehyde oxime

17) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(methyl)oxime

18) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(N-methylcarbamoyl)oxime

19) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(carboxymethyl)oxime

20) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

21) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(tert-butyldimethylsilyl)oxime

22) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-formyl-N-hydroxy-4-trifluoromethylthio-1H-pyrazole-3-carboximidamide

23) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-5-hydroxyiminomethyl-4-trifluoromethylthio-1H-pyrazole-3-carboximidamide

24) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(isopropyl)oxime

25) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(ethoxycarbonylmethyl)oxime

26) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(aminocarbonylmethyl)oxime

27) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-[2-(ethylsulfonyl)ethyl]oxime

28) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(2-cyanoethyl)oxime

29) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylthio-1H-pyrazole-3-carboxaldehyde oxime

30) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

31) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylsulfonyl-1H-pyrazole-3-carboxaldehyde oxime

32) 5-Amino-1-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

33) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylthio-5-methyl-1H-pyrazole-3-carboxaldehyde oxime

34) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-5-methyl-1H-pyrazole-3-carboxaldehyde oxime

35) 1-[2-Chloro-4-(trifluoromethyl)phenyl]-5-[2-ethylsulfonyl(ethylamino]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

36) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-dimethylamino-4-methylthio-1H-pyrazole-3-carboxaldehyde oxime

37) 5-Amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-4-ethylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime

38) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethyl-1H-pyrazole-3-carboxaldehyde oxime

39) 3-Acetyl-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl--1H-pyrazole oxime

40) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-trifluoromethylsulfinyl-1H-pyrazole-3-carboximidamide

41) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-4-trifluoromethylsulfinyl-1H-pyrazole-3-carboximidamide

42) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-ethylsulfinyl-1H-pyrazole-3-carboximidamide

43) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-ethylthio-1H-pyrazole-3-carboximidamide

44) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

45) 5-Amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

46) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylsulfonyl-1H-pyrazole-3-carboximidamide

47) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylthio-1H-pyrazole-3-carboximidamide

48) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-ethylsulfonyl-1H-pyrazole-3-carboximidamide

49) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

50) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-N'-methyl-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

51) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-

(2-fluoroethylsulfinyl)-1H-pyrazole-3-carboximidamide

52) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-(2-fluoroethylsulfonyl)-1H-pyrazole-3-carboximidamide

53) 5-Amino-1-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]-4-ethylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide

54) 5-Amino-1-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide

55) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-5-methylamino-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

56) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-ethylamino-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

57) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-[2-(ethylsulfonyl)ethylamino]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

58) 5-[2-(Cyano)ethylamino]-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

59) 5-(Aminocarbonylmethylamino)-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide

60) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[2-(phenylsulfonyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide

61) 5-Amino-1-[2,6-dibromo-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide

62) 1-[2-Bromo-6-chloro-4-(trifluoromethyl)phenyl]-5-ethylamino-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide

63) 5-Amino-1-[2-bromo-6-chloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide

64) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-5-[2-(methylsulfinyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide

65) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[2-(methylsulfinyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide

66) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-5-[2-(ethylsulfinyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide

67) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[(prop-2-ynyl)amino]- N-hydroxy-1H-pyrazole-3-carboximidamide

68) 5-Amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide.

Other compounds of formula (I) or (I bis) that are provided by the instant invention include:

69) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-amino-1H-pyrazole-3-carboximidamide;

70) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(isopropylcarbonyl)amino-1H-pyrazole-3-carboximidamide;

71) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(n-heptylcarbonyl)amino-1H-pyrazole-3-carboximidamide;

72) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(ethoxycarbonyl)amino-1H-pyrazole-3-carboximidamide;

73) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylsulfinyl-N-amino-1H-pyrazole carboximidamide;

74) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-N-amino-1H-pyrazole carboximidamide;

75) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylsulfinyl-N-acetylamino-1H-pyrazole carboximidamide;

76) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1-methylethenylcarbonylamino)-1H-pyrazole carboximidamide;

77) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tert-butylcarbonylamino)-1H-pyrazole carboximidamide;

78) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(2-methylethenylcarbonylamino)-1H-pyrazole carboximidamide;

79) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(ethylcarbonylamino)-1H-pyrazole carboximidamide;

80) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(propylcarbonylamino)-1H-pyrazole carboximidamide;

81) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1-ethylpropylcarbonylamino)-1H-pyrazole carboximidamide;

82) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(butylcarbonylamino)-1H-pyrazole carboximidamide;

83) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(pentylcarbonylamino)-1H-pyrazole carboximidamide;

84) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(hexylcarbonylamino)-1H-pyrazole carboximidamide;

85) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-N-acetylamino-1H-pyrazole carboximidamide;

86) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-chloroacetylamino-1H-pyrazole carboximidamide;

87) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tridecylcarbonylamino)-1H-pyrazole carboximidamide;

88) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(n-propoxycarbonylamino)-1H-pyrazole carboximidamide;

89) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1,1-dimethylpropyloxycarbonylamino)-1H-pyrazole carboximidamide;

90) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tertbutyloxycarbonylamino)-1H-pyrazole carboximidamide;

91) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(acetyloxy) -1H-pyrazole carboximidamide;

92) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-N-(acetyloxy) -1H-pyrazole carboximidamide;

93) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(ethylcarbonyloxy) -1H-pyrazole carboximidamide;

94) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(propylcarbonyloxy) -1H-pyrazole carboximidamide;

95) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(2-methylethenylcarbonyloxy) -1H-pyrazole carboximidamide;

96) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(benzoyloxy) -1H-pyrazole carboximidamide;

97) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methylamino-4-methylsulfinyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

98) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfonyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

99) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(heptylcarbonyloxy) -1H-pyrazole carboximidamide;

100) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfonyl-N-(heptylcarbonyloxy) -1H-pyrazole carboximidamide;

101) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfenyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

102) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfenyl-N-(heptylcarbonyloxy) -1H-pyrazole carboximidamide;

103) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylsulfinyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

104) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-formylamino-4-ethylsulfenyl-N-(acetyloxy)-1H-pyrazole carboximidamide:

105) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(hexylcarbonyloxy) -1H-pyrazole carboximidamide;

106) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(pentylcarbonyloxy) -1H-pyrazole carboximidamide;

107) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(butylcarbonyloxy) -1H-pyrazole carboximidamide;

108) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfenyl-N-(cyclopentylcarbonyloxy) -1H-pyrazole carboximidamide;

109) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(cyclopentylcarbonyloxy) -1H-pyrazole carboximidamide;

110) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tert-butylcarbonyloxy) -1H-pyrazole carboximidamide;

111) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(iso-propylcarbonyloxy) -1H-pyrazole carboximidamide;

112) 1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-formylamino-4-ethylsulfinyl-N-(acetyloxy)-1H-pyrazole carboximidamide:

113) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(chloroacetyloxy)-1H-pyrazole carboximidamide;

114) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(bromoacetyloxy)-1H-pyrazole carboximidamide;

115) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1-ethylpropylcarbonyloxy)-1H-pyrazole carboximidamide;

116) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-[(3-acetyloxy)phenylcarbonyloxy]-1H-pyrazole carboximidamide;

117) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-trifluoro methylsulfonyl-1H-pyrazole-3-carboximidamide;

118) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-trifluoro methylsulfenyl-1H-pyrazole-3-carboximidamide;

119) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-(methoxycarbonylamino)-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde hydrazone;

120) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-(methylsulfonylamino)-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde hydrazone;

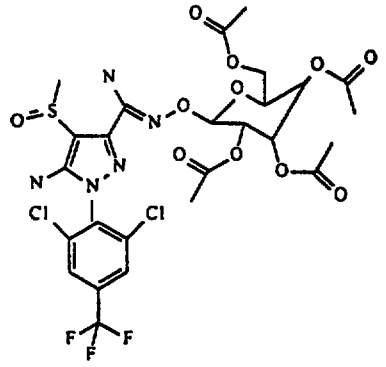
121) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-amino-4-ethylsulfinyl-1H-pyrazole-3-carboxaldehyde hydrazone:

122) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-amino-4-trifluoromethylsulfenyl-1H-pyrazole-3-carboxaldehyde hydrazone:

123) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-amino-4-methylsulfenyl-1H-pyrazole-3-carboximidamide;

124) 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-(furylcarbonylamino)-4-methylsulfinyl-1H-pyrazole-3-carboximidamide; or

125)



DETAILED DESCRIPTION OF THE INVENTION

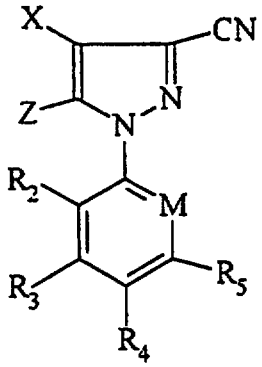
METHODS OR PROCESSES OF SYNTHESIS

The compounds of formula (I) can be prepared according to the manufacturing processes described in International Patent Publications Nos. WO 94/21606 and WO 93/06089 or International Patent Publication No. WO 87/03781 as well as in European Patent Publication No. 0295117 and Hatton et al U.S. Patent No. 5,232,940. Those skilled in the art will choose the proper initial reactant in these known methods and adapt these known methods to the said reactant so as to obtain the corresponding desired products. It is understood that in the description of the following processes the sequences for the introduction of the various groups on the pyrazole ring may be performed in a different order and that suitable protecting groups may be required as will be apparent to those skilled in the art.

In the following description of processes when symbols appearing in formulae are not specifically defined, it is to be understood that they are "as defined above" in accordance with the first definition of each symbol in the specification.

According to a further feature of the present invention compounds of general formula (I) wherein R_2, R_3, R_4, R_5, M, X, Y and Z are as defined above and R_1

represents amino (namely compounds of formula (Ia) or (Ib) in which R_{15} represents hydrogen), may be prepared by the reaction of a compound of formula (II):



(II)

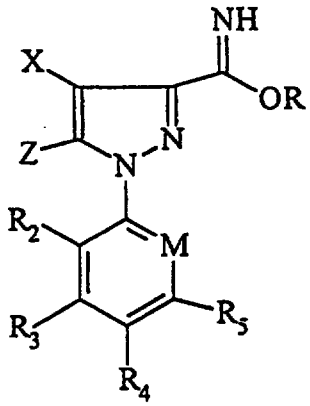
with a compound of formula (III):

$$NH_2OY$$

(III)

in which Y is defined above. The reaction is generally performed using an acid salt of compound (III) for example the hydrochloride salt and in the presence of a base for example pyridine or an alkali metal carbonate (such as sodium carbonate) or an alkali metal acetate (such as sodium acetate) or ammonium acetate in a solvent such as methanol and/or water at a temperature from 0°C to 100°C.

According to a further feature of the present invention compounds of general formula (I) wherein R_2, R_3, R_4, R_5, M, X, Y and Z are as defined above and R_1 represents amino may be prepared by the reaction of a compound of formula (IV):



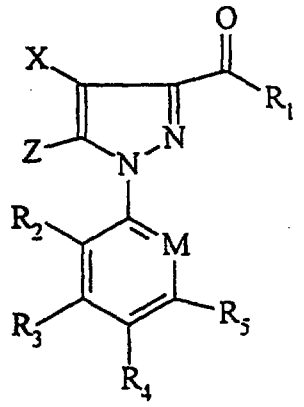
(IV)

wherein R represents alkyl, with a compound of formula (III) in which R is alkyl and Y is defined above. The reaction is generally performed using an using an acid salt of compound (III) for example the hydrochloride salt and optionally in the presence of a base for example pyridine or an alkali metal carbonate (such as sodium carbonate) or

an alkali metal acetate (such as sodium acetate) or ammonium acetate in a solvent such as methanol and/or water at a temperature from 0°C to 100°C.

According to a further feature of the present invention compounds of general formula (I) wherein R_2, R_3, R_4, R_5, M, X, Y and Z are as defined above and R_1 represents alkylamino or dialkylamino may be prepared by the reaction of the corresponding compound of formula (I) wherein R_1 represents amino with an alkylating agent preferably of formula R-hal where R represents alkyl and hal is chloro, bromo or iodo. The reaction is usually carried out in the presence of a strong base such as potassium t-butoxide or sodium hydride in a solvent such as tetrahydrofuran at a temperature from 0°C to 100°C.

According to a further feature of the present invention compounds of general formula (I) wherein R_2, R_3, R_4, R_5, M, X, Y and Z are as defined above and R_1 represents hydrogen or alkyl may be prepared by the reaction of a compound of formula (V):



(V)

in which R_1 represents hydrogen or alkyl with a compound of formula (III) in which Y is defined above and using the same conditions as employed in the reaction of compounds of formula (II) with compounds of formula (III) above.

According to a further feature of the present invention compounds of general formula (I) wherein R_2, R_3, R_4, R_5, M, X and Z are as defined above, R_1 represents hydrogen or alkyl, and Y is defined above with the exclusion of hydrogen, formyl, aryl, pyridinyl and pyrimidinyl (the exclusions being for chemical reasons only), may be prepared by reaction of the corresponding compound of formula (I) wherein Y represents hydrogen with an appropriate alkylating or acylating reagent or Michael acceptor generally in the presence of a base for example triethylamine in an inert solvent such as dichloroethane at a temperature of from 0°C to 100°C.

According to a further feature of the present invention compounds of general formula (I) wherein Z represents $R_{12}NH$- or $R_{13}R_{14}N$- in which R_{12}, R_{13} and/or

R_{14} represent -C(O)alkyl optionally substituted by one or more R_{18} may be prepared by the acylation of the corresponding compound wherein Z represents amino. according to methods described in one or more of International Publications No. WO 94/21606. WO 93/06089 and WO 87/03781. European Patent Publication No. 0295117 and Hatton et al U.S. Patent No. 5,232,940.

For the synthesis of 5-alkylamino and dialkylamino compounds wherein Z represents $R_{12}NH$-or $R_{13}R_{14}N$-in which R_{12}, R_{13} and R_{14} represent alkyl or C-3 to C-6 alkenyl optionally substituted by R_{18}, including the cyclic amino compounds (i.e., the compounds in which R_{13} and R_{14} are joined together) of formula (I), three basic methods are appropriate. The first method includes direct alkylation of precursor compounds of formula (I) in which Z represents amino with alkylating agents. The second method involves a two-step sequence, with formation of the imino ethers. followed by a reduction. The third method of preparation is through a conjugate addition, e.g., a Michael-type addition.

The compounds of formula (I) wherein Z represents $R_{12}NH$-or $R_{13}R_{14}N$ R_{13} in which R_{12}, R_{13} and/or R_{14} are $R_7S(O)_r$, formyl, alkynyl. alkoxycarbonyl, alkylthiocarbonyl or aroyl, and R_7 and r are defined above can be prepared by methods described in one or more of International Publications No. WO 94/21606, WO 93/06089 and WO 87/03781, European Patent Publication No. 0295117 and Hatton et al U.S. Patent No. 5,232,940.

The compounds of formula (I) in which Z represents hydrogen, halogen, -$S(O)_nR_8$, -$C(O)R_7$, -$C(O)OR_9$, alkyl, haloalkyl, -$N=C(R_{10})(R_{11})$, alkylthiocarbonyl and amino. $R_{12}NH$-or $R_{13}R_{14}N$- may be prepared by methods described in one or more of International Publications Numbers WO 94/21606. WO 93/06089 and WO 87/03781, European Patent Publication Numbers EP 0295117, EP 511845, EP 403309 and EP 403300, and Hatton et al U.S.Patent No. 5,232,940, and German Patent Publication No. DE 19511269.

According to a further feature of the present invention compounds of general formula (I) wherein Z represents OR_9 may be prepared by methods described in US Patent Numbers 5,047,550 and 4,918,085.

According to a further feature of the present invention compounds of formula (I) in which the substituent Z is hydrazino. 1H-pyrrol-1-yl or 1H-pyrazol-1-yl may be prepared according to the procedures described in EP 0352944.

The synthesis of higher oxidation states of the compounds of formula (I), i.e., compounds in which m is 1 or 2, can be achieved by oxidation of the corresponding compounds in which m is 0 or 1.

Intermediates of formula (II) may be prepared by known methods (see for example the above listed references).

Certain compounds of formula (II) are novel and as such constitute a further feature of the invention.

Intermediates of formula (IV) wherein R represents alkyl may be prepared by the reaction of compounds of formula (II) with an alcohol of formula ROH where R is alkyl. The alcohol is usually employed in excess as the solvent but a co-solvent such as tetrahydrofuran may be present. The reaction is generally carried out in the presence of a base such as sodium alkoxide at a temperature of from 0°C to 100°C.

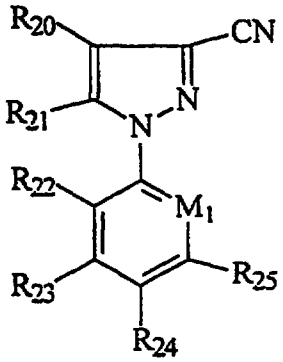
Intermediates of formula (V) wherein R_1 represents hydrogen or alkyl may be prepared by known methods for example as described in WO 8703781 and EP 295117. For example where R_1 represents hydrogen by the reaction of the corresponding compound of formula (II) with diisobutylaluminium hydride, and where R_1 represents alkyl by the reaction of the corresponding compound of formula (II) with an organometallic reagent of formula R_1Q in which Q represents for example Mg-Cl or lithium in an inert solvent such as tetrahydrofuran.

Compounds of formula (IV) are novel and as such constitute a further feature of the invention.

Certain compounds of formula (V) are novel and as such constitute a further feature of the invention.

Intermediates of formula (III) are known or may be prepared by known methods.

According to a further feature of the present invention compounds of general formula (I bis) in which R_{19} is amino may be prepared by the reaction of a compound of formula (II bis):



(II bis)

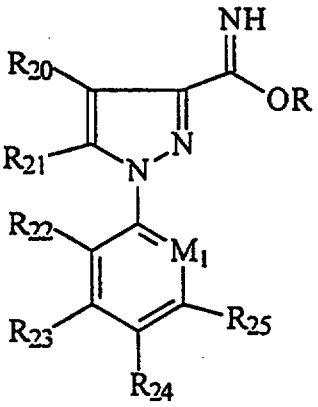
with a compound of formula (III bis):

$H_2NNR_{26}Y_1$

(III bis)

in which Y and A are defined above. The reaction is generally performed using an acid salt of A compound of formula (III bis) for example the hydrochloride salt and in the presence of a base for example pyridine or an alkali metal carbonate (such as sodium carbonate) or an alkali metal acetate (such as sodium acetate) or ammonium acetate in a solvent such as methanol and/or water at a temperature from 0°C to 100°C.

According to a further feature of the present invention compounds of general formula (I bis) wherein R_{19} is amino may be prepared by the reaction of a compound of formula (IV bis):

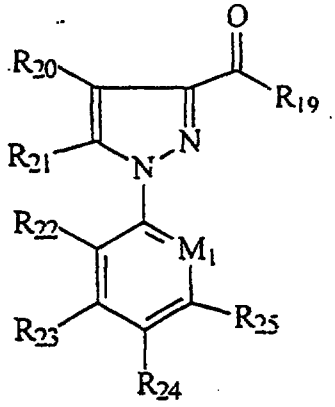


(IV bis)

wherein R represents alkyl. with a compound of formula (III bis). The reaction is generally performed using an using an acid salt of a compound of formula (III bis). for example the hydrochloride salt, and optionally in the presence of a base (for example pyridine or an alkali metal carbonate such as sodium carbonate) or an alkali metal acetate (such as sodium acetate or ammonium acetate) in a solvent such as methanol and/or water and generally at a temperature from 0°C to 100°C.

According to a further feature of the present invention compounds of general formula (I bis) wherein R_{19} represents $NR_{34}R_{35}$ and wherein one or both or of R_{34} and R_{35} are substituted or unsubstituted alkyl may be prepared by the reaction of the corresponding compound of formula (I) wherein R_{19} represents amino with an alkylating agent formula R-hal where R represents alkyl and hal is chloro, bromo or iodo, preferably iodo. The reaction is usually carried out in the presence of a strong base such as potassium t-butoxide or sodium hydride in a solvent such as tetrahydrofuran at a temperature from 0°C to 100°C.

According to a further feature of the present invention compounds of general formula (I bis) with the above definitions wherein R_{19} represents hydrogen or alkyl may be prepared by the reaction of a compound of formula (V bis):



(V bis)

in which R_{19} represents hydrogen or alkyl with a compound of formula (III bis) defined above and using the same conditions as employed in the reaction of compounds of formula (II bis) with compounds of formula (III bis) above.

According to a further feature of the invention, compounds of formula (I bis) wherein Y is $-S(O)_a-R_{28}$, $-P(O)R_{29}R_{31}$, $-P(S)R_{29}R_{30}$, $-Si(R_{31})(R_{32})(R_{33})$, $-C(O)R_{27}$, $-C(S)R_{27}$, cyano or nitro may be prepared by reaction of a compound of formula (I bis) wherein Y_1 is hydrogen, with sulfenylating, sulfinylating, sulfonating phosphorylating, thiophosphorylating, silylating, acylating or thioacylating reagent, respectively, generally in the presence of a base such as triethylamine or sodium carbonate and generally in a solvent at a temperature generally in the range -100 to 100°C.

According to a further feature of the invention for the synthesis of 5-alkylamino and dialkylamino compounds of formula (I bis) wherein R_{21} represents $R_{43}NH-$ or $R_{43}R_{44}N-$ in which R_{43} and R_{44} represent substituted or unsubstituted alkyl or substituted or unsubstituted C-3 or C-6 alkenyl three basic methods are appropriate. The first method includes direct alkylation of precursor compounds of formula (I bis) in which R_{21} represents amino with alkylating agents. The second method involves a two-step sequence, with formation of the imino ethers, followed by a reduction. The third method of preparation is through a conjugate addition, e.g., a Michael-type addition.

The compounds of formula (II bis) wherein R_2, R_3, R_4, R_5, R_6 and M are the above described substituents can be prepared by methods described in one or more of the following: WO 94/21606, WO 93/06089, WO 87/03781, WO 97/22593; European Patent Publications EP 0295117, EP 0511845, EP 0403309, EP 0403300, EP 352944, EP 780378; U.S. Patents 5,232,940, 5,047,550, 4,918,085; German Patent Publication No. 19511269; or by methods known to the skilled in the art.

The synthesis of higher oxidation states of the compounds of formula (I bis), i.e., compounds in which a, b, c, d, e or f are 1 or 2, can be achieved by oxidation of the corresponding compounds in which those variable are is 0 or 1.

Intermediates of formula (II bis) may be prepared by known methods (see for example the above listed references).

REPRESENTATIVE COMPOUNDS OF THE INVENTION

The compounds of TABLE 1 are illustrative of some of the preferred compounds of general formula (I) wherein R_3 and R_5 represent hydrogen and can be prepared by the herein described methods or processes of synthesis, by the appropriate selection of reactants, conditions and procedures, which are commonly known and apparent to one skilled in the art. In Table 1 Me means methyl, Et means ethyl and where subscripts are omitted they should be present, for example CH2 means CH_2 .

TABLE 1

Cmpd No.	M	Z	R_1	R_2	R_4	X	Y
126	C-Cl	$NH(CH_2)_2SO_2Me$	NH_2	Cl	CF_3	$SOCH_3$	H
127	C-Cl	$NHCH_2CN$	NH_2	Cl	CF_3	$SOCH_3$	H
128	C-Cl	$NH(CH_2)_2CONH_2$	NH_2	Cl	CF_3	$SOCH_3$	H
129	C-Cl	NHMe	NH_2	Cl	CF_3	SOMe	Me
130	C-Cl	NHEt	NH_2	Cl	CF_3	SOMe	Me
131	C-Cl	$EtSO_2(CH_2)_2NH$	NH_2	Cl	CF_3	SOMe	Me
132	C-Cl	$NH(CH_2)_2CN$	NH_2	Cl	CF_3	SOMe	Me
133	C-Cl	$NHCH_2CONH_2$	NH_2	Cl	CF_3	SOMe	Me
134	C-Cl	NHMe	NH_2	Cl	CF_3	SMe	Me
135	C-Cl	NHEt	NH_2	Cl	CF_3	SMe	Me
136	C-Cl	$EtSO_2(CH_2)_2NH$	NH_2	Cl	CF_3	SMe	Me
137	C-Cl	$NH(CH_2)_2CN$	NH_2	Cl	CF_3	SMe	Me
138	C-Cl	$NHCH_2CONH_2$	NH_2	Cl	CF_3	SMe	Me
139	C-Br	NHMe	NH_2	Cl	CF_3	SOMe	H
140	C-Br	$EtSO_2(CH_2)_2NH$	NH_2	Cl	CF_3	SOMe	H
141	C-Br	$NH(CH_2)_2CN$	NH_2	Cl	CF_3	SOMe	H
142	C-Br	$NHCH_2CONH_2$	NH_2	Cl	CF_3	SOMe	H
143	C-Cl	NHMe	NH_2	Cl	CF_3O	SOMe	H
144	C-Cl	NHEt	NH_2	Cl	CF_3O	SOMe	H

145	C-Cl	$EtSO_2(CH_2)_2NH$	NH_2	Cl	CF_3O	SOMe	H
146	C-Cl	$NH(CH_2)_2CN$	NH_2	Cl	CF_3O	SOMe	H
147	C-Cl	$NHCH_2CONH_2$	NH_2	Cl	CF_3O	SOMe	H
148	C-Cl	NHMe	NH_2	Cl	CF_3O	SOMe	Me
149	C-Cl	NHEt	NH_2	Cl	CF_3O	SOMe	Me
150	C-Cl	$EtSO_2(CH_2)_2NH$	NH_2	Cl	CF_3O	SOMe	Me
151	C-Cl	$NH(CH_2)_2CN$	NH_2	Cl	CF_3O	SOMe	Me
152	C-Cl	$NHCH_2CONH_2$	NH_2	Cl	CF_3O	SOMe	Me
153	C-Cl	NH_2	NH_2	Cl	CF_3	SOMe	CH_2CO_2Et
154	C-Cl	NHMe	NH_2	Cl	CF_3	SOMe	CH_2CO_2Et
155	C-Cl	NHEt	NH_2	Cl	CF_3	SOMe	CH_2CO_2Et
156	C-Cl	$EtSO_2(CH_2)_2NH$	NH_2	Cl	CF_3	SOMe	CH_2CO_2Et
157	C-Cl	$NH(CH_2)_2CN$	NH_2	Cl	CF_3	SOMe	CH_2CO_2Et
158	C-Cl	$NHCH_2CONH_2$	NH_2	Cl	CF_3	SOMe	CH_2CO_2Et
159	C-Cl	NH_2	NH_2	Cl	CF_3	SOMe	CH_2CONH_2
160	C-Cl	NHMe	NH_2	Cl	CF_3	SOMe	CH_2CONH_2
161	C-Cl	NHEt	NH_2	Cl	CF_3	SOMe	CH_2CONH_2
162	C-Cl	$EtSO_2(CH_2)_2NH$	NH_2	Cl	CF_3	SOMe	CH_2CONH_2
163	C-Cl	$NH(CH_2)_2CN$	NH_2	Cl	CF_3	SOMe	CH_2CONH_2
164	C-Cl	$NHCH_2CONH_2$	NH_2	Cl	CF_3	SOMe	CH_2CONH_2
165	C-Cl	NHMe	NHMe	Cl	CF_3	SOMe	Me
166	C-Cl	NHEt	NHMe	Cl	CF_3	SOMe	Me
167	C-Cl	$EtSO_2(CH_2)_2NH$	NHMe	Cl	CF_3	SOMe	Me
168	C-Cl	$NH(CH_2)_2CN$	NHMe	Cl	CF_3	SOMe	Me
169	C-Cl	$NHCH_2CONH_2$	NHMe	Cl	CF_3	SOMe	Me
170	C-Cl	NH_2	NHEt	Cl	CF_3	SOMe	Me
171	C-Cl	NHMe	NHEt	Cl	CF_3	SOMe	Me
172	C-Cl	NHEt	NHEt	Cl	CF_3	SOMe	Me
173	C-Cl	$EtSO_2(CH_2)_2NH$	NHEt	Cl	CF_3	SOMe	Me
174	C-Cl	$NH(CH_2)_2CN$	NHEt	Cl	CF_3	SOMe	Me
175	C-Cl	$NHCH_2CONH_2$	NHEt	Cl	CF_3	SOMe	Me
176	C-Cl	NH_2	NHMe	Cl	CF_3	SOMe	CH_2CO_2Me
177	C-Cl	NHMe	NHMe	Cl	CF_3	SOMe	CH_2CO_2Me
178	C-Cl	NHEt	NHMe	Cl	CF_3	SOMe	CH_2CO_2Me
179	C-Cl	$EtSO_2(CH_2)_2NH$	NHMe	Cl	CF_3	SOMe	CH_2CO_2Me

180	C-Cl	$NH(CH_2)_2CN$	NHMe	Cl	CF_3	SOMe	CH_2CO_2Me
181	C-Cl	$NHCH_2CONH_2$	NHMe	Cl	CF_3	SOMe	CH_2CO_2Me

DESCRIPTION OF THE PREFERRED EMBODIMENTS

DETAILED EXAMPLES OF COMPOUND SYNTHESIS

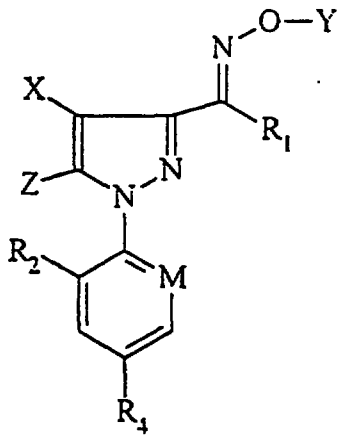
The following EXAMPLES 1 to 17 and REFERENCE EXAMPLES 1 to 24 illustrate detailed methods of synthesis and the physical properties of representative pesticidal compounds of formula (I) (and their chemical intermediates) according to the invention. These example compounds and others prepared in a similar manner, following the detailed procedures or other methods or processes herein described, are shown in Tables 2. Additionally, one or more spectroscopic analyses (IR, H^1 or F^{19} NMR, MS, etc.) have been performed on each compound for characterization and confirmation of the chemical structure. In the following Tables Me means methyl, Et means ethyl, 2-Tolyl means 2-methylphenyl and C_2H means ethynyl.

EXAMPLE 1

A mixture of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde (2.74g), hydroxylamine hydrochloride (0.99g) and pyridine (1.68g) was stirred in methanol at 46° C for 2.8 hours, evaporated, washed (water) and crystallized from ethanol to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (1.74g) as a white solid m.p.219-221° C (decomposition). Compound 1

In a manner similar to that employed above, the following compounds shown in Table 2 were also prepared.

TABLE 2



Cmpd No. #	M	Y	R_1	R_2	R4	X	Z	M.p.°C
35	C-Cl	H	H	H	CF_3	SOMe	$NH(CH_2)_2SO_2Et$	157-157.5
36	C-Cl	H	H	Cl	CF_3	SMe	NMe_2	178-181
37	C-Cl	H	H	Cl	OCF_3	SOEt	NH_2	204-206
38	C-Cl	H	H	Cl	CF_3	CF_3	NH_2	136-146
39	C-Cl	H	Me	Cl	CF_3	SOMe	NH_2	68-71
2	C-Cl	H	H	Cl	CF_3	SOMe	NHEt	158-161
3	C-Cl	H	H	Cl	CF_3	SOMe	NHMe	162
4	C-Cl	H	H	Cl	OCF_3	SOMe	NH_2	144-146
5	C-Cl	H	H	Cl	CF_3	SOEt	NH_2	195
6	C-Cl	H	H	Cl	CF_3	SCF_3	NH_2	163-169
7	C-Cl	H	H	Cl	CF_3	$SCHF_2$	NH_2	146-152
8	C-Cl	H	H	Cl	CF_3	SMe	NH_2	179-181
29	C-Cl	H	H	Cl	CF_3	SMe	Me	160-162.5
32	N	H	H	Cl	CF_3	SOMe	NH_2	195.5-196.5
33	C-Cl	H	H	Cl	CF_3	SEt	Me	155-157
34	C-Cl	H	H	Cl	CF_3	SOEt	Me	210-213

EXAMPLE 2

A mixture of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylthio-1H-pyrazole-3-carboxaldehyde (0.66g), methoxyamine hydrochloride (0.2g) and pyridine was stirred at room temperature for 26 hours. Pyridine was evaporated and the residue dissolved in ethyl acetate/acetonitrile, washed with 1% aqueous HCl, dried ($MgSO_4$) and evaporated.. The residue was purified by silica gel column chromatography, eluting with hexane/ethyl acetate, to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylthio-1H-pyrazole-3-carboxaldehyde O-methyloxime (0.3g) as a white solid m.p. 129-131.5° C. Compound 9.

EXAMPLE 3

Acetyl chloride (0.27ml) was added to a solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (1.0g) and triethylamine (0.56ml) in tetrahydrofuran at 0°C and the mixture stirred for 1 hour. The solvent was evaporated and the residue chromatographed on silica gel eluting with 3:1 dichloromethane/ethyl acetate to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(acetyl)oxime (0.83g)as an orange solid m.p.130-134° C. Compound 10.

In a manner similar to that employed above the following compounds shown in Table 3 were also prepared.

TABLE 3

Cmpd No.	M.p.°C
11	107-110
12	165
13	52-54
14	205.5-206.5
15	171-173
91	156
92	205
93	112
94	149
95	192
96	194
97	127
98	127
99	112
100	oil
101	oil
102	113
103	190
104	167
105	107

EXAMPLE 4

A mixture of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (1.38g), 30% hydrogen peroxide (1.38ml) sodium tungstate dihydrate (0.17g) in methanol/acetic acid was stirred at 20°C overnight, then at 50°C for 4 hours, and again at 20 °C overnight. Water was added and the solid filtered, water-washed and dried to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfonyl-1H-pyrazole-3-carboxaldehyde oxime (0.93g) m.p.209.5-211°C (decomposition). Compound 16.

EXAMPLE 5

A solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)-phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (0.15g) in ethanol was added to

a solution of sodium ethoxide (0.025g)in ethanol at 20 °C. followed by iodomethane (0.023ml). The reaction was monitored by HPLC and over the next 24 hours three additional equivalents of iodomethane were added. The reaction mixture was then concentrated and partitioned between dichloromethane and water. The organic layer was water-washed, dried ($MgSO_4$) and concentrated. This was then combined with crude product from another identical preparation and chromatographed on a silica gel column, eluting with hexane/ethyl acetate, to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(methyl)oxime (0.06g)as a yellow solid m.p.80°C. Compound 17.

EXAMPLE 6

A mixture of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (1.5g), methyl isocyanate (0.705g), and dibutyltin diacetate (2 drops) was stirred in dichloromethane at 20°C in a sealed bottle for 2 days. The mixture was partitioned between water and dichloromethane, the organic layer dried (Na_2SO_4) and evaporated and the residue crystallized from ethyl acetate/hexane to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(N-methylcarbamoyl)oxime (1.22g) m.p.146-147°C.
Compound 18.

EXAMPLE 7

A mixture of 5-amino-1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde (5.15g) and carboxymethoxylamine hemihydrochloride (5.83g) was stirred at 20°C in pyridine/ methanol for 17 hours. The methanol was evaporated and the residue water-washed and subjected to flash column chromatography on silica gel, eluting with acetic acid/ ethyl acetate (1:9) to give 5-amino-1- [2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(carboxymethyl)oxime (1.44g). Mass spectrometric analysis of the product indicated a molecular weight of 458. Compound 19.

EXAMPLE 8

Tert-butyl nitrite (1.25g) was added to 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (2.0g) in tetrahydrofuran and stirred for 4.5 hours. After evaporation the resulting orange solid was triturated with carbon tetrachloride to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (0.24g) m.p.239-240°C. Compound 20.

EXAMPLE 9

A solution of tert-butyldimethylsilyl chloride (0.8g) in N,N-dimethylformamide (DMF) was added to a stirred solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (2.0g) in (DMF), followed by dropwise addition of a solution of imidazole (0.72g) in DMF during 7-minutes. The mixture was heated at 50°C for 3.5-hours and then held at 20 °C for 18 hours. The mixture was diluted (water), extracted (methyl tert-butyl ether) and the organic phase washed in turn with $NaHCO_3$ solution, 5% HCl solution and with $NaHCO_3$ solution, dried ($MgSO_4$), filtered and evaporated. The residue was purified by flash chromatography on silica gel to give 5-amino-1- [2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(tert-butyldimethylsilyl)oxime (0.76g)as a light yellow solid m.p.150-154°C. Compound 21.

EXAMPLE 10

To a stirred solution of 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-formyl-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile (3.0g) in ethanol was added a solution of hydroxylamine hydrochloride (0.46g) and sodium carbonate (0.9g) in water. After 1 hour the mixture was poured into water, extracted (ethyl ether), dried (sodium

sulfate) and evaporated. Purification by column chromatography on silica gel gave 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-5-formyl-N-hydroxy-4-trifluoromethylthio-1H-pyrazole-3-carboximidamide (0.255g), m.p.72-75°C. Compound 22.

The following compounds shown in Table 4 were prepared in a similar manner.

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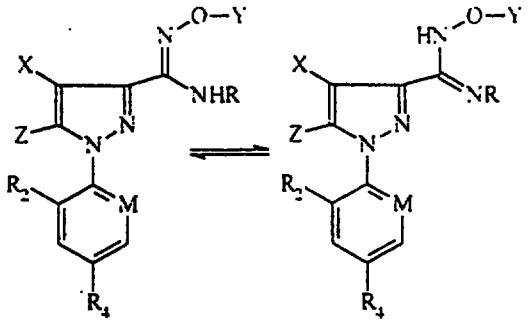
TABLE 4



Cmpd No. #		M	Z	R	R_2	R_4	Y	X	M.p.°C
42		C-Cl	NH_2	H	Cl	CF_3	H	SOEt	186-189
43		C-Cl	NH_2	H	Cl	CF_3	H	SEt	170-175
44		C-Cl	NH_2	H	Cl	CF_3	H	SOMe	225-227
45		C-Cl	NH_2	H	Cl	CF_3O	H	SOMe	198-200
46		C-Cl	NH_2	H	Cl	CF_3	H	SO_2Me	109-111
47		C-Cl	NH_2	H	Cl	CF_3	H	SMe	207-208
48		C-Cl	NH_2	H	Cl	CF_3	H	SO_2Et	109-111
51		C-Cl	NH_2	H	Cl	CF_3	H	$SOCH_2CH_2F$	212-215
52		C-Cl	NH_2	H	Cl	CF_3	H	$SO_2CH_2CH_2F$	107-111
53		N	NH_2	H	Cl	CF_3	H	SOEt	164-168
54		N	NH_2	H	Cl	CF_3	H	SOMe	234-235
55		C-Cl	NHMe	H	Cl	CF_3	H	SOMe	191-192
56		C-Cl	NHEt	H	Cl	CF_3	H	SOMe	192-193
57		C-Cl	$NH(CH_2)_2SO_2Et$	H	Cl	CF_3	H	SOMe	150-152
58		C-Cl	$NH(CH_2)_2CN$	H	Cl	CF_3	H	SOMe	175-176
59		C-Cl	$NHCH_2CONH_2$	H	Cl	CF_3	H	SOMe	119-120
60		C-Cl	$NH(CH_2)_2SO_2Ph$	H	Cl	CF_3	H	SOMe	131-134
61		C-Br	NH_2	H	Br	CF_3	H	SOMe	240-241
62		C-Br	NHEt	H	Cl	CF_3	H	SOMe	213-214
63		C-Br	NH_2	H	Cl	CF_3	H	SOMe	237-238
64		C-Cl	$NH(CH_2)_2SOMe$	H	Cl	CF_3	H	SOEt	108-109
65		C-Cl	$NH(CH_2)_2SOMe$	H	Cl	CF_3	H	SOMe	150-151
66		C-Cl	$NH(CH_2)_2SOEt$	H	Cl	CF_3	H	SOEt	173-175
67		C-Cl	$NHCH_2C_2H$	H	Cl	CF_3	H	SOMe	194-196
68		C-Cl	NH_2	H	H	CF_3	H	SOMe	238-239

EXAMPLE 11

A mixture of 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-formyl-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile (1.0g), hydroxylamine hydrochloride (0.48g) and sodium acetate trihydrate (0.94g) in ethanol was heated under reflux for one hour. After cooling to 20°C the mixture was concentrated and partitioned between water and ether. The organic phase was washed (brine), dried (magnesium sulfate) and evaporated to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-5-hydroxyiminomethyl-4-trifluoromethylthio-1H-pyrazole-3-carboximidamide (0.5g), m.p.68-72°C. Compound 23.

EXAMPLE 12

A suspension of sodium ethoxide (0.34g) in ethanol was added to a stirred solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (2.0g) in ethanol. 2-Iodopropane (1ml) was then added and the mixture stirred overnight at 20°C and evaporated. The residue (in dichloromethane) was water-washed, dried (magnesium sulfate), concentrated and purified by chromatography on silica gel to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(isopropyl)oxime (0.35g), m.p.128-130°C. Compound 24.

By proceeding in a similar manner the following compounds were also prepared:

5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1-H-pyrazole-3-carboxaldehyde O-(ethoxycarbonylmethyl)oxime, Compound 25, m.p.127-128°C ; and

5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1-H-pyrazole-3-carboxaldehyde O-(carbamoylmethyl)oxime, Compound 26, m.p.165-167°C .

EXAMPLE 13

In a manner similar to that employed in Example 12 an ethanol solution of 5-amino-1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime was reacted with sodium ethoxide and ethyl vinyl sulfone to give 5-amino-1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-[2-(ethylsulfonyl)ethyl]oxime, m.p.144-148°C.Compound 27.

EXAMPLE 14

In a manner similar to that employed in Example 12 an ethanol solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime was reacted with sodium ethoxide and acrylonitrile to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(2-cyanoethyl)oxime. Compound 28, as the 85 percent (by weight) component of a mixture containing 8 percent of the oxime starting material. Mass spectrometric analysis of the product indicated the following: MS m/e = 453 (M^+).

EXAMPLE 15

30% Hydrogen peroxide solution (0.32ml) was added to a solution of 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylthio-1H-pyrazole-3-carboxaldehyde oxime (0.8g) in trifluoroacetic acid at 20°C. The reaction solution was partitioned between water and dichloromethane and the organic layer dried (magnesium sulfate), evaporated and flash-chromatographed on silica gel, eluting with dichloromethane/ethyl acetate (3:1) to give 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime (0.29g), m.p.210-214°C. Compound 30 and 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylsulfonyl-1H-pyrazole-3-carboxaldehyde oxime (0.2g), m.p.211-212°C. Compound 31.

EXAMPLE 16

To a stirred solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboximidic acid methyl ester (1.0g) in anhydrous methanol was added anhydrous methoxylamine hydrochloride (0.2g). After 4 hours at 20 °C, the mixture was evaporated and dichloromethane and water added. The organic layer was dried ($MgSO_4$), evaporated and chromatographed on a florisil column, eluting with 3:1 dichloromethane/ethyl acetate to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide(0.28g),m.p.140-145°C.Compound 49. By proceeding in a similar manner the following compounds were prepared:5-amino-1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-4-trifluoromethylsulfinyl-1H-pyrazole-3-carboximidamide, m.p.169-170°C. Compound 41. ; and
5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-trifluoromethylsulfinyl-1H-pyrazole-3-carboximidamide, m.p.222-224°C. Compound 40.

EXAMPLE 17

A solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide (0.5g) in anhydrous THF was stirred at 0-5°C and potassium tert-butoxide (0.13g) and iodomethane (0.081ml) added. After three hours further potassium tert-butoxide (0.068g) and iodomethane (0.08ml) were added at 0-5° C. The mixture was stirred at this temperature for 16 hours, evaporated and the residue purified by chromatography on silica gel eluting with 3:1 dichloromethane/ethyl acetate to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-N'-methyl-4-methylsulfinyl-1H-pyrazole-3-carboximidamide (0.13g), m.p.139-142°C. Compound 50.

EXAMPLE 18

A mixture of 5-amino-3-cyano-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole (550 g), anhydrous hydrazine (700 g) in absolute ethanol (1.55 L) was stirred at ambient temperature for four hours. Water (6.5 L) was added and the precipitate filtered and washed with water. After 12 hours another batch of precipitate was filtered. All solids were combined to provide 568 g of Compound 69 as a white solid, m.p. 210°C.

In a similar manner the following compounds were prepared:
Compound 73 m.p. 170°C;
Compound 74 m.p. 193°C.

EXAMPLE 19

The mixture of Compound 69 (1.0 g) and acetic anhydride(327 mg) in p-dioxane (10 ml) was stirred at room temperature for 2 days. The mixture was evaporated and the residue washed with hexane with small amount of ethyl acetate and the suspension filtered to give 1.08 g of Compound 75, m.p 230°C.

Compound 85 was synthesized using a similar procedure.

EXAMPLE 20

The mixture of Compound 69 (0.2 g) and propionic anhydride (0.07 ml) in tetrahydrofuran (5 ml) was stirred at room temperature for 6 days. The mixture was evaporated and the residue purified by silica gel chromatography to give 70mg of Compound 79, m.p. 155-162°C.

In a similar manner the following compounds were prepared:

Compound #	m.p.
76	95
77	160
70	118
78	160
79	155
80	160
81	110
82	118
83	152
84	130
71	122
86	oil

EXAMPLE 21

The mixture of Compound 69 (0.2 g) and di-t-amyldicarbonate (0.13 ml) in tetrahydrofuran (4.5 ml) was stirred at room temperature for 5 days. The mixture was evaporated and the residue purified by silica gel chromatography to give 20 mg (0.038 mmol) of Compound 89, m.p. 95-98°C.

The following compounds were synthesized with the similar procedure using an appropriate dicarbonates: Compound 88, m.p. 135°C. Compound 90, m.p. 155°C. Compound 72, m.p. 196°C.

EXAMPLE 22

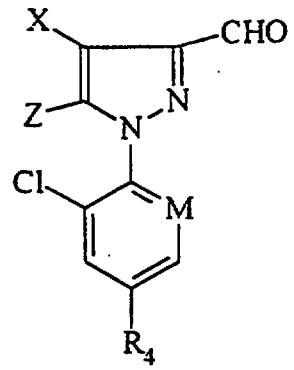
To a suspension of 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-methylsulfinylpyrazole (20g) in methanol (120 ml) was added hydroxylamine hydrochloride (3.99g) , followed by addition of triethylamine (8.0 ml). The mixture was stirred at room temperature overnight then evaporated. The residue was partitioned between water and ethyl acetate. The organic layer was washed with water, followed by wash with brine. The organic layer was dried over anhydrous sodium sulfate. The solution was concentrated by evaporation of solvent. A precipitate was formed and collected by filtration. The solid was washed with small amount of ethyl acetate to give Compound 44 (16.1 g), m.p. 225-226°C.

REFERENCE EXAMPLE 1

Diisobutylaluminum hydride (1M in toluene. 391ml) was added dropwise during 1.5 hours to 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-3-carbonitrile (50g) in dry THF at -20° C. The partially evaporated mixture was then quenched by addition to acetonitrile/water at 0-5° C. Aluminum salts were filtered, the filtrate evaporated and the residue extracted with dichloromethane. The extract was dried ($MgSO_4$), and evaporated to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde (47.1g).

By proceeding in a similar manner the following compounds shown in Table 5 were also prepared.

TABLE 5



M	R_2	R_4	X	Z	HPLC Retention Time [a] (Min.)
C-Cl	Cl	CF_3	SOMe	NHEt	3.76
C-Cl	Cl	CF_3	SOMe	NHMe	3.49
C-Cl	Cl	CF_3	SOEt	NH_2	(M.p.166-168°C)
C-Cl	Cl	CF_3	SMe	NH_2	4.04
C-Cl	Cl	CF_3O	SOMe	NH_2	3.41
C-Cl	Cl	CF_3	SMe	Me	7.64
N	Cl	CF_3	SOMe	NH_2	3.04
C-Cl	Cl	CF_3	SEt	Me	8.22
C-Cl	Cl	CF_3	SMe	NMe_2	10.08
C-Cl	Cl	CF_3	SCF_3	NH_2	4.83
C-Cl	Cl	CF_3	CF_3	NH_2	(b)
C-Cl	H	CF_3	SOMe	$NH(CH_2)_2SO_2Et$	(b)
C-Cl	Cl	CF_3O	SOEt	NH_2	(b)
C-Cl	I	CF_3	$SCHF_2$	NH_2	(b)
C-Cl	Cl	CF_3	SOEt	NH_2	(b)

(a) 25.0 cm x 4.6 mm SUPELCOSIL LC-18 Column. Eluant: MeCN/H_2O (3:1)at one ml/minute.

(b) used without purification in the next stage

REFERENCE EXAMPLE 2

A 1.4 M solution of methyllithium (31ml) in ethyl ether was added to a stirred solution of 5-bromo-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carbonitrile (17.67g) in dry tetrahydrofuran (THF) at-65°C over 15-

minutes and allowed to warm to 0°C over 3-hours. After recooling to -65°C. methyl iodide (3.06ml) in THF was added over 3 minutes. the mixture warmed to -20°C over 1.5 hours. and then partitioned between aqueous ammonium chloride and dichloromethane. The organic phase was dried (magnesium sulfate). evaporated and purified by flash chromatography on silica gel eluting with hexane/methyl tert-butylether to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylthio-1H-pyrazole-3-carbonitrile (6.2g) having a purity of 90.7 area percent by HPLC. .

By proceeding in a similar manner the following compound was also prepared: 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylthio-5-methyl-1-H-pyrazole-3-carbonitrile m.p.79-82°C..

REFERENCE EXAMPLE 3

30% Hydrogen peroxide (1.82ml) was added to a stirred solution of 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylthio-1H-pyrazole-3-carbonitrile (6.2g) in methanol, containing i-PrOH/H_2SO_4 catalyst (5.31ml) described by Drabowicz, et al (above) at 0-5° C. The mixture was allowed to warm to 20°C over 17 hours. Additional hydrogen peroxide (5.46 ml) was added in three portions over the next 24 hours. along with the catalyst (5ml). After stirring for a further 60 hours water was added to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylsulfinyl-1H-pyrazole-3-carbonitrile (6.72 g) as a yellow oil (91.7% area purity by HPLC) having a retention time of 3.61 minutes on a 25.0 centimeter by 4.6 millimeter SUPELCOSIL LC-18 column. eluting with CH_3CN / H_2O (3:1) solvent at 1 ml/minute..

By proceeding in a similar manner the following compounds were also obtained:

1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-5-methyl-1-H-pyrazole-3-carbonitrile, m.p.109-115°C;

5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[2-(fluoroethyl)sulfinyl]-1-H-pyrazole-3-carbonitrile, m.p.182-183°C;

1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(methylsulfinyl)ethylamino]-4-ethylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.106-108 °C, from 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(methylthio)ethylamino]-4-ethylsulfinyl-1H-pyrazole-3-carbonitrile;

1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(methylsulfinyl)ethylamino]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.114-116 °C. from 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(methylthio)ethylamino]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile;

1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(ethylsulfinyl)ethylamino]-4-ethylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.138-140 °C. from 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(ethylthio)ethylamino]-4-ethylsulfinyl-1H-pyrazole-3-carbonitrile;

5-amino-1-[3-chloro-5-(trifluoromethyl)pyrid-2-yl]-4-ethylsulfinyl-1H-pyrazole-3-carbonitrile. m.p.150-152 °C; and

5-amino-1-[2,6-dibromo-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile. m.p.165-166 °C.

REFERENCE EXAMPLE 4

90% Tertiary-butyl nitrite (27.9ml) was slowly added to a stirred solution of 5-amino-1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylthio-1H-pyrazole-3-carbonitrile (49.8g) in bromoform (600ml) at 0-5°C. The mixture was stirred for three hours whilst warming to 20°C evaporated and re-evaporated after addition of hexane/ethyl acetate (1:1) to give 5-bromo-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylthio-1H-pyrazole-3-carbonitrile (32.65g), showing 93.3 area % purity by HPLC and with a retention time of 11.26 minutes on a 25.0 cm by 4.6 mm SUPELCOSIL LC-18 column, eluting with CH_3CN/H_2O (3:1) solvent at 1 ml/minute.

By proceeding in a similar manner the following compound was prepared:
5-bromo-1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carbonitrile, m.p.134-140 °C.

REFERENCE EXAMPLE 5

Ozone was bubbled through a solution of 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-(E-2-methoxycarbonylethenyl)-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile (36.6g) in dichloromethane at -78°C for 3 hours. The intensely blue solution was decolorized with oxygen gas, then treated with dimethylsulfide (19 ml) and allowed to warm to 20°C during 14 hours The mixture was then washed with water, dried (magnesium sulfate), filtered and evaporated to give 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-formyl-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile as white crystals (30.7g). m.p.90°C.

REFERENCE EXAMPLE 6

1.8-Diazabicyclo-[5.4,0]-undec-7-ene (13 ml) was added to a solution of 5-(2'-bromo-2'-carbomethoxy)ethyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile (45g) in toluene and stirred for 0.5

hour. The mixture was diluted (ethyl acetate), and washed with water, hydrochloric acid solution, saturated sodium hydrogen carbonate solution and brine. The organic phase was dried (magnesium sulfate), concentrated and triturated with cold pentane to give 1-(2,6-dichloro-4-trifluoromethylphenyl)-5-(E-2-methoxycarbonylethenyl)-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile as a white solid (36.6 g), m.p.90°C.

REFERENCE EXAMPLE 7

A solution of 5-amino-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile (100g) in acetonitrile was added dropwise to a mixture of methyl acrylate (430 ml), copper (II) bromide (80 g) and 90% tert-butylnitrite (51 ml) in acetonitrile at 0°C, warmed to 20°C and stirred for 12 hours. The mixture was diluted (ether), washed (water), dried (magnesium sulfate) and concentrated. Trituration with hexane gave 5-(2'-bromo-2'-carbomethoxy)ethyl-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylthio-1H-pyrazole-3-carbonitrile as a white solid (72.7g) m.p.122°C.

REFERENCE EXAMPLE 8

To a stirred suspension of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile (5.0g) in anhydrous methanol was added a 25% w/w solution of sodium methoxide (8.95ml) in methanol, at 20 °C. The mixture was stirred for 16-hours, cooled to 0 °C and diluted with ice-cold anhydrous methanol. Carbon dioxide was passed into the solution for 15-minutes until a pH of 8 was attained. The precipitate was filtered off, washed (ethyl acetate) and evaporated to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboximidic acid methyl ester (3.65g), ^{1}H NMR ($CDCl_3$) in ppm: 8.34(s,1H), 7.79(s,2H), 5.11(brs,2H), 3.93(s,3H), 2.94(s,3H). By proceeding in a similar manner the following compound was prepared:5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylsulfinyl-1H-pyrazole-3-carboximidic acid methyl ester, m.p.179-180 °C.

REFERENCE EXAMPLE 9

To a stirred solution of 4,4'-dithiobis [5-amino-3-cyano-1-{2,6-dichloro-4-(trifluoromethyl)phenyl}-1H-pyrazole (1.0g) in methanol was added sodium borohydride (0.03g). After 7-minutes 1-bromo-2-fluoroethane (0.05ml) was added. Five further portions of sodium borohydride (0.15g) and 1-bromo-2-fluoroethane (0.25ml) were added over 5 hours. The mixture was evaporated, dichloromethane and water added and the organic phase dried ($MgSO_4$) and re-evaporated to give 5-amino-

1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-[2-(fluoroethyl)thio]-1H-pyrazole-3-carbonitrile (1.09g). m.p.130-131.5° C. By proceeding in a similar manner the following compound was obtained:
5-amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-4-ethylthio-1H-pyrazole-3-carbonitrile. m.p.127-128°C. 4,4'-Dithiobis [5-amino-3-cyano-1-{2.6-dichloro-4-(trifluoromethoxy)phenyl}-1H-pyrazole used above may be prepared in a similar manner to 4,4'-dithiobis [5-amino-3-cyano-1-{2,6-dichloro-4-(trifluoromethyl)phenyl}-1H-pyrazole as described in French Patent Application Numbers 8816710 and 8913371.

REFERENCE EXAMPLE 10

In a manner similar to that of Example 15. 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-[2-(fluoroethyl)thio]-1H-pyrazole-3-carbonitrile was oxidized with hydrogen peroxide in trifluoroacetic acid solution to give 5-amino-1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-[2-(fluoroethyl)sulfonyl]-1H-pyrazole-3-carbonitrile, m.p.192-193°C By proceeding in a similar manner the following compounds were prepared:
5-amino-1-[2-bromo-6-chloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.150-151°C. 5-amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.137-138°C. 5-amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.146-147°C.

REFERENCE EXAMPLE 11

A mixture of 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-amino-1H-pyrazole-3-carbonitrile (5.0g), trimethyl orthoacetate (100ml) and p-toluenesulfonic acid (0.2g) in toluene was heated to 145°C for 2 hours and then at 130°C with distillation of the methanol.. The mixture was evaporated and the residue purified by column chromatography using 20% ethyl acetate in hexane to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[1-(methoxyethylene)amino]-1H-pyrazole-3-carbonitrile (3.31g) m.p.164 to 165°C.

REFERENCE EXAMPLE 12

To a suspension of 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[1-(methoxyethylene)amino]-1H-pyrazole-3-carbonitrile (6.0g) in methanol was added sodium borohydride (0.79g) in three portions over 15 min. at 20°C then stirred under nitrogen for 45 mins..After evaporation the residue was

purified by column chromatography on silica gel using 15% ethyl acetate in methylene chloride to give 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-ethylamino-1H-pyrazole-3-carbonitrile (1.1g) , m.p.130-131°C(decomp.).

By proceeding in a similar manner was prepared:
1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-5-methylamino-4-methylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.147-150° C (decomposition).

By proceeding in a similar manner but replacing sodium borohydride with sodium cyanoborohydride was prepared:
1-[2-bromo-6-chloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-ethylamino-1H-pyrazole-3-carbonitrile, m.p.125-126.5°C.

REFERENCE EXAMPLE 13

A solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile (4.92g) in triethyl orthoformate (100ml) was heated under reflux for two hours, then stirred at 20°C for 16 hours and evaporated. Trituration with boiling hexane gave 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[(ethoxymethylene)amino]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile (4.05g), m.p.93-95° C. By proceeding in a similar manner the following compound was prepared:
1-[2-bromo-6-chloro-4-(trifluoromethyl)phenyl]-5-[1-(methoxyethylene)amino]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile. This was used directly in the next stage.

REFERENCE EXAMPLE 14

To a suspension of 35% potassium hydride in oil (0.7g) in dry N,N-dimethylformamide (DMF) was added a solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-(methylsulfinyl)-1H-pyrazole-3-carbonitrile (10.0g) in dry DMF dropwise at 4°C over 10 minutes. After stirring for 20 minutes, vinyl ethyl sulfone (3.13g) in dry DMF was added during 5 hours at 4°C. The mixture was stirred overnight under nitrogen with warming to 20°C. Ammonium chloride was added at 4°C, and the mixture extracted (ethyl acetate), washed twice with water, dried (sodium sulfate) and evaporated. Crystallization from ethyl acetate/methanol/hexane gave 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(ethylsulfonyl)ethylamino]-4-(methylsulfinyl)-1H-pyrazole-3-carbonitrile (4.08g), m.p.131-132°C. By proceeding in a similar manner the following compounds were prepared:

1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-5-[2-(cyanoethyl)amino]-4-(methylsulfinyl)-1H-pyrazole-3-carbonitrile. m.p.55-57°C; 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[2-(phenylsulfonyl)ethylamino]-1H-pyrazole-3-carbonitrile, m.p.138-139°C; and
1-[2-chloro-4-(trifluoromethyl)phenyl]-5-[2-(ethylsulfonyl)ethylamino]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile.m.p.139-140°C.

REFERENCE EXAMPLE 15

To a solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile (0.5g) in acetonitrile was added 2-bromoacetamide (0.18g) in water and calcium carbonate (0.13g). The mixture was heated under reflux for 1.5 hours, cooled to 25°C and a solution of sodium hydroxide (0.05g) in water added. This was then heated under reflux for one hour, evaporated and the residue purified by preparative thin-layer chromatography eluting first with 20% methanol in dichloromethane to give 1-[2.6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[(aminocarbonylmethyl)amino]-1H-pyrazole-3-carbonitrile (0.089g), m.p.155-157°C.

REFERENCE EXAMPLE 16

To a suspension of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile (2g) in toluene was added methyl magnesium bromide (7ml of a 1.4M solution in toluene/THF). The mixture was stirred at 20°C (1 hr.) and neutralised with saturated ammonium chloride solution. The organic layer was dried (sodium sulfate), evaporated and the residue purified by chromatography using 40% ethyl acetate in hexane to give 3-acetyl-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole (0.68g), m.p. 166°C.

REFERENCE EXAMPLE 17

To a suspension of 35% potassium hydride in oil (1.4g) in dry N,N-dimethylformamide (DMF) was added a solution of 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-amino-4-(ethylsulfinyl)-1H-pyrazole-3-carbonitrile (5.0g) in dry DMF at 4°C and stirred for 40 min. 2-Chloroethyl methyl sulfide (1.39g) was added at 4°C and the stirred mixture allowed to warm to 20°C over 40 minutes, then heated to 50°C for 4 hours and at 20°C for 3 days. Ammonium chloride solution and ethyl acetate were added and the organic layer dried (sodium sulfate), evaporated and purified by column chromatography using 80% methyl t-butyl ether in hexane to give

1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[[-2-(methylthio)ethyl]amino]-4-(ethylsulfinyl)-1H-pyrazole-3-carbonitrile (0.26g), m.p.126-127°C.

By proceeding in a similar manner there were prepared: 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[-2-(methylthio)ethylamino]-4-methylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.111-113°C. 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-[-2-(ethylthio)ethylamino]-4-ethylsulfinyl-1H-pyrazole-3-carbonitrile, m.p.27.5-29°C. 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-(2-propynyl)amino-1H-pyrazole-3-carbonitrile, m.p.140-141°C

REFERENCE EXAMPLE 18

Sulfuryl chloride (1.48g) was added to methyl disulfide (3.16g) in methyl t-butyl ether and stirred for 5 hours to give methyl sulfenyl chloride. This was added dropwise over 5 minutes to a solution of 5-amino-1-[2-bromo-6-chloro-4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carbonitrile (4.0g) heated under reflux in methyl t-butyl ether under nitrogen. After 1 hour the cooled mixture was washed in turn with water, sodium bicarbonate solution and water, dried (sodium sulfate) and evaporated. Purification by chromatography on silica gel eluting with hexane/ethyl acetate (9:1) gave 5-amino-1-[2-bromo-6-chloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carbonitrile (3.15g), m.p.178-180°C. By proceeding in a similar manner the following compound was prepared: 5-amino-1-[3-chloro-5-(trifluoromethyl)pyrid-2-yl]-4-ethylthio-1H-pyrazole-3-carbonitrile.

REFERENCE EXAMPLE 19

Step 1

Bromine (0.5 ml) was added over 10 minutes to a stirred solution of sodium thiocyanate (1.7 g) in anhydrous methanol at -65° C. A solution of 5-amino-1-(2-chloro-4-(trifluoromethyl)phenyl]-1-H-pyrazole-3-carbonitrile (1.5 g) in anhydrous methanol was added over 10-minutes and the stirred mixture allowed to warm to 20° C over 16-hours. After pouring into water the precipitate was collected and dried to give 5-amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-thiocyanato-1H-pyrazole-3-carbonitrile (1.64 g). HPLC (C-18 column, eluting with 3:1 CH_3CN/H_2O at 1.0 ml/min.) showed the compound as a peak of 86.6% area at 5.11 minutes.

Step 2

Iodomethane (0.7 ml) was injected into a stirred suspension of 5-amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-thiocyanato-1H-pyrazole-3-carbonitrile (1.64 g), in methanol at 4° C. A 10% aqueous solution of sodium hydroxide (2.8 ml) was

added and the reaction mixture stirred for 1 hour at 4° C , poured into water and extracted with dichloromethane and ethyl acetate. The dried (Na_2SO_4) combined organic phase was evaporated and purified by flash-chromatography on silica gel eluting with 4:1 hexane/ethyl acetate to give, after trituration with hexane/dichloromethane, 5-amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carbonitrile (0.4 g), m.p.129-132°C.

By proceeding in a similar manner as step 1 above there was obtained:

A) 5-amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-4-thiocyanato-1H-pyrazole, which was used in Step 2 with iodomethane to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carbonitrile, m.p. 147-148°C.

B) 5-amino-1-[2,6-dibromo-4-(trifluoromethyl)phenyl]-4-thiocyanato-1H-pyrazole-3-carbonitrile, which was used directly in step 2 with iodoethane and methanol as solvent to give the 5-amino-1-[2,6-dibromo-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carbonitrile, m.p.211-214°C .

REFERENCE EXAMPLE 20

A suspension of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-1H-pyrazole-3-carbonitrile (9.8g) and N-iodosuccinimide (8.87g) was heated at reflux in carbon tetrachloride for 3.5 hours, cooled and washed with sodium bisulfite solution, NaOH solution and water. The dried (magnesium sulfate) solution was evaporated and purified by chromatography on silica gel eluting with dichloromethane to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-iodo-1H-pyrazole-3-carbonitrile (4.0g), m.p.212-214 °C.

REFERENCE EXAMPLE 21

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-iodo-1H-pyrazole-3-carbonitrile (1.96g) was stirred with dimethylformamide dimethyl acetal (10ml) at 20 °C for 2 hours, then excess ice/water added and the solid filtered and oven-dried to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-iodo-5-N-(dimethylaminomethyleneamino)-1H-pyrazole-3-carbonitrile (1.53g), m.p.177-180 °C.

REFERENCE EXAMPLE 22

Activated cadmium was prepared by washing cadmium with hydrochloric acid (10%), water, ethanol and ether and drying. Dibromodifluoromethane (317.2g) in dry N,N-dimethylformamide (DMF) was added during 1 hour to a mixture of activated

cadmium (212.5g) in dry DMF initially at 0-5°C and when initiated at below 35°C with stirring under nitrogen. Hexamethylphosphoramide (1l.dry) was added followed by copper (I) bromide (108.5g) and, after 15 minutes, 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-iodo-5-N-(dimethylaminomethyleneamino)-1H-pyrazole-3-carbonitrile (100.0g) and the mixture heated at 75°C for 2 hours. The cooled mixture was filtered (celite), concentrated, diluted (water) and filtered. The product was washed (hot water) to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-N-(dimethylaminomethyleneamino)-4-trifluoromethyl-1H-pyrazole-3-carbonitrile (80.9g), m.p.156-157.5°C.

REFERENCE EXAMPLE 23

A solution of 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-N-(dimethylaminomethyleneamino)-4-trifluoromethyl-1H-pyrazole-3-carbonitrile (120.5g) in tetrahydrofuran and hydrochloric acid (6N) was heated at reflux for 24 hours, concentrated and filtered. The solid was mixed with dichloromethane and filtered to give 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethyl-1H-pyrazole-3-carbonitrile (88.2g), m.p.191-193°C.

REFERENCE EXAMPLE 24

A solution of 5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carbonitrile (1.0g) in tetrahydrofuran was added to anhydrous sodium hydride (0.13g) stirred under nitrogen in tetrahydrofuran at 4°C. After 2 hours iodomethane (0.34ml) was added and the mixture stirred at 20°C overnight and treated with ammonium chloride solution. Extraction (ethyl acetate), drying (sdium sulfate) and evaporation was followed by chromatography on silica gel eluting with ethyl acetate/dichloromethane (1:9) to give 1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-5-dimethylamino-4-methylthio-1H-pyrazole-3-carbonitrile (0.5g), m.p.118-119°C.

MITICIDE, INSECTICIDE, APHICIDE, AND NEMATICIDE USE

The following representative test procedures, using compounds of the invention, were conducted to determine the pesticidal use and activity of compounds of the invention against: mites; certain insects, including aphids, two species of caterpillar, a fly, and three species of beetle larvae (one foliar feeding and two root feeding); and nematodes. The specific species tested were as follows:

GENUS, SPECIES	COMMON NAME	(ABBREVIATION)
Tetranychus urticae	twospotted spider mite	TSM

Aphis nasturtii	buckthorn aphid	BA
Spodoptera eridania	southern armyworm	SAW
Epilachna varivestis	Mexican bean beetle	MBB
Musca domestica	housefly	HF
Diabrotica u. howardi	southern corn rootworm	SCRW
Diabrotica virgifera	western corn rootworm	WCRW
Meloidogyne incognita	southern root-knot nematode	SRKN
Aphis gossypii	cotton aphid	CA
Schizaphis graminum	greenbug (aphid)	GB
Heliothis virescens	tobacco budworm	TBW

Formulations:

The test compounds were formulated for use according to the following methods used for each of the test procedures.

For mite, aphid, southern armyworm, Mexican bean beetle, and tobacco budworm tests, a solution or suspension was prepared by adding 10 mg of the test compound to a solution of 160 mg of dimethylformamide, 838 mg of acetone, 2 mg of a 3:1 ratio of Triton X-172 : Triton X-152 (respectively, mainly anionic and nonionic low foam emulsifiers which are each anhydrous blends of alkylaryl polyether alcohols with organic sulfonates), and 98.99 g of water. The result was a concentration of 100 ppm of the test compound.

For housefly tests, the formulation was initially prepared in a similar manner to the above, but in 16.3 g of water with corresponding adjustment of other components, providing a 200 ppm concentration. Final dilution with an equal volume of a 20% by weight aqueous solution of sucrose provided a 100 ppm concentration of the test compound. When necessary, sonication was provided to insure complete dispersion.

For southern and western corn rootworm tests, a solution or suspension was prepared in the same manner as that used for the initial 200 ppm concentration for housefly. Aliquots of this 200 ppm formulation were then used by dilution with water according to the required test concentration.

For southern root-knot nematode and systemic tests for southern armyworm, cotton aphid, tobacco budworm and greenbug, a stock solution or suspension was prepared by adding 15 mg of the test compound to 250 mg of dimethylformamide, 1250 mg of acetone and 3 mg of the emulsifier blend referenced above. Water was then added to provide a test compound concentration of 150 ppm. When necessary, sonication was provided to insure complete dispersion.

For tobacco budworm contact tests. a stock solution was prepared by dissolving the compound in acetone and then further diluted to provide the required serial dilution concentrations.

Test Procedures:

The above formulated test compounds were then evaluated for their pesticidal activity at the specified concentrations, in ppm (parts per million) by weight. according to the following test procedures:

Twospotted spider mite: Leaves infested with adult and nymphal stages of the two-spotted spider mite, obtained from a stock culture were placed on the primary leaves of two bean plants growing in a 6 cm. peat pot. A sufficient number of mites (150-200) for testing were transferred to the fresh plants within a period of twenty-four hours. The potted plants (one pot per compound) were placed on a revolving turntable and sprayed, sufficient to wet the plants to runoff, with 100 ml of the 100 ppm test compound formulation by use of a DeVilbiss spray gun set at 40 psig. air pressure. As an untreated control, 100 ml of the water-acetone-DMF-emulsifier solution, containing no test compound, were also sprayed on infested plants. A treated control with a commercial technical compound, either dicofol or hexythiazox, formulated in the same manner, was tested as a standard. The sprayed plants were held for six days, after which a mortality count of motile forms was made.

Twospotted spider mite (ovicide test): Eggs were obtained from adults of the twospotted spider mite from a stock culture. Heavily infested leaves from the stock culture were placed on uninfested bean plants. Females were allowed to oviposit for a period of about 24 hours, after which the leaves of the plant were dipped into a solution of TEPP (tetraethyl diphosphate) in order to kill the motile forms and prevent additional egg laying. This dipping procedure, which was repeated after the plants dried, did not affect the viability of the eggs. The potted plants (one pot per compound) were placed on a revolving turntable and sprayed, sufficient to wet the plants to runoff, with 100 ml of the 100 ppm test compound formulation by use of a DeVilbiss spray gun set at 40 psig. air pressure. As an untreated control, 100 ml of the water-acetone-DMF-emulsifier solution, containing no test compound, were also sprayed on infested plants. A treated control with a commercial technical compound, typically demeton, formulated in the same manner, was tested as a standard. The sprayed plants were held for seven days, after which a mortality count of egg forms was made along with notations on residual activity on hatched larvae.

Buckthorn or cotton aphid: Adult and nymphal stages of buckthorn or cotton aphid were reared on potted dwarf nasturtium or cotton plants, respectively. The

potted plants (one pot per compound tested) infested with 100-150 aphids, were placed on a revolving turntable and sprayed with 100 ml of the 100 ppm test compound formulation by use of a DeVilbiss spray gun set at 40 psig air pressure. As an untreated control, 100 ml of a water-acetone-DMF-emulsifier solution, containing no test compound, were also sprayed on infested plants. A treated control with a commercial technical compound, malathion or cyhalothrin, formulated in the same manner, was tested as a standard. After spraying, the pots were stored for one day on buckthorn aphid or three days for cotton aphid, after which the dead aphids were counted.

Southern armyworm: Potted bean plants, were placed on a revolving turntable and sprayed with 100 ml of the 100 ppm test compound formulation by use of a DeVilbiss spray gun set at 40 psig air pressure. As an untreated control, 100 ml of a water-acetone-DMF-emulsifier solution, containing no test compound, were also sprayed on plants. A treated control with a commercial technical compound, either cypermethrin or sulprofos, formulated in the same manner, was tested as a standard. When dry, the leaves were placed in plastic cups lined with moistened filter paper. Five randomly selected second instar southern armyworm larvae were introduced into each cup which was closed and held for five days. Larvae which were unable to move the length of the body, even upon stimulation by prodding, were considered dead.

Tobacco budworm: Potted cotton plants were placed on a revolving turntable and sprayed with 100 ml of the 100 ppm test compound formulation by use of a DeVilbiss spray gun set at 40 psig air pressure. As an untreated control, 100 ml of a water-acetone-DMF-emulsifier solution, containing no test compound, were also sprayed on plants. A treated control with a commercial technical compound, either cypermethrin or sulprofos, formulated in the same manner, was tested as a standard. When dry, the leaves were placed in plastic dishes containing a piece of filter paper and a moistened dental wick. One randomly selected second instar tobacco budworm larva was then introduced into each cup which was closed and held for five days. Larvae unable to move the length of their body, even upon stimulation by prodding, were considered dead.

Mexican bean beetle: Potted bean plants were placed on a revolving turntable and sprayed with 100 ml of the 100 ppm test compound formulation, sufficient to wet the plants to runoff, by use of a DeVilbiss spray gun set at 40 psig air pressure. As an untreated control, 100 ml of a water-acetone-DMF-emulsifier solution, containing no test compound, were also sprayed on plants. A treated control with a commercial technical compound, either cypermethrin or sulprofos, formulated in the same manner, was tested as a standard. When dry, the leaves were placed in plastic cups

lined with moistened filter paper. Five randomly selected second instar Mexican bean beetle larvae were introduced into each cup which was closed and held for five days. Larvae which were unable to move the length of the body, even upon stimulation by prodding, were considered dead.

House fly: Four to six day old adult house flies were reared according to the specifications of the Chemical Specialties Manufacturing Association (Blue Book, McNair-Dorland Co., N.Y. 1954; pages 243-244, 261) under controlled conditions. The flies were immobilized by anesthetizing with carbon dioxide and twenty five immobilized individuals, males and females, were transferred to a cage consisting of a standard food strainer and a wrapping-paper-covered surface. Ten ml of the 100 ppm test compound formulation were added to a soufflé cup containing an absorbent cotton pad. As an untreated control, 10 ml of a water-acetone-DMF-emulsifier-sucrose solution, containing no test compound, were applied in a similar manner. A treated control with a commercial technical compound, malathion, formulated in the same manner, was tested as a standard. The bait cup was introduced inside the food strainer prior to admitting the anesthetized flies. After 24 hours, flies which showed no sign of movement on stimulation were considered dead.

Southern or western corn rootworm: Into a jar containing 60g of sandy loam soil was added 1.5 ml of an aqueous formulation consisting of an aliquot of the 200 ppm test compound formulation, diluted with water as appropriate for the final soil concentration of the test compound, 3.2 ml of water and five pregerminated corn seedlings. The jar was shaken thoroughly to obtain an even distribution of the test formulation. Following this, twenty corn rootworm eggs (or optionally ten first instar larvae in the case of WCRW) were placed into a cavity, which was made in the soil. Vermiculite (1 ml), used optionally in the case of WCRW tests, and water (1.7ml) were then added to this cavity. In a similar manner, an untreated control was prepared by application of the same size aliquot of a water-acetone-DMF-emulsifier solution, containing no test compound. Additionally, a treated control with a commercial technical compound (selected typically from terbufos, fonofos, phorate, chlorpyrifos, carbofuran, isazophos, or ethoprop), formulated in the same manner was used as needed as a test standard. After 7 days, the living rootworm larvae were counted using a well known "Berlese" funnel extraction method.

Southern root-knot nematode: Infected roots of tomato plants, containing egg masses of southern root-knot nematode, were removed from a stock culture and cleaned of soil by shaking and washing with tap water. The nematode eggs were separated from the root tissue and rinsed with water. Samples of the egg suspension were placed on a fine screen over a receiving bowl, in which the water level was

adjusted to be in contact with the screen. From the bowl, juveniles were collected on a fine screen. The bottom of a cone-shaped container was plugged with coarse vermiculite and then filled to within 1.5 cm of the top with about a 200 ml volume of pasteurized soil. Then into a hole made in the center of the soil in the cone was pipetted an aliquot of the 150 ppm test compound formulation. A treated control with a commerical technical compound, fenamifos, formulated in a similar manner, was tested as a standard. As an untreated control, an aliquot of a water-acetone-DMF-emulsifier solution, containing no test compound, was applied in a similar manner. Immediately after treatment of the soil with the test compound there were added to the top of each cone 1000 second stage juvenile southern root-knot nematodes. After 3 days, a single healthy tomato seedling was then transplanted into the cone. The cone, containing the infested soil and tomato seedling, was kept in the greenhouse for 3 weeks. At the termination of the test, roots of the tomato seedling were removed from the cone and evaluated for galling on a rating scale relative to the untreated control as follows:

1- severe galling, equal to untreated control
3- light galling
4- very light galling
5- no galling, ie, complete control

These results were then converted to an ED_3 or ED_5 value (effective dose to provide a 3 or 5 gall rating).

Southern armyworm on tomato - systemic evaluation: This test was conducted in conjunction with the southern root-knot nematode evaluation (discussed below). The tomato plants, grown in the soil (at an initial compound test screening rate of 6.6 ppm soil concentration or about 150 ppm solution concentration) for nematode evaluation, were then utilized for evaluation of a compound's uptake via roots and subsequent systemic transport to the tomato foliage. At the termination of the nematode test, 21 days after treatment, the tomato foliage was excised, placed into a plastic container, and infested with second instar larvae of southern armyworm. After about 5 days, the larvae were examined for percent mortality.

Cotton aphid and tobacco budworm (on cotton) and greenbug and tobacco budworm (on sorghum) - systemic evaluation: A 7.0 ml aliquot of the 150 ppm nematode test solution was applied to deliver the equivalent of 10.0 ppm soil concentration dose as a drench to 6 cm pots containing cotton and sorghum plants. The cotton plants were previously infested with cotton aphids about two days before treatment and greenbug one day before treatment. After holding the plants about three days, the plants were rated for aphid activity. Again at six days, the plants were rated

for aphid activity and the cotton aphids and greenbugs were counted and mortality was assessed. Portions of the cotton and sorghum foliage were excised, placed in separate plastic containers, and infested with second instar larvae of tobacco budworm. The potted plants were dipped in sulfotepp to kill the remaining aphids and returned to the greenhouse for regrowth. Thirteen days after treatment, the remaining foliage was excised and fed to tobacco budworms. Mortality was assessed six days after infestation.

Cotton aphid and southern armyworm (on cotton) and greenbug and southern armyworm (on sorghum) - systemic evaluation: A stock solution or suspension was prepared to deliver 5 ml of a 20 ppm soil concentration dose (and subsequent dilutions) as a drench to 6 cm pots containing cotton and sorghum plants. The cotton plants were previously infested with cotton aphids about two days before treatment and greenbug one day before treatment. After holding the plants about three days, the plants were rated for aphid activity. Again at six days, the plants were rated for aphid activity and the cotton aphids and greenbugs were counted and mortality was assessed. Portions of the cotton and sorghum foliage were excised, placed in separate plastic containers, and infested with second instar larvae of southern armyworms. The potted plants were dipped in sulfotepp to kill the remaining aphids and returned to the greenhouse for regrowth. Thirteen days after treatment the remaining foliage was excised and fed to southern armyworm. Mortality was assessed six days after infestation.

Cotton aphid and southern armyworm (on cotton and oats) - seed treatment evaluation: Technical material was applied to the seed of oats and cotton by placing the compound and the seed in an appropriate sized jar and rolling the jar on a ball mill. Assay of the material applied to the seed was by weight. Seed was then planted. When germinated and emerged, the plants were infested at the appropriate intervals with host insects. Mortality was assessed on those insects.

Tobacco budworm - contact evaluation: The following topical application method provides an assessment of contact toxicity of a compound to tobacco budworm larvae. The test compound solution at sequential two-fold dilution concentrations from 10 down to 0.16 µg/µl was applied by a microinjector in replicated 1 µl portions to the dorsum of approximately 20 mg tobacco budworm larvae. This is equivalent to applied doses of 500 down to 8 µg/g body weight. An acetone treated control, without any test compounds, was also applied. A treated control with a commercial technical compound, cypermethrin or thiodicarb, also in acetone was used as a standard. The treated larvae were placed, individually, in separate plastic petri dishes containing an untreated cotton leaf and a moist dental

wick. The treated larvae were maintained at about 27°C and 50% relative humidity. The percent mortality was rated 1 and 4 days after treatment.

All of the Compound Numbers 1 to 118 of the invention showed insecticidal activity in one or more of the above evaluation methods, with particularly good activity in the systemic tests. Compounds

METHODS AND COMPOSITIONS

The present invention provides a method for the systemic control of arthropods at a locus, especially some insects or mites which feed on the above ground portions of plants. Control of such foliar pests may be provided by direct foliar application or by application by for example soil spray or granule application to the plant roots or plant seeds with subsequent systemic translocation to the above ground portions of the plants. Such systemic activity includes the control of insects which reside not only at the point of application but at a remote part of the plant for example by translocation from one side of a leaf to the other or from a treated leaf to an untreated leaf. Examples of the classes of insect pests which may be systemically controlled by the arylpyrazoles of the invention include the Homoptera order (piercing-sucking), Hemiptera order (piercing-sucking), and Thysanoptera order. The invention is especially appropriate for aphids and thrips.

As is evident from the foregoing pesticidal uses, the present invention provides pesticidally active arylpyrazoles and methods of use of said arylpyrazoles for the control of a number of pest species which includes: arthropods, especially insects or mites; plant nematodes; or helminth or protozoan pests. The arylpyrazoles of formula (I) or pesticidally acceptable salts thereof thus are advantageously employed in practical uses, for example, in agricultural or horticultural crops, forestry, veterinary medicine or livestock husbandry, or in public health. From this point forward, whenever the term "arylpyrazoles of formula (I)" is used this term embraces arylpyrazoles of formula (I) and their pesticidally acceptable salts. The term "arylpyrazole of formula (I)" embraces a arylpyrazole of formula (I) and a pesticidally acceptable salt thereof.

The present invention therefore provides a method of control of pests at a locus which comprises the treatment of the locus (e.g., by application or administration) with an effective amount of a arylpyrazole of formula (I) or a pesticidally acceptable salt thereof, wherein the substituent groups are as hereinbefore defined. The locus includes, for example, the pest itself or the place (plant, animal, field, structure, premises, forest, orchard, waterway, soil, plant or animal product, or the like) where the pest resides or feeds.

The arylpyrazoles of this invention may in addition be used to control soil insects, such as corn rootworm, termites (especially for protection of structures), root maggots, wireworms, root weevils, stalkborers, cutworms, root aphids, or grubs. They may also be used to provide activity against plant pathogenic nematodes, such as root-knot, cyst, dagger, lesion, or stem or bulb nematodes, or against mites. For the control of soil pests, for example corn rootworm, the arylpyrazoles are advantageously applied to or incorporated at an effective rate into the soil in which crops are planted or to be planted or to the seeds or growing plant roots.

In the area of public health, the arylpyrazoles are especially useful in the control of many insects, especially filth flies or other Dipteran pests, such as houseflies, stableflies, soldierflies, hornflies, deerflies, horseflies, midges, punkies, blackflies, or mosquitoes.

Arylpyrazoles of the invention may be used in the following applications and on the following pests including arthropods, especially insects or mites, nematodes, or helminth or protozoan pests:

In the protection of stored products, for example cereals, including grain or flour, groundnuts, animal feedstuffs, timber or household goods, e.g. carpets and textiles, arylpyrazoles of the invention are useful against attack by arthropods, more especially beetles, including weevils, moths or mites, for example Ephestia spp. (flour moths), Anthrenus spp. (carpet beetles), Tribolium spp. (flour beetles), Sitophilus spp. (grain weevils) or Acarus spp. (mites).

In the control of cockroaches, ants or termites or similar arthropod pests in infested domestic or industrial premises or in the control of mosquito larvae in waterways, wells, reservoirs or other running or standing water.

For the treatment of foundations, structures or soil in the prevention of the attack on building by termites, for example, Reticulitermes spp., Heterotermes spp., Coptotermes spp..

In agriculture against adults, larvae and eggs of Lepidoptera (butterflies and moths), e.g. Heliothis spp. such as Heliothis virescens (tobacco budworm), Heliothis armigera and Heliothis zea. Against adults and larvae of Coleoptera (beetles) e.g. Anthonomus spp. e.g. grandis (cotton boll weevil), Leptinotarsa decemlineata (Colorado potato beetle), Diabrotica spp. (corn rootworms). Against Heteroptera (Hemiptera and Homoptera) e.g. Psylla spp., Bemisia spp., Trialeurodes spp., Aphis spp., Myzus spp., Megoura viciae, Phylloxera spp., Nephotettix spp. (rice leaf hoppers), Nilaparvata spp..

Against Diptera e.g. Musca spp.. Against Thysanoptera such as Thrips tabaci. Against Orthoptera such as Locusta and Schistocerca spp., (locusts and crickets) e.g.

Gryllus spp.. and Acheta spp. for example. Blatta orientalis, Periplaneta americana, Blatella germanica, Locusta migratoria migratorioides, and Schistocerca gregaria. Against Collembola e.g. Periplaneta spp. and Blattela spp. (roaches). Against Isoptera e.g. Coptotermes spp. (termites).

Against arthropods of agricultural significance such as Acari (mites) e.g. Tetranychus spp., and Panonychus spp..

Against nematodes which attack plants or trees of importance to agriculture, forestry or horticulture either directly or by spreading bacterial, viral, mycoplasma or fungal diseases of the plants. For example root-knot nematodes such as Meloidogyne spp. (e.g. M. incognita).

In the field of veterinary medicine or livestock husbandry or in the maintenance of public health against arthropods, helminths or protozoa which are parasitic internally or externally upon vertebrates, particularly warm-blooded vertebrates, for example domestic animals, e.g. cattle, sheep, goats, equines, swine, poultry, dogs or cats, for example Acarina, including ticks (e.g. Ixodes spp., Boophilus spp. e.g. Boophilus microplus, Rhipicephalus spp. e.g. Rhipicephalus appendiculatusOrnithodorus spp. (e.g. Ornithodorus moubata) and mites (e.g. Damalinia spp.); Diptera (e.g. Aedes spp., Anopheles spp., Musca spp., Hypoderma spp.); Hemiptera.; Dictyoptera (e.g. Periplaneta spp., Blatella spp.); Hymenoptera; for example against infections of the gastro-intestinal tract caused by parasitic nematode worms, for example members of the family Trichostrongylidae; in the control and treatment of protozoal diseases caused by, for example, Eimeria spp. e.g. Trypanosoms cruzi, Leishaminia spp., Plasmodium spp., Babesis spp., Trichomonadidae spp., Toxoplasma spp. and Theileria spp..

In practical use for the control of arthropods, especially insects or mites, or nematode pests of plants, a method, for example, comprises applying to the plants or to the medium in which they grow an effective amount of a arylpyrazole of the invention. For such a method, the active arylpyrazole is generally applied to the locus in which the arthropod or nematode infestation is to be controlled at an effective rate in the range of about 5 g to about 1 kg of the active arylpyrazole per hectare of locus treated. Under ideal conditions, depending on the pest to be controlled, a lower rate may offer adequate protection. On the other hand, adverse weather conditions, resistance of the pest or other factors may require that the active ingredient be used at higher rates. The optimum rate depends usually upon a number of factors, for example, the type of pest being controlled, the type or the growth stage of the infested plant, the row spacing or also the method of application. More preferably an effective rate range of the active arylpyrazole is from about 50g/ha to about 400 g/ha.

When a pest is soil-borne, the active arylpyrazole generally in a formulated composition, is distributed evenly over the area to be treated (ie. for example broadcast or band treatment) in any convenient manner and is applied at rates from about 5 to about 1kg ai/ha, preferably from about 50 to about 250 g ai/ha. When applied as a root dip to seedlings or drip irrigation to plants the liquid solution or suspension contains from about 0.075 to about 1000 mg ai/l, preferably from about 25 to about 200 mg ai/l. Application may be made, if desired, to the field or crop-growing area generally or in close proximity to the seed or plant to be protected from attack. The active component can be washed into the soil by spraying with water over the area or can be left to the natural action of rainfall. During or after application, the formulated arylpyrazole can, if desired, be distributed mechanically in the soil, for example by ploughing, disking, or use of drag chains. Application can be prior to planting, at planting, after planting but before sprouting has taken place, or after sprouting.

The arylpyrazoles of the invention and methods of control of pests therewith are of particular value in the protection of field, forage, plantation, glasshouse, orchard or vineyard crops, of ornamentals, or of plantation or forest trees, for example: cereals (such as wheat or rice), cotton, vegetables (such as peppers), field crops (such as sugar beets, soybeans or oil seed rape), grassland or forage crops (such as maize or sorghum), orchards or groves (such as of stone or pit fruit or citrus), ornamental plants, flowers or vegetables or shrubs under glass or in gardens or parks, or forest trees (both deciduous and evergreen) in forests, plantations or nurseries.

They are also valuable in the protection of timber (standing, felled, converted, stored or structural) from attack, for example, by sawflies or beetles or termites.

They have applications in the protection of stored products such as grains, fruits, nuts, spices or tobacco, whether whole, milled or arylpyrazoleed into products, from moth, beetle, mite or grain weevil attack. Also protected are stored animal products such as skins, hair, wool or feathers in natural or converted form (e.g. as carpets or textiles) from moth or beetle attack as well as stored meat, fish or grains from beetle, mite or fly attack.

Additionally, the arylpyrazoles of the invention and methods of use thereof are of particular value in the control of arthropods, helminths or protozoa which are injurious to, or spread or act as vectors of diseases domestic animals, for example those hereinbefore mentioned, and more especially in the control of ticks, mites, lice, fleas, midges, or biting, nuisance or myiasis flies. The arylpyrazoles of the invention are particularly useful in controlling arthropods, helminths or protozoa which are present inside domestic host animals or which feed in or on the skin or suck the blood

of the animal, for which purpose they may be administered orally, parenterally, percutaneously or topically.

Furthermore, arylpyrazoles of the invention may be useful for coccidiosis, a disease caused by infections from protozoan parasites of the genus Eimeria. It is an important potential cause of economic loss in domestic animals and birds, particularly those raised or kept under intensive conditions. For example, cattle, sheep, pigs or rabbits may be affected, but the disease is especially important in poultry, particularly in chickens. Administration of a small amount of a arylpyrazole of the invention, preferably by a combination with feed is effective in preventing or greatly reducing the incidence of coccidiosis. The arylpyrazoles are effective against both the cecal form and the intestinal forms. Furthermore, the arylpyrazoles of the invention may also exert an inhibiting effect on oocytes by greatly reducing the number and sporulation of those produced. The poultry disease is generally spread by the birds picking up the infectious organism in droppings in or on contaminated litter, ground, food, or drinking water. The disease is manifested by hemorrhage, accumulation of blood in the ceca, passage of blood to the droppings, weakness and digestive disturbances. The disease often terminates in the death of the animal, but the fowl which survive severe infections have had their market value subtantially reduced as a result of the infection.

The compositions hereinafter described for application to growing crops or crop growing loci or as a seed dressing may, in general, alternatively be employed for topical application to animals or in the protection of stored products, household goods, property or areas of the general environment. Suitable means of applying the arylpyrazoles of the invention include:

to growing crops as foliar sprays, dusts, granules, fogs or foams or also as suspensions of finely divided or encapsulated compositions as soil or root treatments by liquid drenches, dusts, granules, smokes or foams; to seeds of crops via application as seed dressings by liquid slurries or dusts;

to animals infested by or exposed to infestation by arthropods, helminths or protozoa, by parenteral, oral or topical application of compositions in which the active ingredient exhibits an immediate and/or prolonged action over a period of time against the arthropods, helminths or protozoa, for example by incorporation in feed or suitable orally-ingestible pharmaceutical formulations, edible baits, salt licks, dietary supplements, pour-on formulations, sprays, baths, dips, showers, jets, dusts, greases, shampoos, creams, wax smears or livestock self-treatment systems;

to the environment in general or to specific locations where pests may lurk, including stored products, timber, household goods, or domestic or industrial

premises, as sprays, fogs, dusts, smokes, wax-smears, lacquers, granules or baits, or in tricklefeeds to waterways, wells, reservoirs or other running or standing water;

- to domestic animals in feed to control fly larvae feeding in their feces;

In practice, the arylpyrazoles of the invention most frequently form parts of compositions. These compositions can be employed to control: arthopods, especially insects or mites; nematodes: or helminth or protozoan pests. The compositions may be of any type known in the art suitable for application to the desired pest in any premises or indoor or outdoor area or by internal or external administration to vertebrates. These compositions contain at least one arylpyrazole of formula (I) or a pesticidally acceptable salt thereof, such as described earlier, as the active ingredient in combination or association with one or more other compatible components which are for example, solid or liquid carriers or diluents, adjuvants, surface-active-agents, or the like appropriate for the intended use and which are agronomically or medicinally acceptable. These compositions, which may be prepared by any manner known in the art, likewise form a part of this invention.

These compositions may also contain other kinds of ingredients such as protective colloids, adhesives, thickeners, thixotropic agents, penetrating agents, spray oils (especially for acaridical use), stabilizers, preservative agents (especially mold preservatives), sequestering agents, or the like, as well as other known active ingredients with pesticidal properties (particularly insecticidal, miticidal, nematicidal, or fungicidal) or with properties regulating the growth of plants. More generally, the arylpyrazoles employed in the invention may be combined with all the solid or liquid additives corresponding to the usual techniques of formulation.

Compositions, suitable for applications in agriculture, horticulture, or the like include formulations suitable for use as, for example, sprays, dusts, granules, fogs, foams, emulsions, or the like.

The effective use doses of the arylpyrazoles employed in the invention can vary within wide limits, particularly depending on the nature of the pest to be eliminated or degree of infestation, for example, of crops with these pests. In general, the compositions according to the invention usually contain about 0.05 to about 95% (by weight) of one or more active ingredients according to the invention, about 1 to about 95% of one or more solid or liquid carriers and, optionally, about 0.1 to about 50% of one or more other compatible components, such as surface-active agents or the like.

In the present account, the term "carrier" denotes an organic or inorganic ingredient, natural or synthetic, with which the active ingredient is combined to facilitate its application, for example, to the plant, to seeds or to the soil. This carrier

is therefore generally inert and it must be acceptable (for example, agronomically acceptable, particularly to the treated plant).

The carrier may be a solid, for example, clays, natural or synthetic silicates, silica, resins, waxes, solid fertilizers (for example ammonium salts), ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite, bentonite or diatomaceous earth, or ground synthetic minerals, such as silica, alumina, or silicates especially aluminium or magnesium silicates. As solid carriers for granules the following are suitable: crushed or fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite; synthetic granules of inorganic or organic meals; granules of organic material such as sawdust, coconut shells, corn cobs, corn husks or tobacco stalks; kieselguhr, tricalcium phosphate, powdered cork, or absorbent carbon black; water soluble polymers, resins, waxes; or solid fertilizers. Such solid compositions may, if desired, contain one or more compatible wetting, dispersing, emulsifying or colouring agents which, when solid, may also serve as a diluent.

The carrier may also be liquid, for example: water; alcohols, particularly butanol or glycol, as well as their ethers or esters, particularly methylglycol acetate; ketones, particularly acetone, cyclohexanone, methylethyl ketone, methylisobutylketone, or isophorone; petroleum fractions such as paraffinic or aromatic hydrocarbons, particularly xylenes or alkyl naphthalenes; mineral or vegetable oils; aliphatic chlorinated hydrocarbons, particularly trichloroethane or methylene chloride; aromatic chlorinated hydrocarbons, particularly chlorobenzenes; water-soluble or strongly polar solvents such as dimethylformamide, dimethyl sulphoxide, or N-methylpyrrolidone; liquefied gases; or the like or a mixture thereof.

The surface-active agent may be an emulsifying agent, dispersing agent or wetting agent of the ionic or non-ionic type or a mixture of such surface-active agents. Amongst these are e.g., salts of polyacrylic acids, salts of lignosulphonic acids, salts of phenolsulphonic or naphthalenesulphonic acids, polycondensates of ethylene oxide with fatty alcohols or fatty acids or fatty esters or fatty amines, substituted phenols (particularly alkylphenols or arylphenols), salts of sulphosuccinic acid esters, taurine derivatives (particularly alkyltaurates), phosphoric esters of alcohols or of polycondensates of ethylene oxide with phenols, esters of fatty acids with polyols, or sulphate, sulphonate or phosphate functional derivatives of the above arylpyrazoles. The presence of at least one surface-active agent is generally essential when the active ingredient and/or the inert carrier are only slightly water soluble or are not water soluble and the carrier agent of the composition for application is water.

Compositions of the invention may further contain other additives such as adhesives or colorants. Adhesives such as carboxymethylcellulose or natural or synthetic polymers in the form of powders, granules or lattices, such as arabic gum, polyvinyl alcohol or polyvinyl acetate, natural phospholipids, such as cephalins or lecithins, or synthetic phospholipids can be used in the formulations. It is possible to use colorants such as inorganic pigments, for example: iron oxides, titanium oxides or Prussian Blue; organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs or metal phthalocyanine dyestuffs; or trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum or zinc.

Compositions containing arylpyrazoles of formula (I), or pesticidally acceptable salts thereof, which may be applied to control arthropod, plant nematode, helminth or protozoan pests, may also contain synergists (e.g. piperonyl butoxide or sesamex), stabilizing substances, other insecticides, acaricides, plant nematocides, anthelmintics or anticoccidials, fungicides (agricultural or veterinary as appropriate, e.g. benomyl and iprodione), bactericides, arthropod or vertebrate attractants or repellents or pheromones, deodorants, flavouring agents, dyes, or auxiliary therapeutic agents, e.g. trace elements. These may be designed to improve potency, persistence, safety, uptake where desired, spectrum of pests controlled or to enable the composition to perform other useful functions in the same animal or area treated.

Examples of other pesticidally-active arylpyrazoles which may be included in, or used in conjunction with the compositions of the present invention are: acephate, chlorpyrifos, demeton-S-methyl, disulfoton, ethoprofos, fenitrothion, fenamiphos, fonofos, isazophos, isofenphos, malathion, monocrotophos, parathion, phorate, phosalone, pirimiphos-methyl, terbufos, triazophos, cyfluthrin, cypermethrin, deltamethrin, fenpropathrin, fenvalerate, permethrin, tefluthrin, aldicarb, carbosulfan, methomyl, oxamyl, pirimicarb, bendiocarb, teflubenzuron, dicofol, endosulfan, lindane, benzoximate, cartap, cyhexatin, tetradifon, avermectins, ivermectins, milbemycins, thiophanate, trichlorfon, dichlorvos, diaveridine or dimetriadazole.

For their agricultural application, the arylpyrazoles of the formula (I), or pesticidally acceptable salts thereof, are therefore generally in the form of compositions, which are in various solid or liquid forms.

Solid forms of compositions which can be used are dusting powders (with a content of the arylpyrazole of formula (I), or a pesticidally acceptable salt thereof, ranging up to 80%), wettable powders or granules (including water dispersible granules), particularly those obtained by extrusion, compacting, impregnation of a granular carrier, or granulation starting from a powder (the content of the arylpyrazole of formula (I), or a pesticidally acceptable salt thereof, in these wettable powders or

granules being between about 0.5 and about 80%). Solid homogenous or heterogenous compositions containing one or more arylpyrazoles of formula (I), or pesticidally acceptable salts thereof, for example granules, pellets, briquettes or capsules, may be used to treat standing or running water over a period of time. A similar effect may be achieved using trickle or intermittent feeds of water dispersible concentrates as described herein.

Liquid compositions, for example, include aqueous or non-aqueous solutions or suspensions (such as emulsifiable concentrates, emulsions, flowables, dispersions, or solutions) or aerosols. Liquid compositions also include, in particular, emulsifiable concentrates, dispersions, emulsions, flowables, aerosols, wettable powders (or powder for spraying), dry flowables or pastes as forms of compositions which are liquid or intended to form liquid compositions when applied, for example as aqueous sprays (including low and ultra-low volume) or as fogs or aerosols.

Liquid compositions, for example, in the form of emulsifiable or soluble concentrates most frequently comprise about 5 to about 80% by weight of the active ingredient, while the emulsions or solutions which are ready for application contain, in their case, about 0.01 to about 20% of the active ingredient. Besides the solvent, the emulsifiable or soluble concentrates may contain, when required, about 2 to about 50% of suitable additives, such as stabilizers, surface-active agents, penetrating agents, corrosion inhibitors, colorants or adhesives. Emulsions of any required concentration, which are particularly suitable for application, for example, to plants, may be obtained from these concentrates by dilution with water. These compositions are included within the scope of the compositions which may be employed in the present invention. The emulsions may be in the form of water-in-oil or oil-in-water type and they may have a thick consistency.

The liquid compositions of this invention may, in addition to normal agricultural use applications be used for example to treat substrates or sites infested or liable to infestation by arthropods (or other pests controlled by arylpyrazoles of this invention) including premises, outdoor or indoor storage or processing areas, containers or equipment or standing or running water.

All these aqueous dispersions or emulsions or spraying mixtures can be applied, for example, to crops by any suitable means, chiefly by spraying, at rates which are generally of the order of about 100 to about 1,200 liters of spraying mixture per hectare, but may be higher or lower (eg. low or ultra-low volume) depending upon the need or application technique. The arylpyrazoles or compositions according to the invention are conveniently applied to vegetation and in particular to roots or leaves having pests to be eliminated. Another method of application of the arylpyrazoles or

compositions according to the invention is by chemigation, that is to say, the addition of a formulation containing the active ingredient to irrigation water. This irrigation may be sprinkler irrigation for foliar pesticides or it can be ground irrigation or underground irrigation for soil or for systemic pesticides.

The concentrated suspensions, which can be applied by spraying, are prepared so as to produce a stable fluid product which does not settle (fine grinding) and usually contain from about 10 to about 75% by weight of active ingredient, from about 0.5 to about 30% of surface-active agents, from about 0.1 to about 10% of thixotropic agents, from about 0 to about 30% of suitable additives, such as anti-foaming agents, corrosion inhibitors, stabilizers, penetrating agents, adhesives and, as the carrier, water or an organic liquid in which the active ingredient is poorly soluble or insoluble Some organic solids or inorganic salts may be dissolved in the carrier to help prevent settling or as antifreezes for water.

The wettable powers (or powder for spraying) are usually prepared so that they contain from about 10 to about 80% by weight of active ingredient, from about 20 to about 90% of a solid carrier, from about 0 to about 5% of a wetting agent, from about 3 to about 10% of a dispersing agent and, when necessary, from about 0 to about 80% of one or more stabilizers and/or other additives, such as penetrating agents, adhesives, anti-caking agents, colorants, or the like. To obtain these wettable powders, the active ingredient(s) is(are) thoroughly mixed in a suitable blender with additional substances which may be impregnated on the porous filler and is(are) ground using a mill or other suitable grinder. This produces wettable powders, the wettability and the suspendability of which are advantageous. They may be suspended in water to give any desired concentration and this suspension can be employed very advantageously in particular for application to plant foliage.

The "water dispersible granules (WG)" (granules which are readily dispersible in water) have compositions which are substantially close to that of the wettable powders. They may be prepared by granulation of formulations described for the wettable powders, either by a wet route (contacting finely divided active ingredient with the inert filler and a little water, e.g. 1 to 20% by weight, or with an aqueous solution of a dispersing agent or binder, followed by drying and screening), or by a dry route (compacting followed by grinding and screening).

The rates and concentrations of the formulated compositions may vary according to the method of application or the nature of the compositions or use thereof. Generally speaking, the compositions for application to control arthropod, plant nematode, helminth or protozoan pests usually contain from about 0.00001% to about 95%, more particularly from about 0.0005% to about 50% by weight of one or

more arylpyrazoles of formula (I), or pesticidally acceptable salts thereof, or of total active ingredients (that is to say the arylpyrazole of formula (I), or a pesticidally acceptable salt thereof, together with: other substances toxic to arthropods or plant nematodes, anthelmintics, anticoccidials, synergists, trace elements or stabilizers). The actual compositions employed and their rate of application will be selected to achieve the desired effect(s) by the farmer, livestock producer, medical or veterinary practitioner, pest control operator or other person skilled in the art.

Solid or liquid compositions for application topically to animals, timber, stored products or household goods usually contain from about 0.00005% to about 90%, more particularly from about 0.001% to about 10%, by weight of one or more arylpyrazoles of formula (I) or pesticidally acceptable salts thereof. For administration to animals orally or parenterally, including percutaneously solid or liquid compositions, these normally contain from about 0.1% to about 90% by weight of one or more arylpyrazoles of formula (I) or pesticidally acceptable salts thereof. Medicated feedstuffs normally contain from about 0.001% to about 3% by weight of one or more arylpyrazoles of formula (I) or pesticidally acceptable salts thereof. Concentrates or supplements for mixing with feedstuffs normally contain from about 5% to about 90%, preferably from about 5% to about 50%, by weight of one or more arylpyrazoles of formula (I) or pesticidally acceptable salts thereof. Mineral salt licks normally contain from about 0.1% to about 10% by weight of one or more arylpyrazoles of formula (I) or pesticidally acceptable salts thereof.

Dusts or liquid compositions for application to livestock, goods, premises or outdoor areas may contain from about 0.0001% to about 15%, more especially from about 0.005% to about 2.0%, by weight, of one or more arylpyrazoles of formula (I) or pesticidally acceptable salts thereof. Suitable concentrations in treated waters are between about 0.0001 ppm and about 20 ppm, more particularly about 0.001 ppm to about 5.0 ppm, of one or more arylpyrazoles of formula (I), or pesticidally acceptable salts thereof, and may be used therapeutically in fish farming with appropriate exposure times. Edible baits may contain from about 0.01% to about 5%, preferably from about 0.01% to about 1.0%, by weight, of one or more arylpyrazoles of formula (I) or pesticidally acceptable salts thereof.

When administered to vertebrates parenterally, orally or by percutaneous or other means, the dosage of arylpyrazoles of formula (I), or pesticidally acceptable salts thereof, will depend upon the species, age, or health of the vertebrate and upon the nature and degree of its actual or potential infestation by arthropod, helminth or protozoan pests. A single dose of about 0.1 to about 100 mg, preferably about 2.0 to about 20.0 mg, per kg body weight of the animal or doses of about 0.01 to about 20.0

mg. preferably about 0.1 to about 5.0 mg. per kg body weight of the animal per day. for sustained medication. are generally suitable by oral or parenteral administration. By use of sustained release formulations or devices. the daily doses required over a period of months may be combined and administered to animals on a single occasion.

The following composition EXAMPLES 2A - 2M illustrate compositions for use against arthropods, especially mites or insects, plant nematodes. or helminth or protozoan pests which comprise. as active ingredient, arylpyrazoles of formula (I). or pesticidally acceptable salts thereof, such as those described in preparative examples. The compositions described in EXAMPLES 2A - 2M can each be diluted to give a sprayable compositon at concentrations suitable for use in the field. Generic chemical descriptions of the ingredients (for which all of the following percentages are in weight percent), used in the composition EXAMPLES 2A - 2M exemplified below. are as follows:

Trade Name	Chemical Description
Ethylan BCP	Nonylphenol ethylene oxide condensate
Soprophor BSU	Tristyrylphenol ethylene oxide condensate
Arylan CA	A 70% w/v solution of calcium dodecylbenzenesulfonate
Solvesso 150	Light C_{10} aromatic solvent
Arylan S	Sodium dodecylbenzenesulfonate
Darvan No2	Sodium lignosulphonate
Celite PF	Synthetic magnesium silicate carrier
Sopropon T36	Sodium salts of polycarboxylic acids
Rhodigel 23	Polysaccharide xanthan gum
Bentone 38	Organic derivative of magnesium montmorillonite
Aerosil	Microfine silicon dioxide

EXAMPLE 2A

A water soluble concentrate is prepared with the composition as follows:

Active ingredient	7%
Ethylan BCP	10%
N-methylpyrrolidone	83%

To a solution of Ethylan BCP dissolved in a portion of N-methylpyrrolidone is added the active ingredient with heating and stirring until dissolved. The resulting solution is made up to volume with the remainder of the solvent.

EXAMPLE 2B

An emulsifiable concentrate (EC) is prepared with the composition as follows:

Active ingredient	25%(max)
Soprophor BSU	10%
Arylan CA	5%
N-methylpyrrolidone	50%
Solvesso 150	10%

The first three components are dissolved in N-methylpyrrolidone and to this is then added the Solvesso 150 to give the final volume.

EXAMPLE 2C

A wettable powder (WP) is prepared with the composition as follows:

Active ingredient	40%
Arylan S	2%
Darvan No2	5%
Celite PF	53%

The ingredients are mixed and ground in a hammer-mill to a powder with a particle size of less than 50 microns.

EXAMPLE 2D

An aqueous-flowable formulation is prepared with the composition as follows:

Active ingredient	40.00%
Ethylan BCP	1.00%
Sopropon T360.	0.20%
Ethylene glycol	5.00%
Rhodigel 230.	0.15%
Water	53.65%

The ingredients are intimately mixed and are ground in a bead mill until a mean particle size of less than 3 microns is obtained.

EXAMPLE 2E

An emulsifiable suspension concentrate is prepared with the composition as follows:

Active ingredient	30.0%
Ethylan BCP	10.0%
Bentone 38	0.5%
Solvesso 150	59.5%

The ingredients are intimately mixed and ground in a beadmill until a mean particle size of less than 3 microns is obtained.

EXAMPLE 2F

A water dispersible granule is prepared with the composition as follows:

Active ingredient	30%
Darvan No 2	15%
Arylan S	8%
Celite PF	47%

The ingredients are mixed, micronized in a fluid-energy mill and then granulated in a rotating pelletizer by spraying with water (up to 10%). The resulting granules are dried in a fluid-bed drier to remove excess water.

EXAMPLE 2G

A dusting powder is prepared with the composition as follows:

Active ingredient	1 to 10%
Talc powder-superfine	99 to 90%

The ingredients are intimately mixed and further ground as necessary to achieve a fine powder. This powder may be appplied to a locus of arthropod infestation. for example refuse dumps. stored products or household goods or animals infested by. or at risk of infestation by, arthropods to control the arthropods by oral ingestion. Suitable means for distributing the dusting powder to the locus of arthropod infestation include mechanical blowers, handshakers or livestock self treatment devices.

EXAMPLE 2H

An edible bait is prepared with the composition as follows:

Active ingredient	0.1 to 1.0%
Wheat flour	80%
Molasses	19.9 to 19%

The ingredients are intimately mixed and formed as required into a bait form. This edible bait may be distributed at a locus, for example domestic or industrial premises, e.g. kitchens, hospitals or stores, or outdoor areas, infested by arthropods, for example ants, locusts, cockroaches or flies, to control the arthropods by oral ingestion.

EXAMPLE 2I

A solution formulation is prepared with a composition as follows:

Active ingredient	15%
Dimethyl sulfoxide	85%

The active ingredient is dissolved in dimethyl sulfoxide with mixing and or heating as required. This solution may be applied percutaneously as a pour-on application to domestic animals infested by arthropods or, after sterilization by filtration through a polytetrafluoroethylene membrane (0.22 micrometer pore size), by

parenteral injection. at a rate of application of from 1.2 to 12 ml of solution per 100 kg of animal body weight.

EXAMPLE 2J

A wettable powder is prepared with the composition as follows:

Active ingredient	50%
Ethylan BCP	5%
Aerosil	5%
Celite PF	40%

The Ethylan BCP is absorbed onto the Aerosil which is then mixed with the other ingredients and ground in a hammer-mill to give a wettable powder, which may be diluted with water to a concentration of from 0.001% to 2% by weight of the active arylpyrazole and applied to a locus of infestation by arthropods, for example, dipterous larvae or plant nematodes, by spraying, or to domestic animals infested by, or at risk of infection by arthropods, helminths or protozoa, by spraying or dipping, or by oral administration in drinking water, to control the arthropods, helminths or protozoa.

EXAMPLE 2K

A slow release bolus composition is formed from granules containing the following components in varying percentages(similar to those described for the previous compositions) depending upon need:

Active ingredient
Density agent
Slow-release agent
Binder

The intimately mixed ingredients are formed into granules which are compressed into a bolus with a specific gravity of 2 or more. This can be administered orally to ruminant domestic animals for retention within the reticulo-rumen to give a continual slow release of active arylpyrazole over an extended period of time to control infestation of the ruminant domestic animals by arthropods. helminths or protozoa.

EXAMPLE 2L

A slow release composition in the form of granules, pellets, brickettes or the like can be prepared with compositions as follows:

Active ingredient	0.5 to 25%
Polyvinyl chloride	75 to 99.5%
Dioctyl phthalate (plasticizer)	

The components are blended and then formed into suitable shapes by melt-extrusion or molding. These composition are useful, for example, for addition to standing water or for fabrication into collars or eartags for attachment to domestic animals to control pests by slow release.

EXAMPLE 2M

A water dispersible granule is prepared with the composition as follows:

Active ingredient	85%(max)
Polyvinylpyrrolidone	5%
Attapulgite clay	6%
Sodium lauryl sulfate	2%
Glycerine	2%

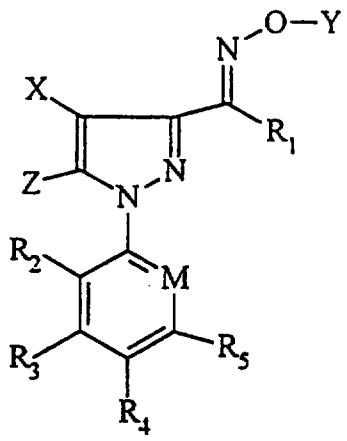
The ingredients are mixed as a 45% slurry with water and wet milled to a particle size of 4 microns, then spray-dried to remove water.

While the present invention has been set forth in specific and illustrative details and described with preferred particularity, it is susceptible to changes, modifications or alternations, obvious to one of ordinary skill in the art, without departing from the scope and spirit of the invention, which is defined by the claims appended hereto.

While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions and changes can be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims, including equivalents thereof.

What is claimed is:

1. A compound having the formula:



(I)

wherein:

X is $-S(O)_mR_6$ or R_7,

Y is hydrogen, C-3 to C-6 alkenyl, alkynyl, formyl, alkylcarbonyl, cycloalkylcarbonyl, halocycloalkyl carbonyl, aroyl, arylalkylcarbonyl, alkylsulfonyl, arylsulfonyl, haloalkylcarbonyl, aminoalkylcarbonyl, alkylaminoalkylcarbonyl, dialkylaminoalkylcarbonyl, alkoxyalkylcarbonyl, aryloxyalkylcarbonyl, alkylthioalkylcarbonyl, alkylsulfonylalkylcarbonyl, arylthioalkylcarbonyl, N-alkylcarbamoyl, N-arylcarbamoyl, N-alkylthiocarbamoyl, N-arylthiocarbamoyl, alpha-hydroxyarylalkylcarbonyl, hydroxyalkylcarbonyl, carboxyalkylcarbonyl, alkoxycarbonylalkylcarbonyl, $-P(=O)(O\text{-Alkyl})_2$, $-P(=S)(O\text{-alkyl})_2$, $-P(=O)(S\text{-alkyl})_2$, $-P(=S)(S\text{-alkyl})_2$, trialkylsilyl, alkylcarbonylaminoalkylcarbonyl, alkylcarbonyloxyalkylcarbonyl, aryl, pyridinyl, pyrimidinyl, -C(=O)S-alkyl, -C(=O)S-aryl, -C(=O)S-alkylaryl, alkoxyalkoxycarbonyl, alkylthioalkoxycarbonyl, alkylsulfonylalkoxycarbonyl, arylthioalkoxycarbonyl, alkoxycarbonyl, aryloxycarbonyl and aryloxycarbonylalkylcarbonyl; or alkyl or haloalkyl both of which are unsubstituted or substituted by alkoxy, alkoxycarbonyl, carboxy, cyano, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthio, nitro, alkylsulfinyl, alkylsulfonyl, alkylcarbonyl, amino, alkylamino, dialkylamino, hydroxy, alkylcarbonylamino or alkylcarbonyloxy;

Z is hydrogen, halogen, $-C(O)R_7$-,$-S(O)_nR_8$, $-C(O)OR_9$, alkyl, haloalkyl, $-OR_9$, $-N=C(R_{10})(R_{11})$, alkenyl, hydrazino, alkylthiocarbonyl, 1H-pyrrol-1-yl or 1H-pyrazol-1-yl, -CHO, -CH=NOH, amino, $R_{12}NH$-or $R_{13}R_{14}N$-;

* C L M S *

R_1 is hydrogen, alkyl or -$NR_{15}R_{16}$;

R_2 is hydrogen or halogen;

R_3 and R_5 are hydrogen, halogen or alkyl;

R_4 is halogen, haloalkyl, haloalkoxy, $R_{17}S(O)_p$- or SF_5;

R_6 is alkyl or haloalkyl, alkenyl or haloalkenyl, alkynyl or haloalkynyl or cycloalkyl having 3 to 5 carbon atoms;

R_7 is alkyl or haloalkyl;

R_8 is R_7 or phenyl;

R_9 and R_{10} are hydrogen, alkyl or haloalkyl;

R_{11} is alkyl, haloalkyl, alkoxy, or a phenyl group which is unsubstituted or substituted by one or more groups selected from hydroxy, halogen, alkoxy, cyano, R_7 or
-$S(O)_qR_7$;

R_{12}, R_{13} and R_{14}, which are identical or different, are $R_7S(O)_r$-, formyl, alkynyl, alkoxycarbonyl, alkylthiocarbonyl or aroyl; or alkyl, C-3 to C-6 alkenyl or -C(O)alkyl wherein the alkyl and alkenyl portions are unsubstituted or substituted by one or more R_{18};or

R_{13} and R_{14} are joined so as together form a divalent radical having 4 to 6 atoms in the chain, this divalent radical being alkylene, alkyleneoxyalkylene or alkyleneaminoalkylene;

R_{15} and R_{16} are independently hydrogen or alkyl;

R_{17} is haloalkyl;

R_{18} is cyano, nitro, alkoxy, haloalkoxy, -C(O)R_7, $R_8S(O)_s$-, -C(O)OR_9, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, halogen, hydroxy, aminosulfonyl, alkylaminosulfonyl or dialkylaminosulfonyl;

m, n, p, q, r and s are independent of one another zero, one or two;

M is C-halo, C-CH_3, C-CH_2F, C-CH_2Cl, C-NO_2, or N;

or a geometric isomer, tautomeric form or pesticidally active salt thereof.

2. A compound of formula (I) according to Claim 1, in which:

X is -$S(O)_mR_6$;

Y is hydrogen; alkyl having 1 to 4 carbon atoms, cycloalkyl having up to 4 carbons both of which are unsubstituted or substituted by aminocarbonyl, alkylsulfonyl, alkoxy, alkoxycarbonyl, alkylcarbonyl, cyano or nitro; C-3 to C-4 alkenyl; C-3 to C-5 alkynyl; alkylcarbonyl; unsubstituted or substituted aroyl; arylalkylcarbonyl; alkylsulfonyl; alkoxycarbonylalkylcarbonyl; haloalkylcarbonyl; N-alkylcarbamoyl; alkoxycarbonyl; aryloxycarbonyl;

* C L M S *

alkoxyalkylcarbonyl: alpha-hydroxyarylalkylcarbonyl: hydroxyalkylcarbonyl: aminoalkylcarbonyl: -C(=O)S-alkyl and trialkylsilyl:

Z is amino, $R_{12}NH$-, $R_{13}R_{14}N$-, halogen or methyl;

R_1 is hydrogen, methyl, amino or methylamino;

R_2 is F, Cl, Br or H;

R_3 and R_5 are hydrogen;

R_4 is CF_3, CF_3O, CHF_2, $CF_3S(O)_p$, CF_2Cl, $CFCl_2$, CF_2ClO, $CFCl_2O$, Cl, Br, or F;

R_6 is methyl or ethyl optionally substituted by F, Cl or Br;

M is CCl, CF, CBr, or N;

R_{12}, R_{13} and R_{14} are $CF_3S(O)_r$-, alkynyl or alkoxycarbonyl; or alkyl, C-3 to C-6 alkenyl or -C(O)alkyl wherein the alkyl and alkenyl portions are unsubstituted or substituted by one or more R_{18}; and

R_{18} is cyano, nitro, alkoxy, haloalkoxy, -C(O)R_7, $R_8S(O)_s$-, -C(O)OR_9, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, halogen, hydroxy, aminosulfonyl, alkylaminosulfonyl or dialkylaminosulfonyl.

3. The compound of formula (I) according to Claim 1 or Claim 2, which is:

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-ethylamino-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methylamino-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylthio-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-difluoromethylthio-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylthio-1H-pyrazole-3-carboxaldehyde O-(methyl)oxime;

* C L M S *

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(acetyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(2-methylbenzoyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(methoxycarbonyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-[2-(ethoxycarbonyl)propionyl]oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carboxaldehyde O-(acetyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylthio-1H-pyrazole-3-carboxaldehyde O-(methoxycarbonyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfonyl-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(methyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(N-methylcarbamoyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(carboxymethyl)oxime;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(tert-butyldimethylsilyl)oxime;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-formyl-N-hydroxy-4-trifluoromethylthio-1H-pyrazole-3-carboximidamide;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-5-hydroxyiminomethyl-4-trifluoromethylthio-1H-pyrazole-3-carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(isopropyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(ethoxycarbonylmethyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(aminocarbonylmethyl)oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-[2-(ethylsulfonyl)ethyl]oxime;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde O-(2-cyanoethyl)oxime;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylthio-1H-pyrazole-3-carboxaldehyde oxime;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methyl-4-methylsulfonyl-1H-pyrazole-3-carboxaldehyde oxime;
5-Amino-1-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylthio-5-methyl-1H-pyrazole-3-carboxaldehyde oxime;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-5-methyl-1H-pyrazole-3-carboxaldehyde oxime;
1-[2-Chloro-4-(trifluoromethyl)phenyl]-5-[2-(ethylsulfonyl)ethylamino]-4-methylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-dimethylamino-4-methylthio-1H-pyrazole-3-carboxaldehyde oxime;
5-Amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-4-ethylsulfinyl-1H-pyrazole-3-carboxaldehyde oxime;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethyl-1H-pyrazole-3-carboxaldehyde oxime;
3-Acetyl-5-amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl--1H-pyrazole oxime;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-trifluoromethylsulfinyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-4-trifluoromethylsulfinyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-ethylsulfinyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-ethylthio-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethoxy)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methyl-

* C L M S *

sulfonyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylthio-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-ethylsulfonyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-methoxy-N'-methyl-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-[2-(fluoroethyl)sulfinyl]-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-[2-(fluoroethyl)sulfonyl]-1H-pyrazole-3-carboximidamide;
5-Amino-1-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]-4-ethylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide;
5-Amino-1-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-5-methylamino-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-ethylamino-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-[2-(ethylsulfonyl)ethylamino]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
5-[2-(Cyano)ethylamino]-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
5-(Aminocarbonylmethylamino)-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[2-(phenylsulfonyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2,6-dibromo-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide;
1-[2-Bromo-6-chloro-4-(trifluoromethyl)phenyl]-5-ethylamino-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide;
5-Amino-1-[2-bromo-6-chloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-1H-pyrazole-3-carboximidamide;

* C L M S *

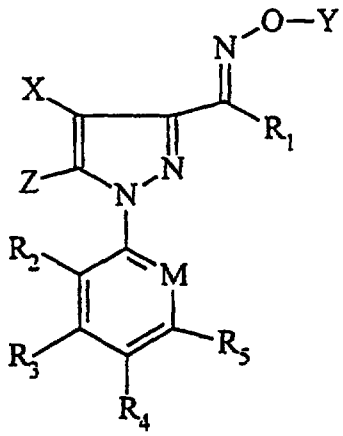
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-5-[2-(methylsulfinyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[2-(methylsulfinyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-5-[2-(ethylsulfinyl)ethylamino]-N-hydroxy-1H-pyrazole-3-carboximidamide;
1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-5-[(prop-2-ynyl)amino]-N-hydroxy-1H-pyrazole-3-carboximidamide; and
5-Amino-1-[2-chloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-hydroxy-1H-pyrazole-3-carboximidamide.

4. A pesticidal composition comprising:

(a) a compound of formula (I)



(I)

wherein:

X is $-S(O)_mR_6$ or R_7,

Y is hydrogen, C-3 to C-6 alkenyl, alkynyl, formyl, alkylcarbonyl, aroyl, arylalkylcarbonyl, alkylsulfonyl, arylsulfonyl, haloalkylcarbonyl, aminoalkylcarbonyl, alkylaminoalkylcarbonyl, dialkylaminoalkylcarbonyl, alkoxyalkylcarbonyl, aryloxyalkylcarbonyl, alkylthioalkylcarbonyl, alkylsulfonylalkylcarbonyl, arylthioalkylcarbonyl, N-alkylcarbamoyl, N-arylcarbamoyl, N-alkylthiocarbamoyl, N-arylthiocarbamoyl, alpha-hydroxyarylalkylcarbonyl, hydroxyalkylcarbonyl, carboxyalkylcarbonyl, alkoxycarbonylalkylcarbonyl, $-P(=O)(O\text{-Alkyl})_2$, $-P(=S)(O\text{-alkyl})_2$, $-P(=O)(S\text{-alkyl})_2$, $-P(=S)(S\text{-alkyl})_2$, trialkylsilyl,

* C L M S *

alkylcarbonylaminoalkylcarbonyl, alkylcarbonyloxyalkylcarbonyl, aryl, pyridinyl, pyrimidinyl, -C(=O)S-alkyl, -C(=O)S-aryl, -C(=O)S-alkylaryl, alkoxyalkoxycarbonyl, alkylthioalkoxycarbonyl, alkylsulfonylalkoxycarbonyl, arylthioalkoxycarbonyl, alkoxycarbonyl, aryloxycarbonyl and aryloxycarbonylalkylcarbonyl; or alkyl or haloalkyl both of which are unsubstituted or substituted by alkoxy, alkoxycarbonyl, carboxy, cyano, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthio, nitro, alkylsulfinyl, alkylsulfonyl, alkylcarbonyl, amino, alkylamino, dialkylamino, hydroxy, alkylcarbonylamino or alkylcarbonyloxy;

Z is hydrogen, halogen, $-C(O)R_7-$,$-S(O)_nR_8$, $-C(O)OR_9$, alkyl, haloalkyl, $-OR_9$, $-N=C(R_{10})(R_{11})$, alkenyl, hydrazino, alkylthiocarbonyl, 1H-pyrrol-1-yl or 1H-pyrazol-1-yl, -CHO, -CH=NOH, amino, $R_{12}NH$-or $R_{13}R_{14}N$-;

R_1 is hydrogen, alkyl or-$NR_{15}R_{16}$;

R_2 is hydrogen or halogen;

R_3 and R_5 are hydrogen, halogen or alkyl;

R_4 is halogen, haloalkyl, haloalkoxy, $R_{17}S(O)_p$-or SF_5;

R_6 is alkyl or haloalkyl, alkenyl or haloalkenyl, alkynyl or haloalkynyl or cycloalkyl having 3 to 5 carbon atoms;

R_7 is alkyl or haloalkyl;

R_8 is R_7 or phenyl;

R_9 and R_{10} are hydrogen, alkyl or haloalkyl;

R_{11} is alkyl, haloalkyl, alkoxy, or a phenyl group which is unsubstituted or substituted by one or more groups selected from hydroxy, halogen, alkoxy, cyano, R_7 or $-S(O)_qR_7$;

R_{12}, R_{13} and R_{14}, which are identical or different, are $R_7S(O)_r$-, formyl, alkynyl, alkoxycarbonyl, alkylthiocarbonyl or aroyl; or alkyl, C-3 to C-6 alkenyl or -C(O)alkyl wherein the alkyl and alkenyl portions are unsubstituted or substituted by one or more R_{18};or

R_{13} and R_{14} are joined so as together form a divalent radical having 4 to 6 atoms in the chain, this divalent radical being alkylene, alkyleneoxyalkylene or alkyleneaminoalkylene;

R_{15} and R_{16} are independently hydrogen or alkyl;

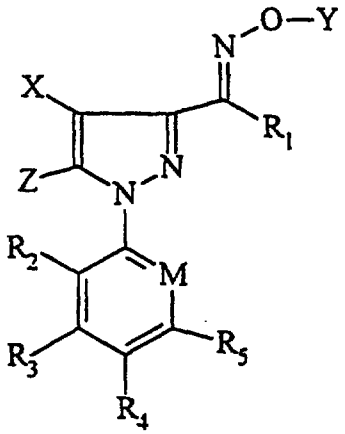
R_{17} is haloalkyl;

R_{18} is cyano, nitro, alkoxy, haloalkoxy, $-C(O)R_7$, $R_8S(O)_s$-, $-C(O)OR_9$, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, halogen, hydroxy, aminosulfonyl, alkylaminosulfonyl or dialkylaminosulfonyl;

* C L M S *

m. n. p. q. r and s are independent of one another zero. one or two:
M is C-halo. C-CH_3. C-CH_2F. C-CH_2Cl. C-NO_2. or N;
or a geometric isomer. tautomeric form or pesticidally active salt thereof: and
(b) an agriculturally acceptable inert carrier therefor.

5. A method for the control of pests at a locus comprising applying to said locus a pesticidally effective amount of a compound of formula (I)



(I)

wherein:
X is $-S(O)_mR_6$ or R_7,
Y is hydrogen, C-3 to C-6 alkenyl. alkynyl. formyl, alkylcarbonyl, aroyl. arylalkylcarbonyl, alkylsulfonyl, arylsulfonyl, haloalkylcarbonyl. aminoalkylcarbonyl, alkylaminoalkylcarbonyl, dialkylaminoalkylcarbonyl. alkoxyalkylcarbonyl, aryloxyalkylcarbonyl, alkylthioalkylcarbonyl, alkylsulfonylalkylcarbonyl, arylthioalkylcarbonyl, N-alkylcarbamoyl, N-arylcarbamoyl, N-alkylthiocarbamoyl, N-arylthiocarbamoyl, alpha-hydroxyarylalkylcarbonyl, hydroxyalkylcarbonyl, carboxyalkylcarbonyl, alkoxycarbonylalkylcarbonyl, $-P(=O)(O\text{-Alkyl})_2$, $-P(=S)(O\text{-alkyl})_2$, $-P(=O)(S\text{-alkyl})_2$, $-P(=S)(S\text{-alkyl})_2$, trialkylsilyl, alkylcarbonylaminoalkylcarbonyl, alkylcarbonyloxyalkylcarbonyl, aryl, pyridinyl, pyrimidinyl, -C(=O)S-alkyl, -C(=O)S-aryl, -C(=O)S-alkylaryl, alkoxyalkoxycarbonyl, alkylthioalkoxycarbonyl, alkylsulfonylalkoxycarbonyl, arylthioalkoxycarbonyl, alkoxycarbonyl, aryloxycarbonyl and aryloxycarbonylalkylcarbonyl; or alkyl or haloalkyl both of which are unsubstituted or substituted by alkoxy, alkoxycarbonyl, carboxy, cyano, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, alkylthio, nitro,

* C L M S *

alkylsulfinyl, alkylsulfonyl, alkylcarbonyl, amino, alkylamino, dialkylamino, hydroxy, alkylcarbonylamino or alkylcarbonyloxy;

Z is hydrogen, halogen, $-C(O)R_7$-, $-S(O)_nR_8$, $-C(O)OR_9$, alkyl, haloalkyl, $-OR_9$, $-N=C(R_{10})(R_{11})$, alkenyl, hydrazino, alkylthiocarbonyl, 1H-pyrrol-1-yl or 1H-pyrazol-1-yl, -CHO, -CH=NOH, amino, $R_{12}NH$- or $R_{13}R_{14}N$-;

R_1 is hydrogen, alkyl or $-NR_{15}R_{16}$;

R_2 is hydrogen or halogen;

R_3 and R_5 are hydrogen, halogen or alkyl;

R_4 is halogen, haloalkyl, haloalkoxy, $R_{17}S(O)_p$- or SF_5;

R_6 is alkyl or haloalkyl, alkenyl or haloalkenyl, alkynyl or haloalkynyl or cycloalkyl having 3 to 5 carbon atoms;

R_7 is alkyl or haloalkyl;

R_8 is R_7 or phenyl;

R_9 and R_{10} are hydrogen, alkyl or haloalkyl;

R_{11} is alkyl, haloalkyl, alkoxy, or a phenyl group which is unsubstituted or substituted by one or more groups selected from hydroxy, halogen, alkoxy, cyano, R_7 or $-S(O)_qR_7$;

R_{12}, R_{13} and R_{14}, which are identical or different, are $R_7S(O)_r$-, formyl, alkynyl, alkoxycarbonyl, alkylthiocarbonyl or aroyl; or alkyl, C-3 to C-6 alkenyl or -C(O)alkyl wherein the alkyl and alkenyl portions are unsubstituted or substituted by one or more R_{18};or

R_{13} and R_{14} are joined so as together form a divalent radical having 4 to 6 atoms in the chain, this divalent radical being alkylene, alkyleneoxyalkylene or alkyleneaminoalkylene;

R_{15} and R_{16} are independently hydrogen or alkyl;

R_{17} is haloalkyl;

R_{18} is cyano, nitro, alkoxy, haloalkoxy, $-C(O)R_7$, $R_8S(O)_s$-, $-C(O)OR_9$, aminocarbonyl, alkylaminocarbonyl, dialkylaminocarbonyl, halogen, hydroxy, aminosulfonyl, alkylaminosulfonyl or dialkylaminosulfonyl;

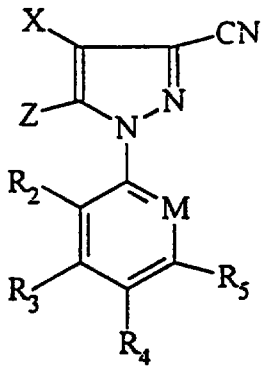
m, n, p, q, r and s are independent of one another zero, one or two;

M is C-halo, $C-CH_3$, $C-CH_2F$, $C-CH_2Cl$, $C-NO_2$, or N;

or a geometric isomer, tautomeric form or pesticidally active salt thereof.

6. A process for preparing a compound of formula (I) as defined in Claim 1 which comprises:

(a) when R_2, R_3, R_4, R_5, M, X, Y and Z are defined in Claim 1 and R_1 represents amino, reacting a compound of formula (II):



(II)

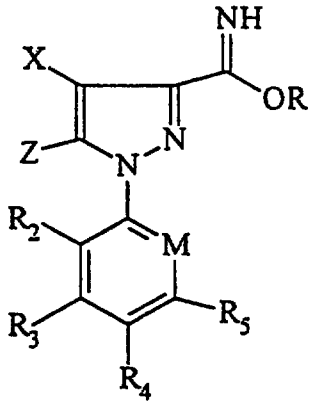
with a compound of formula (III):

$$NH_2OY$$

(III)

wherein Y is defined in Claim 1;

(b) when R_2, R_3, R_4, R_5, M, X, Y and Z are as defined in Claim 1and R_1 represents amino, reacting a compound of formula (IV):



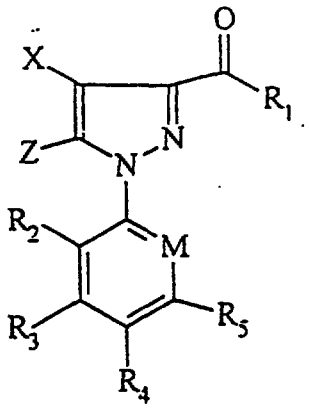
(IV)

wherein R represents alkyl, with a compound of formula (III) in which R is alkyl and Y is defined in Claim 1;

(c) when R_2, R_3, R_4, R_5, M, X, Y and Z are as defined in Claim 1 and R_1 represents alkylamino or dialkylamino, reacting the corresponding compound of formula (I) wherein R_1 represents amino with an alkylating agent preferably of formula R-hal where R represents alkyl and hal is Cl, Br or I;

(d) when R_2, R_3, R_4, R_5, M, X, Y and Z are as defined in Claim 1 and R_1 represents hydrogen or alkyl, reacting a compound of formula (V):

* C L M S *



(V)

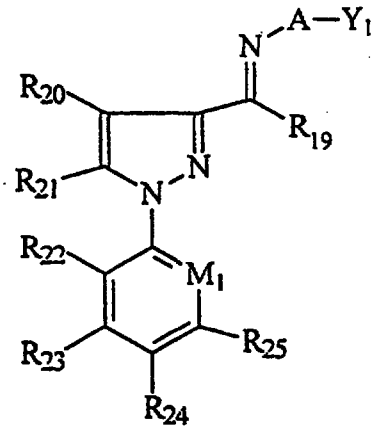
in which R_1 represents hydrogen or alkyl with a compound of formula (III) in which Y is defined above;

(e) when R_2, R_3, R_4, R_5, M, X and Z are as defined in Claim 1, R_1 represents hydrogen or alkyl, and Y is defined as in Claim 1 with the exclusion of hydrogen, formyl, aryl, pyridinyl and pyrimidinyl, reacting the corresponding compound of formula (I) wherein Y represents hydrogen with an appropriate alkylating or acylating reagent or Michael acceptor.

(f) when Z is $R_{12}NH$-or $R_{13}R_{14}N$-in which R_{12}, R_{13} and R_{14} are alkyl or C-3 to C-6 alkenyl optionally substituted by R_{18}, including the cyclic amino compounds of formula (I), alkylating a compound of formula (I) in which Z represents amino; or by forming the imino ether followed by reducing the imino ether; or by Michael addition;

(g) when m is 1 or 2 , oxidizing the corresponding compound of formula (I) in which m is 0 or 1.

7. A compound of formula (I bis):



(I bis)

wherein:

A is $-NR_{26}-$;

Y_1 is hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aryl, $-S(O)_aR_{28}$, $-P(O)R_{29}R_{30}$, $-P(S)R_{29}R_{30}$, $-Si(R_{31})(R_{32})(R_{33})$, $-C(O)R_{27}$, $-C(S)R_{27}$, cyano or nitro;

R_{19} is hydrogen, alkyl, haloalkyl, or $-NR_{34}R_{35}$;

R_{20} is $-S(O)_bR_{36}$ or R_{37};

R_{21} is hydrogen, halogen, $-C(O)R_{38}$, $-S(O)_cR_{39}$, alkyl, haloalkyl, $-OR_{40}$, $-N=C(R_{41})(R_{42})$, alkenyl, $-NR_{43}R_{44}$, 1H-pyrrol-1-yl, 1H-pyrazol-1-yl, or -CH=NOH;

R_{22}, R_{23} and R_{25} are independently selected from hydrogen, halogen or alkyl;

R_{24} is halogen, haloalkyl, haloalkoxy, $-S(O)_dR_{45}$ or SF_5;

R_{26} is hydrogen or substituted or unsubstituted alkyl;

R_{27} is hydrogen, substituted or unsubstituted alkyl of C_1 to C_{20}, substituted or unsubstituted aryl, $-OR_{46}$, $-NR_{47}R_{48}$, or $-SR_{49}$;

R_{28} is substituted or unsubstituted alkyl or substituted or unsubstituted aryl;

R_{29} and R_{30} are independently selected from alkoxy and thioalkoxy;

R_{31}, R_{32} and R_{33} are independently selected from alkyl, haloalkyl and aryl;

R_{34} and R_{35} are independently selected from hydrogen or substituted or unsubstituted alkyl;

R_{36} is alkyl, alkenyl, alkynyl, or C_3-C_6 cycloalkyl each of which is optionally substituted by one or more halogens;

R_{37} is alkyl or haloalkyl;

R_{38} is hydrogen, alkyl, haloalkyl, alkoxy or thioalkoxy;

R_{39} is alkyl haloalkyl or aryl;

R_{40} and R_{41} are independently selected from hydrogen, alkyl and haloalkyl;

R_{42} is alkyl, haloalkyl, alkoxy or phenyl each of which is optionally substituted by one or more groups selected from hydroxy, halogen, alkoxy, -CN, alkyl, $-S(O)_e$alkyl;

R_{43} and R_{44} are independently selected from hydrogen, NH_2, $-S(O)_fR_{50}$, $-C(O)R_{51}$, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl and alkynyl; or R_{43} and R_{44} form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_{45} is haloalkyl;

R_{46} and R_{49} are independently selected from substituted or unsubstituted alkyl and substituted or unsubstituted aryl:

R_{47} and R_{48} are independently selected from hydrogen, substituted or unsubstituted alkyl and substituted or unsubstituted aryl; or R_{47} and R_{48} may form together a divalent alkylene radical which may be interrupted by one or more heteroatoms;

R_{50} is substituted or unsubstituted alkyl;

R_{51} is hydrogen, alkyl, haloalkyl, aryl, alkenyl, $-OR_{52}$, $-SR_{53}$, or $-NR_{54}R_{55}$;

R_{52} and R_{53} are independently selected from alkyl and haloalkyl;

R_{54} and R_{55} are independently selected from hydrogen, alkyl, haloalkyl and aryl;

a, b, c, d, e and f independently represent zero, one or two;

M_1 is C-halo, $C\text{-}CH_3$, $C\text{-}CH_2F$, $C\text{-}CH_2Cl$, $C\text{-}NO_2$, or N;

or a pesticidally acceptable salt thereof.

8. A compound according to Claim 7 wherein the compound of formula (I bis) has one or more of the following features:

A is $-NR_{26}-$;

Y_1 is hydrogen, alkyl, or $-C(O)R_{27}$;

R_{19} is hydrogen or NH_2;

R_{20} is $-S(O)_bR_{36}$;

R_{21} is $-NR_{43}R_{44}$;

R_{22} is halogen;

R_{23} and R_{25} are hydrogen;

R_{24} is haloalkyl;

R_{27} is alkyl or O-alkyl; or

M is C-halo.

9. A compound according to Claims 1, 2, 3, 7 or 8 wherein the compound of formula (I) or (I bis) is:

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(acetyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-N-(acetyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(ethylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(propylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(2-methylethenylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(benzoyloxy) -1H-pyrazole carboximidamide;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-methylamino-4-methylsulfinyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfonyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(heptylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfonyl-N-(heptylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfenyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfenyl-N-(heptylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylsulfinyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-formylamino-4-ethylsulfenyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(hexylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(pentylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(butylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfenyl-N-(cyclopentylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(cyclopentylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tert-butylcarbonyloxy) -1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(iso-propylcarbonyloxy) -1H-pyrazole carboximidamide;

1-[2,6-Dichloro-4-(trifluoromethyl)phenyl]-5-formylamino-4-ethylsulfinyl-N-(acetyloxy)-1H-pyrazole carboximidamide;

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5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(chloroacetyloxy)-1H-pyrazole carboximidamide:

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(bromoacetyloxy)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1-ethylpropylcarbonyloxy)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-[(3-acetyloxy)phenylcarbonyloxy]-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-trifluoro methylsulfonyl-1H-pyrazole-3-carboximidamide; or

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-N-hydroxy-4-trifluoro methylsulfenyl-1H-pyrazole-3-carboximidamide.

10. A compound according to Claim 7 or Claim 8 wherein the compound of formula (I bis) is:

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-amino-1H-pyrazole-3-carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(isopropylcarbonyl)amino-1H-pyrazole-3-carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(n-heptylcarbonyl)amino-1H-pyrazole-3-carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(ethoxycarbonyl)amino-1H-pyrazole-3-carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylsulfinyl-N-amino-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-N-amino-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-trifluoromethylsulfinyl-N-acetylamino-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1-methylethenylcarbonylamino)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tert-butylcarbonylamino)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(2-methylethenylcarbonylamino)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(ethylcarbonylamino)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(propylcarbonylamino)-1H-pyrazole carboximidamide:

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1-ethylpropylcarbonylamino)-1H-pyrazole carboximidamide:

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(butylcarbonylamino)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(pentylcarbonylamino)-1H-pyrazole carboximidamide:

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(hexylcarbonylamino)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-ethylsulfinyl-N-acetylamino-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-chloroacetylamino-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tridecylcarbonylamino)-1H-pyrazole carboximidamide;

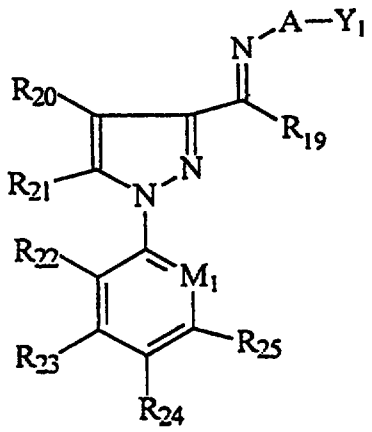
5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(n-propoxycarbonylamino)-1H-pyrazole carboximidamide;

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(1,1-dimethylpropyloxycarbonylamino)-1H-pyrazole carboximidamide; or

5-Amino-1-[2,6-dichloro-4-(trifluoromethyl)phenyl]-4-methylsulfinyl-N-(tertbutyloxycarbonylamino)-1H-pyrazole carboximidamide;

11. A pesticidal composition comprising:

(a) a compound of formula (I bis)



(I bis)

wherein:

A is $-NR_{26}-$;

Y_1 is hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aryl, $-S(O)_aR_{28}$, $-P(O)R_{29}R_{30}$, $-P(S)R_{29}R_{30}$, $-Si(R_{31})(R_{32})(R_{33})$, $-C(O)R_{27}$, $-C(S)R_{27}$, cyano or nitro;

R_{19} is hydrogen, alkyl, haloalkyl, or $-NR_{34}R_{35}$;

R_{20} is $-S(O)_bR_{36}$ or R_{37};

R_{21} is hydrogen, halogen, $-C(O)R_{38}$, $-S(O)_cR_{39}$, alkyl, haloalkyl, $-OR_{40}$, $-N=C(R_{41})(R_{42})$, alkenyl, $-NR_{43}R_{44}$, 1H-pyrrol-1-yl, 1H-pyrazol-1-yl, or -CH=NOH;

R_{22}, R_{23} and R_{25} are independently selected from hydrogen, halogen or alkyl;

R_{24} is halogen, haloalkyl, haloalkoxy, $-S(O)_dR_{45}$ or SF_5;

R_{26} is hydrogen or substituted or unsubstituted alkyl;

R_{27} is hydrogen, substituted or unsubstituted alkyl of C_1 to C_{20}, substituted or unsubstituted aryl, $-OR_{46}$, $-NR_{47}R_{48}$, or $-SR_{49}$;

R_{28} is substituted or unsubstituted alkyl or substituted or unsubstituted aryl;

R_{29} and R_{30} are independently selected from alkoxy and thioalkoxy;

R_{31}, R_{32} and R_{33} are independently selected from alkyl, haloalkyl and aryl;

R_{34} and R_{35} are independently selected from hydrogen or substituted or unsubstituted alkyl;

R_{36} is alkyl, alkenyl, alkynyl, or C_3-C_6 cycloalkyl each of which is optionally substituted by one or more halogens;

R_{37} is alkyl or haloalkyl;

R_{38} is hydrogen, alkyl, haloalkyl, alkoxy or thioalkoxy;

R_{39} is alkyl haloalkyl or aryl;

R_{40} and R_{41} are independently selected from hydrogen, alkyl and haloalkyl;

R_{42} is alkyl, haloalkyl, alkoxy or phenyl each of which is optionally substituted by one or more groups selected from hydroxy, halogen, alkoxy, -CN, alkyl, $-S(O)_e$alkyl;

R_{43} and R_{44} are independently selected from hydrogen, NH_2, $-S(O)_fR_{50}$, $-C(O)R_{51}$, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl and alkynyl; or R_{43} and R_{44} form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_{45} is haloalkyl;

R_{46} and R_{49} are independently selected from substituted or unsubstituted alkyl and substituted or unsubstituted aryl;

R_{47} and R_{48} are independently selected from hydrogen, substituted or unsubstituted alkyl and substituted or unsubstituted aryl; or R_{47} and R_{48} may form together a divalent alkylene radical which may be interrupted by one or more heteroatoms;

R_{50} is substituted or unsubstituted alkyl;

R_{51} is hydrogen, alkyl, haloalkyl, aryl, alkenyl, $-OR_{52}$, $-SR_{53}$, or $-NR_{54}R_{55}$;

R_{52} and R_{53} are independently selected from alkyl and haloalkyl;

R_{54} and R_{55} are independently selected from hydrogen, alkyl, haloalkyl and aryl;

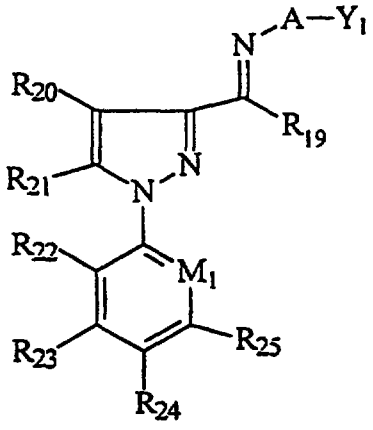
a, b, c, d, e and f independently represent zero, one or two;

M_1 is C-halo, C-CH_3, C-CH_2F, C-CH_2Cl, C-NO_2, or N;

or a pesticidally acceptable salt thereof; and

(b) an agriculturally acceptable carrier therefor.

12. A method for the control of pests at a locus comprising applying to said locus a pesticidally effective amount of a compound of formula (I bis):



(I bis)

wherein:

A is $-NR_{26}-$;

Y_1 is hydrogen, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl, substituted or unsubstituted alkynyl, substituted or unsubstituted aryl, $-S(O)_aR_{28}$, $-P(O)R_{29}R_{30}$, $-P(S)R_{29}R_{30}$, $-Si(R_{31})(R_{32})(R_{33})$, $-C(O)R_{27}$, $-C(S)R_{27}$, cyano or nitro;

R_{19} is hydrogen, alkyl, haloalkyl, or $-NR_{34}R_{35}$;

R_{20} is $-S(O)_bR_{36}$ or R_{37};

R_{21} is hydrogen, halogen, -C(O)R_{38}, -S(O)$_c$$R_{39}$, alkyl, haloalkyl, -O$R_{40}$, -N=C($R_{41}$)($R_{42}$), alkenyl, -N$R_{43}R_{44}$, 1H-pyrrol-1-yl, 1H-pyrazol-1-yl, or -CH=NOH;

R_{22}, R_{23} and R_{25} are independently selected from hydrogen, halogen or alkyl;

R_{24} is halogen, haloalkyl, haloalkoxy, -S(O)$_d$$R_{45}$ or SF_5;

R_{26} is hydrogen or substituted or unsubstituted alkyl;

R_{27} is hydrogen, substituted or unsubstituted alkyl of C_1 to C_{20}, substituted or unsubstituted aryl, -OR_{46}, -N$R_{47}R_{48}$, or -SR_{49};

R_{28} is substituted or unsubstituted alkyl or substituted or unsubstituted aryl;

R_{29} and R_{30} are independently selected from alkoxy and thioalkoxy;

R_{31}, R_{32} and R_{33} are independently selected from alkyl, haloalkyl and aryl;

R_{34} and R_{35} are independently selected from hydrogen or substituted or unsubstituted alkyl;

R_{36} is alkyl, alkenyl, alkynyl, or C_3-C_6 cycloalkyl each of which is optionally substituted by one or more halogens;

R_{37} is alkyl or haloalkyl;

R_{38} is hydrogen, alkyl, haloalkyl, alkoxy or thioalkoxy;

R_{39} is alkyl haloalkyl or aryl;

R_{40} and R_{41} are independently selected from hydrogen, alkyl and haloalkyl;

R_{42} is alkyl, haloalkyl, alkoxy or phenyl each of which is optionally substituted by one or more groups selected from hydroxy, halogen, alkoxy, -CN, alkyl, -S(O)$_e$alkyl;

R_{43} and R_{44} are independently selected from hydrogen, NH_2, -S(O)$_f$$R_{50}$, -C(O)$R_{51}$, substituted or unsubstituted alkyl, substituted or unsubstituted alkenyl and alkynyl; or R_{43} and R_{44} form together a divalent alkylene radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulfur;

R_{45} is haloalkyl;

R_{46} and R_{49} are independently selected from substituted or unsubstituted alkyl and substituted or unsubstituted aryl;

R_{47} and R_{48} are independently selected from hydrogen, substituted or unsubstituted alkyl and substituted or unsubstituted aryl; or R_{47} and R_{48} may form together a divalent alkylene radical which may be interrupted by one or more heteroatoms;

R_{50} is substituted or unsubstituted alkyl;

R_{51} is hydrogen, alkyl, haloalkyl, aryl, alkenyl, -OR_{52}, -SR_{53}, or -N$R_{54}R_{55}$;

R_{52} and R_{53} are independently selected from alkyl and haloalkyl;

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R_{54} and R_{55} are independently selected from hydrogen, alkyl. haloalkyl and aryl:
a. b. c. d. e and f independently represent zero, one or two;
M_1 is C-halo, C-CH_3, C-CH_2F, C-CH_2Cl. C-NO_2, or N;
or a pesticidally acceptable salt thereof.

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