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(54) Title: ARTHROPODICIDAL PYRAZOLE SULFONATES

(57) Abstract

Arthropodicidal compounds having the formula R^1-SO_2-O-Q where R^1 and Q are as defined in the text, compositions containing said compounds and use of the compounds to control arthropods.

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TITLE

ARTHROPODICIDAL PYRAZOLE SULFONATES

U.S. Patent 3,966,574 discloses insecticidal sulfonates that contain a heteroaromatic ring having three heteroatoms. U.S. Patent 4,791,127 discloses insecticidal thiazole sulfonates and Jacobsen, et al., *Pest. Sci.*, (1990), 29, 96-100 discloses insecticidal oxazole sulfonates. Arthropodicidal pyrazole sulfonates of Formula I have hitherto been unknown.

SUMMARY OF THE INVENTION

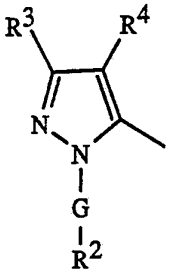
This invention pertains to compounds of Formula I, including all geometric and stereoisomers, agriculturally suitable salts thereof, agricultural compositions containing them and their use for the control of arthropods and nematodes in both agronomic and nonagronomic environments. The compounds are

$$R^1—SO_2—O—Q$$

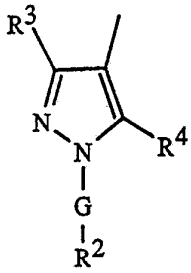
I

wherein:

Q is selected from the group

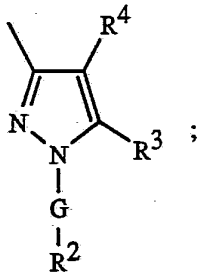


Q-1



Q-2

and



Q-3

G is selected from the group S, S(=O), $S(=O)_2$, C=S and C=O;

R^1 is selected from the group C_1–C_3 alkyl and C_1-C_3 haloalkyl;

R^2 is selected from the group C_1–C_6 alkyl, C_3-C_6 cycloalkyl, C_2–C_6 alkenyl and C_2–C_6 alkynyl each of which can be optionally substituted with R^5; or R^2 is selected from the group C_1–C_6 haloalkyl, $N(R^7)R^8$, C_3-C_6 cyclohaloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_4-C_7 cycloalkylalkyl and C_4–C_7 cycloalkylalkyl substituted with R^6;

R^3 and R^4 are independently selected from the group H, C_1–C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, C_1–C_6 alkylthio, C_1–C_6 haloalkylthio, C_3-C_6 cyclohaloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_4-C_7 cycloalkylalkyl, C_1-C_6 alkylsulfinyl, C_1–C_6 haloalkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1–C_6 haloalkylsulfonyl, C_2-C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyl, formyl, halogen, OH, NO_2, $N(R^{14})R^{15}$, $C(O)N(R^{14})R^{15}$, CN and phenyl optionally substituted with W; C_1-C_6 alkyl; C_3-C_6 cycloalkyl; C_2-C_6 alkenyl; C_2–C_6 alkynyl; wherein each of C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_2-C_6 alkenyl and C_2-C_6 alkynyl can be optionally substituted with R^{13};

R^5 and R^{13} are independently selected from the group CN, SCN, NO_2, OR^9, SR^9, $S(O)R^9$, SO_2R^9, $OC(O)R^9$, OSO_2R^9, $Si(R^9)(R^{10})(R^{11})$, CO_2R^9, $C(O)N(R^9)R^{10}$, $C(O)R^9$, $N(R^9)R^{10}$ and phenyl optionally substituted with R^{12};

R^6 is selected from the group halogen, CN and C_1-C_2 alkyl;

R^7 is selected from the group C_1-C_6 alkyl optionally substituted with R^{16}, C_3-C_6 cycloalkyl optionally substituted with R^{19}, and C_4-C_7 cycloalkylalkyl optionally substituted with R^{19};

R^8 is selected from the group H, CN, C_1-C_6 haloalkyl and C_1–C_6 alkyl optionally substituted with CN;

R^7 and R^8 can be taken together to form $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$ or $-CH_2CH_2-O-CH_2CH_2-$;

R^9, R^{10} and R^{11} are independently selected from the group C_1-C_3 alkyl and C_1–C_3 haloalkyl;

R^{12} and W are independently selected from the group halogen, C_1–C_2 alkyl, C_1-C_2 haloalkyl, C_1–C_2 alkoxy, C_1–C_2 haloalkoxy, C_1-C_2 alkylthio, C_1-C_2 haloalkylthio, C_1-C_2 alkylsulfinyl, C_1-C_2 haloakylsulfinyl, C_1-C_2 alkylsulfonyl, C_1-C_2 haloalkylsulfonyl, NO_2 and CN;

R^{14} and R^{15} are independently selected from the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkylcarbonyl, C_2-C_6 alkoxycarbonyl, C_1-C_6 alkylsulfonyl and $C(O)N(R^{17})R^{18}$; or

R^{14} and R^{15} can be taken together to form $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$ or $-CH_2CH_2-O-CH_2CH_2-$;

R^{16} is selected from the group 1 to 5 halogens, CN, C_1-C_2 alkoxy, C_1-C_2 alkylthio, C_1-C_2 alkylsulfonyl and C_3-C_6 trialkylsilyl;

R^{17} and R^{18} are independently selected from the group H and C_1-C_3 alkyl; and

R^{19} is selected from the group 1 to 5 halogens, C_1-C_3 alkyl, CN, C_1-C_2 alkoxy, C_1-C_2 alkylthio, C_1-C_2 alkylsulfonyl and C_3-C_6 trialkylsilyl.

Preferred compounds A are those compounds of Formula I wherein:

G is selected from the group $S(=O)_2$ and C=O

R^1 is selected from the group CH_3 and $ClCH_2$;

R^2 is selected from the group C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl and $N(R^7)R^8$;

R^3 and R^4 are independently selected from the group H, C_1-C_2 alkyl, C_1-C_2 haloalkyl, C_1-C_2 alkoxy, $N(R^{14})R^{15}$ and halogen; and

R^{14} and R^{15} are independently selected from the group H and C_1-C_6 alkyl.

Preferred Compounds B are compounds of Preferred A wherein Q is Q-1.

Preferred Compounds C are compounds of Preferred A wherein Q is Q-2.

Preferred Compounds D are compounds of Preferred A wherein Q is Q-3.

Some of the compounds of this invention can exist as one or more stereoisomers. The various stereoisomers include enantiomers, diastereomers and geometric isomers. One skilled in the art will appreciate that one stereoisomer may be more active than the others and how to separate said stereoisomers. Accordingly, the present invention comprises mixtures, individual stereoisomers, and optically active mixtures of compounds of Formula I as well as agriculturally suitable salts thereof.

In the above recitations, the term "alkyl" used either alone or in compound word such as "haloalkyl", denotes straight or branched alkyl such as methyl, ethyl, *n*-propyl, isopropyl, or the different butyl, pentyl or hexyl isomers. Alkoxy denotes methoxy and ethoxy. Alkenyl denotes straight or branched chain alkenes such as vinyl, 1-propenyl, 2-propenyl and the different butenyl, pentenyl and hexenyl isomers. Cycloalkylalkyl denotes cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl attached to a straight or branched C_1-C_4 alkylene group. The term "trialkylsilyl" denotes silicon with three alkyl substituents. The term"Alkoxy" denotes methoxy, ethoxy, *n*-propyloxy, isopropyloxy and the different butoxy, pentoxy and hexyloxy isomers.

The term "alkoxycarbonyl" denotes $CH_3OC(=O)$, $CH_3CH_2OC(=O)$, $CH_3CH_2CH_2OC(=O)$, $(CH_3)_2CHOC(=O)$ and the different butoxy-, pentoxy- or hexyloxycarbonyl isomers. The term "alkylcarbonyl" denotes $CH_3C(=O)$, $CH_3CH_2C(=O)$, $CH_3CH_2CH_2C(=O)$, $(CH_3)_2CHC(=O)$ and the different butyl-, pentyl- or hexylcarbonyl isomers.

The term "alkylsulfonyl" denotes $CH_3S(O)_2$, $CH_3CH_2S(O)_2$, $CH_3CH_2CH_2S(O)_2$, $(CH_3)_2CHS(O)_2$ and the different butylsulfonyl, pentylsulfonyl and hexylsulfonyl isomers. The term "alkylsulfinyl" denotes $CH_3S(O)$ and $CH_3CH_2S(O)$.

The term "halogen", either alone or in compound words such as "haloalkyl", denotes fluorine, chlorine, bromine or iodine. Further, when used in compound words such as "haloalkyl" said alkyl may be partially or fully

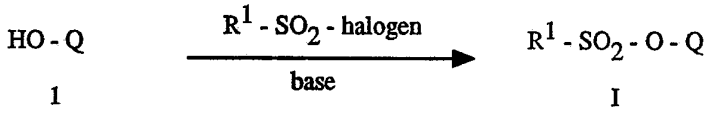
substituted with halogen atoms, which may be the same or different. Examples of haloalkyl include CH_2CH_2F, CF_2CF_3 and CH_2CHFCl. The terms "haloalkenyl" and "haloalkynyl" are defined analogously to the term "haloalkyl".

The total number of carbon atoms in a substituent group is indicated by the "C_i-C_j" prefix where i and j are numbers from 1 to 7. For example, C_2 alkoxycarbonyl designates $C(O)OCH_3$ and C_3 alkoxycarbonyl designates $C(O)OCH_2CH_3$.

DETAILS OF THE INVENTION

Compounds of Formula I can be prepared by reaction of the corresponding hydroxypyrazole (1) with the appropriate sulfonyl halide and a base such as triethylamine or pyridine in a solvent such as dichloromethane or tetrahydrofuran as shown in Equation 1. It is known to one skilled in the art that the hydroxy compounds (1) may exist as the pyrazolone tautomer. In Equations 1-8 R^1, R^2, R^3, R^4 and G are as previously defined.

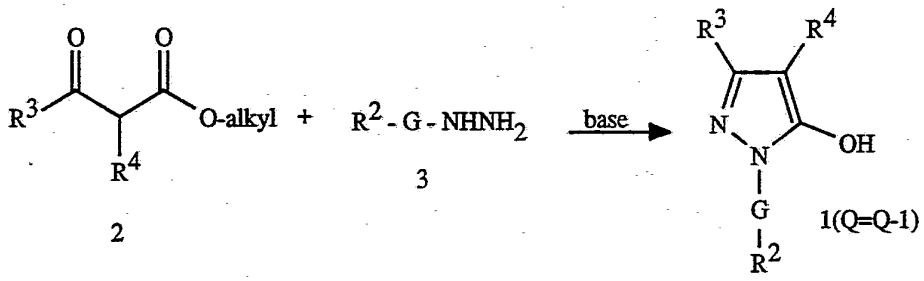
Equation 1



1 I

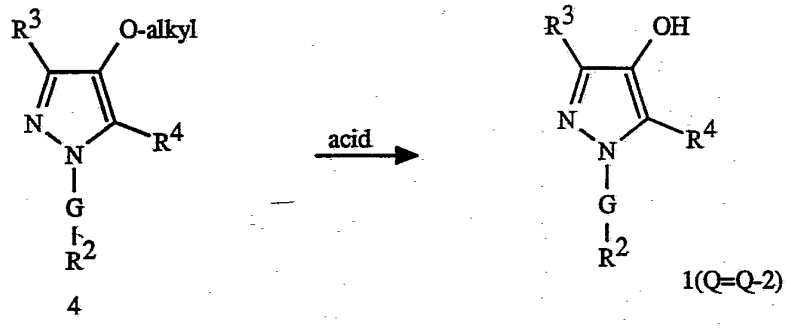
A general review for the synthesis of hydroxypyrazoles can be found in Wiley, et at., *The Chemistry of Hetrocyclic Compounds, Pyrazolones, Pyrazolidones and Derivatives:*, Vol. 20, Wiley, New York, (1964). More specifically, the hydroxy pyrazoles 1 wherein Q is Q-1 can be prepared from the appropriate β-dicarbonyl compound 2 or a synthetic equivalent such as acetylenic ester or α-oxodithioketene acetal and the appropriate hydrazide (3, wherein G is C=O), thiohydrazide (3, wherein G is C=S), sulfonylhydrazide (3, wherein G is $S(=O)_2$),sulfinylhydrazide (3, wherein G is S(=O), or sulfenylhydrazide (3, wherein G is S), in the presence of base as shown in Equation 2. The synthesis of the compounds 3 is known.

Equation 2



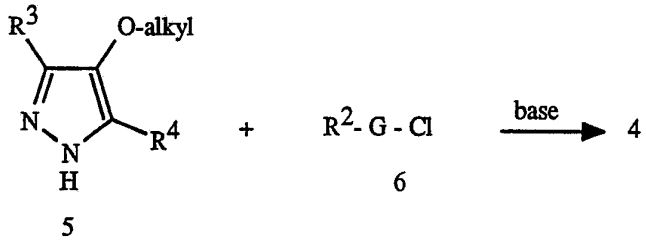
The hydroxy pyrazoles 1 wherein Q is Q-2 can be prepared from alkoxy compounds 4 by treatment with iodotrimethylsilane or aqueous acid such as hydrobromic acid in acetic acid as shown in Equation 3.

Equation 3



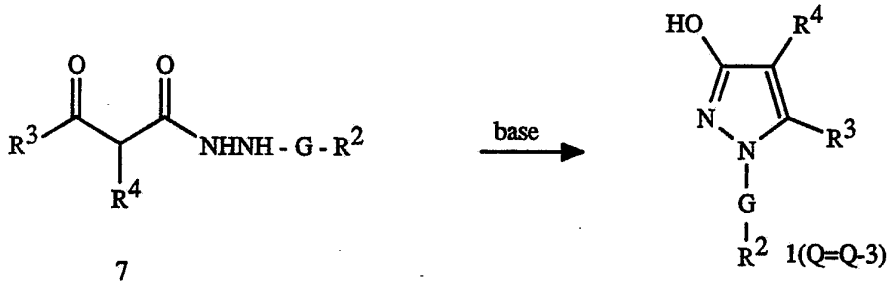
The compounds of Formula 4 can be prepared by treatment of an alkoxypyrazole 5 with the appropriate acid chloride, sulfonyl chloride, sulfinylchloride or sulfenyl chloride (6) and base as shown in Equation 4. The compounds of Formula 4 wherein G is C=S can be prepared from the compounds of Formula 4 wherein G is C=O by treatment with a thiation reagent such as P_2S_5 or 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide. The synthesis of 4-alkoxypyrazoles is known to one skilled in the art. (For instance see: Pluempe, H. and Schegk, E., *Arch. Pharm.*, 300, 704, (1967).

Equation 4



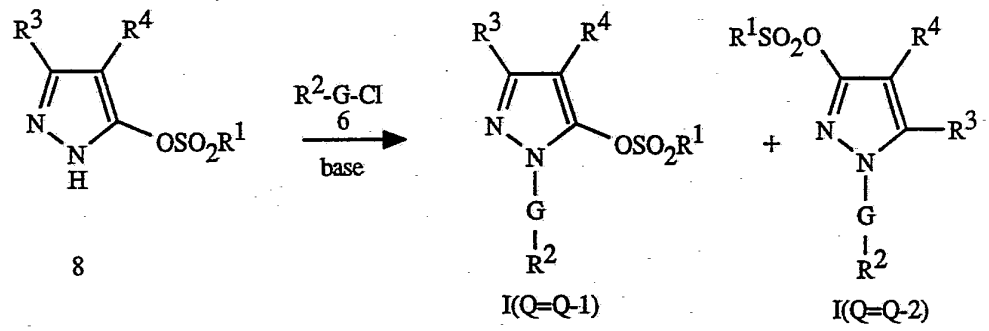
The hydroxy pyrazoles 1 wherein Q is Q-3 can be prepared by cyclization of β-oxohydrazides (7) with a base such as sodium ethoxide in a solvent such as ethanol as shown in Equation 5. The compounds of Formula 7 are prepared by known methods.

Equation 5



Alternatively, compounds of Formula I wherein Q is Q-1 or Q-3 can be prepared by reaction of a pyrazole sulfonate 8 with a compound of Formula 6 and base as shown in Equation 6. The ratio of products obtained will depend on the nature of the R^3 and R^4 groups. In some instances, only one product will be obtained.

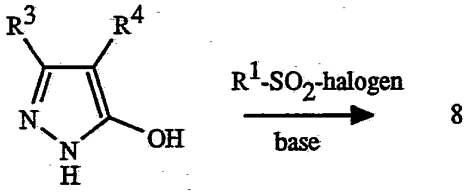
Equation 6



8 I(Q=Q-1) I(Q=Q-2)

The compounds of Formula 8 can be prepared by the reaction of a hydroxypyrazole 9 with a sulfonyl halide and base as shown in Equation 7. The synthesis of compounds of Formula 9 is known.

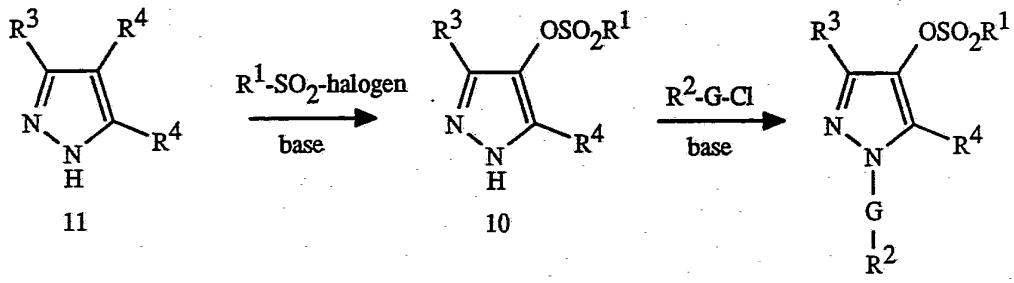
Equation 7



9 8

Analogously, compounds of Formula I wherein Q is Q-2 can be prepared from pyrazole sulfonates of Formula 10 which in turn can be prepared from hydroxy pyrazoles of Formula II as shown in Equation 8.

Equation 8



11 10 I(Q=Q-2)

EXAMPLE 1

Preparation of 3-Methyl-1-(propylsulfonyl)-1H-pyrazol-5-ol Methanesulfonate (Ester)

Intermediate 1

3-Methyl-1-(propylsulfonyl)-1H-pyrazol-5-ol

To a solution of 10 g (72 mmol) of 1-propanesulfonic acid, hydrazide in 150 mL of ethanol was added 9.2 mL (72 mmol) of ethyl acetoacetate and 27 mL (72 mmol) of a 2.68 M solution of sodium ethoxide in ethanol. The reaction mixture was refluxed overnight. After cooling, the solvent was removed with a rotary evaporator. The residue was taken up in water, acidified and extracted with dichloromethane. After drying with sodium sulfate, the solvent was removed with a rotary evaporator to give the product (11.36 g) as an orange solid. ^1H NMR ($CDCl_3$): d 0.94 (t, 3), 1.62 (m, 2), 2.10 (s, 3), 3.46 (t, 2), 5.2 (br, 1).

3-Methyl-1-(propylsulfonyl)-1H-pyrazol-5-ol, Methanesulfonate (Ester)

To a solution of 1 g (4.9 mmol) of 3-methyl-1-(propylsulfonyl)-1H-pyrazol-5-ol in 50 mL of dichloromethane at 0°C was added 0.96 mL (6.9 mmol) of triethylamine followed by 0.56 mL (6.9 mmol) of methanesulfonyl chloride. The reaction mixture was allowed to stand at room temperature overnight. Dichloromethane was added. The organic layer was washed with water, dried (sodium sulfate) and the solvent was removed with a rotary evaporator. The residue was purified by flash chromatography to give 0.79 g of the title compound as a yellow oil. ^1H NMR ($CDCl_3$): δ 1.08 (t, 3), 1.62 (m, 2), 2.31 (s, 3), 3.33 (s, 3), 3.43 (t, 2), 6.12 (s, 1).

EXAMPLE 2

Preparation of 5-Methyl-1-(propylsulfonyl)-1H-pyrazol-3-ol Methanesulfonate (Ester)

Intermediate 1

5-Methyl-1H-pyrazol-3-ol Methanesulfonate (Ester)

To a solution of 10 g (102 mmol) of 2,4-dihydro-3H-pyrazol-3-one in 250 mL of dichloromethane at 0°C was added 15.6 mL (112 mmol) of triethylamine followed by 8.7 mL (112 mmol) of methanesulfonyl chloride dropwise. The reaction mixture was stirred overnight at room temperature. It was washed with water, dried (Na_2SO_4) and the solvent was removed with a rotary evaporator. The residue was purified by flash chromatography (45-60%

ethyl acetate in hexanes as eluant) to afford 4.98 g of the title compound as a white solid (m.p. 104-106°C) ^{1}H NMR ($CDCl_3$) δ 2.32 (s,3), 3.28 (s,3), 5.94 (s,1) 9.6 (br,1).

5-Methyl-1H (propylsulfonyl)-1H-pyrazol-3-ol Methanesulfonate (Ester)

To a solution of 1.70 g (9.6 mmol) of 5-methyl-1H-pyrazol-3-ol, methanesulfonate (ester) in 50 mL of dichloromethane at 0°C was added 1.87 mL (13.4 mmol) of triethylamine followed by 1.5 mL (13.4 mmol) of propanesulfonyl chloride. The reaction mixture was stirred overnight at room temperature. An additional 0.67 mL of triethylamine was added. The reaction mixture was cooled in an ice bath of 0.54 mL of propanesulfonyl chloride was added. It was stirred at room temperature for 4 h. Water was added. The organic layer was dried (Na_2SO_4) and the solvent was removed with a rotary evaporator. The residue was purified by flash chromatography (30% ethyl acetate in hexanes as eluant) to afford 2.15 g of the title compound as a white solid (m.p. 84-85°C) ^{1}H NMR ($CDCl_3$) δ 1.4 (t,3), 1.77 (m,2), 2.54 (s,3) 3.34 (s,3), 3.45 (m,2), 6.10 (s,1).

By applying the procedures of Examples 1 and 2 and Equations 1 through 8, one skilled in the art can prepare the compounds in Tables 1 through 3. In the following Tables, abbreviations for G, various alkyl chains and rings have been used with the following corresponding definitions.

iPr = isopropyl = $CH(CH_3)_2$

nPr = *n*-propyl = $CH_2CH_2CH_3$

cPr = cylopropyl = $CH(CH_2)_2$

iBu = isobutyl = $CH_2CH(CH_3)_2$

sBu = *s*-butyl = $CH(CH_3)CH_2CH_3$

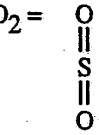
tBu = *tert*-butyl = $C(CH_3)_3$

nBu = *n*-butyl = $(CH_2)_3CH_3$

iAm = isoamyl = $CH_2CH_2CH(CH_3)_2$

Ph = phenyl = C_6H_5

cPrCH$_3$ = 2-cyclopropylmethyl = $CH(CHCH_3)CH_2$

SO_2 = 

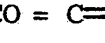
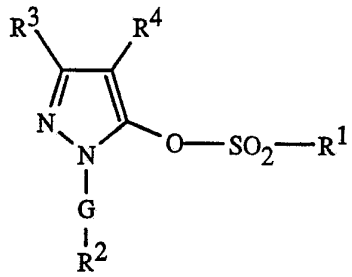
CO = 

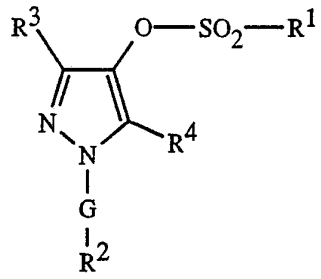
Table 1



$G=SO_2$, $R^1=CH_3$, $R^3=CH_3$, $R^4=H$, R^2 =	$G=SO_2$, $R^1=CH_3$, $R^3=H$, $R^4=H$, R^2 =	$G=CO$, $R^1=CH_3$, $R^3=CH_3$, $R^4=H$, R^2 =	$G=CO$, $R^1=CH_3$, $R^3=H$, $R^4=H$, R^2 =
CH_3	CH_3	CH_3	CH_3
C_2H_5	C_2H_5	C_2H_5	C_2H_5
nPr	nPr	nPr	nPr
iPr	iPr	iPr	iPr
cPr	cPr	cPr	cPr
nBu	nBu	nBu	nBu
iBu	iBu	iBu	iBu
tBu	tBu	tBu	tBu
sBu	sBu	sBu	sBu
iAm	iAm	iAm	iAm
$CH_2CH=CH_2$	$CH_2CH=CH_2$	$CH_2CH=CH_2$	$CH_2CH=CH_2$
$CH_2C\equiv CH$	$CH_2C\equiv CH$	$CH_2C\equiv CH$	$CH_2C\equiv CH$
$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$
$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$
CH_2cPr	CH_2cPr	CH_2cPr	CH_2cPr
N(H)iPr	N(H)iPr	N(H)iPr	N(H)iPr
N(H)sBu	N(H)sBu	N(H)sBu	N(H)sBu

$G=SO_2$, $R^1=CH_3$, R^2=nPr,		$G=CO$, $R^1=CH_3$, R^2=N(H)iPr,	
R^3 =	R^4 =	R^3 =	R^4 =
H	CO_2CH_3	H	CO_2CH_3
H	$CO_2C_2H_5$	H	$CO_2C_2H_5$
H	$C(O)CH_3$	H	$C(O)CH_3$
H	CN	H	CN
CH_3	CH_3	CH_3	CH_3
CH_3	CO_2CH_3	CH_3	CO_2CH_3
CH_3	$C(O)CH_3$	CH_3	$C(O)CH_3$
CH_3	CN	CH_3	CN
CF_3	H	CF_3	H
OCH_3	H	OCH_3	H
OCH_3	CH_3	OCH_3	CH_3
OCF_2H	H	OCF_2H	H
SCH_3	H	SCH_3	H
SCH_3	CO_2CH_3	SCH_3	CO_2CH_3
Cl	H	Cl	H
F	H	F	H

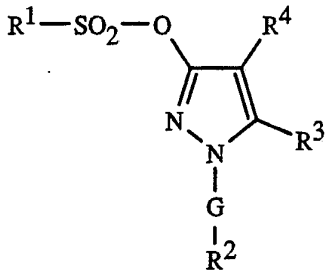
Table 2



$G=SO_2$, $R^1=CH_3$, $R^3=CH_3$, $R^4=H$, R^2 =	$G=SO_2$, $R^1=CH_3$, $R^3=H$, $R^4=H$, R^2 =	$G=CO$, $R^1=CH_3$, $R^3=CH_3$, $R^4=H$, R^2 =	$G=CO$, $R^1=CH_3$, $R^3=H$, $R^4=H$, R^2 =
CH_3	CH_3	CH_3	CH_3
C_2H_5	C_2H_5	C_2H_5	C_2H_5
nPr	nPr	nPr	nPr
iPr	iPr	iPr	iPr
cPr	cPr	cPr	cPr
nBu	nBu	nBu	nBu
iBu	iBu	iBu	iBu
tBu	tBu	tBu	tBu
sBu	sBu	sBu	sBu
iAm	iAm	iAm	iAm
$CH_2CH=CH_2$	$CH_2CH=CH_2$	$CH_2CH=CH_2$	$CH_2CH=CH_2$
$CH_2C\equiv CH$	$CH_2C\equiv CH$	$CH_2C\equiv CH$	$CH_2C\equiv CH$
$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$
$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$
CH_2cPr	CH_2cPr	CH_2cPr	CH_2cPr
N(H)iPr	N(H)iPr	N(H)iPr	N(H)iPr
N(H)sBu	N(H)sBu	N(H)sBu	N(H)sBu

$G=SO_2$, $R^1=CH_3$, R^2=nPr,		$G=CO$, $R^1=CH_3$, $R^2=N(H)iPr$,	
R^3 =	R^4 =	R^3 =	R^4 =
H	CO_2CH_3	H	CO_2CH_3
H	$CO_2C_2H_5$	H	$CO_2C_2H_5$
H	$C(O)CH_3$	H	$C(O)CH_3$
H	CN	H	CN
CH_3	CH_3	CH_3	CH_3
CH_3	CO_2CH_3	CH_3	CO_2CH_3
CH_3	$C(O)CH_3$	CH_3	$C(O)CH_3$
CH_3	CN	CH_3	CN
CF_3	H	CF_3	H
OCH_3	H	OCH_3	H
OCH_3	CH_3	OCH_3	CH_3
OCF_2H	H	OCF_2H	H
SCH_3	H	SCH_3	H
SCH_3	CO_2CH_3	SCH_3	CO_2CH_3
Cl	H	Cl	H
F	H	F	H

Table 3



$G=SO_2$, $R^1=CH_3$, $R^3=CH_3$, $R^4=H$, R^2 =	$G=SO_2$, $R^1=CH_3$, $R^3=H$, $R^4=H$, R^2 =	$G=CO$, $R^1=CH_3$, $R^3=CH_3$, $R^4=H$, R^2 =	$G=CO$, $R^1=CH_3$, $R^3=H$, $R^4=H$, R^2 =
CH_3	CH_3	CH_3	CH_3
C_2H_5	C_2H_5	C_2H_5	C_2H_5
nPr	nPr	nPr	nPr
iPr	iPr	iPr	iPr
cPr	cPr	cPr	cPr
nBu	nBu	nBu	nBu
iBu	iBu	iBu	iBu
tBu	tBu	tBu	tBu
sBu	sBu	sBu	sBu
iAm	iAm	iAm	iAm
$CH_2CH=CH_2$	$CH_2CH=CH_2$	$CH_2CH=CH_2$	$CH_2CH=CH_2$
$CH_2C\equiv CH$	$CH_2C\equiv CH$	$CH_2C\equiv CH$	$CH_2C\equiv CH$
$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$	$CH_2CH_2CH_2Cl$
$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$	$CH_2CH_2C(F)=CF_2$
CH_2cPr	CH_2cPr	CH_2cPr	CH_2cPr
N(H)iPr	N(H)iPr	N(H)iPr	N(H)iPr
N(H)sBu	N(H)sBu	N(H)sBu	N(H)sBu
CH_2SCH_3	CH_2SCH_3	$N(CH_3)iPr$	$N(CH_3)iPr$
$CH_2Si(CH_3)_3$	$CH_2Si(CH_3)_3$	N(H)cPr	N(H)cPr
CH_2CN	CH_2CN	$N(CH_3)C_2H_5$	$N(CH_3)C_2H_5$
$CH_2S(O)_2CH_3$	$CH_2S(O)_2CH_3$	$N(H)CH(CH_3)CH_2CN$	$N(H)CH(CH_3)CH_2CN$

$G=SO_2$, $R^1=CH_3$, R^2=nPr,		$G=CO$, $R^1=CH_3$, $R^2=N(H)iPr$	
R^3 =	R^4 =	R^3 =	R^4 =
H	CO_2CH_3	H	CO_2CH_3
H	$CO_2C_2H_5$	H	$CO_2C_2H_5$
H	$C(O)CH_3$	H	$C(O)CH_3$
H	CN	H	CN
CH_3	CH_3	CH_3	CH_3
CH_3	CO_2CH_3	CH_3	CO_2CH_3
CH_3	$C(O)CH_3$	CH_3	$C(O)CH_3$
CH_3	CN	CH_3	CN
CF_3	H	CF_3	H
OCH_3	H	OCH_3	H
OCH_3	CH_3	OCH_3	CH_3
OCF_2H	H	OCF_2H	H
SCH_3	H	SCH_3	H
SCH_3	CO_2CH_3	SCH_3	CO_2CH_3
Cl	H	Cl	H
F	H	F	H

Formulation/Utility

Compounds of this invention will generally be used in formulation with an agriculturally suitable carrier comprising a liquid or solid diluent or an organic solvent. Useful formulations include dusts, granules, baits, pellets, solutions, suspensions, emulsions, wettable powders, emulsifiable concentrates, dry flowables and the like, consistent with the physical properties of the active ingredient, mode of application and environmental factors such as soil type, moisture and temperature. Sprayable formulations can be extended in suitable media and used at spray volumes from about one to several hundred liters per hectare. High strength compositions are primarily used as intermediates for further formulation. The formulations will typically contain effective amounts of active ingredient, diluent and surfactant within the following approximate ranges which add up 100 weight percent.

	Weight Percent		
	Active Ingredient	Diluent	Surfactant
Wettable Powders	25-90	0-74	1-10
Oil Suspensions, Emulsions, Solutions, (including Emulsifiable Concentrates)	5-50	40-95	0-15
Dusts	1-25	70-99	0-5
Granules, Baits and Pellets	0.01-99	5-99.99	0-15
High Strength Compositions	90-99	0-10	0-2

Typical solid diluents are described in Watkins, et al., *Handbook of Insecticide Dust Diluents and Carriers*, 2nd Ed., Dorland Books, Caldwell, New Jersey. Typical liquid diluents and solvents are described in Marsden, *Solvents Guide*, 2nd Ed., Interscience, New York, 1950. *McCutcheon's Detergents and Emulsifiers Annual*, Allured Publ. Corp., Ridgewood, New Jersey, as well as Sisely and Wood, *Encyclopedia of Surface Active Agents*, Chemical Publ. Co., Inc., New York, 1964, list surfactants and recommended uses. All formulations can contain minor amounts of additives to reduce foam, caking, corrosion, microbiological growth, etc.

Solutions are prepared by simply mixing the ingredients. Fine solid compositions are made by blending and, usually, grinding as in a hammer mill or fluid energy mill. Water-dispersible granules can be produced by agglomerating a fine powder composition; see for example, Cross et al., *Pesticide Formulations*, Washington, D.C., 1988, pp 251-259. Suspensions are prepared by wet-milling; see, for example, U.S. 3,060,084. Granules and pellets can be made by spraying the active material upon preformed granular carriers or by agglomeration techniques. See Browning, "Agglomeration", *Chemical Engineering*, December 4, 1967, pp 147–148, *Perry's Chemical Engineer's Handbook*, 4th Ed., McGraw-Hill, New York, (1963), pages 8–57 and following, and WO 91/13546. Pellets can be prepared as described in U.S. 4,172,714. Water-dispersible and water-soluble granules can also be prepared as taught in DE 3,246,493.

For further information regarding the art of formulation, see U.S. 3,235,361, Col. 6, line 16 through Col. 7, line 19 and Examples 10–41; U.S. 3,309,192, Col. 5, line 43 through Col. 7, line 62 and Examples 8, 12, 15, 39, 41, 52, 53, 58, 132, 138-140, 162-164, 166, 167 and 169-182; U.S. 2,891,855, Col. 3, line 66 through Col. 5, line 17 and Examples 1-4; Klingman, *Weed Control as a Science*, John Wiley and Sons, Inc., New York, (1961), pp 81-96; and Hance et al., *Weed Control Handbook*, 8th Ed., Blackwell Scientific Publications, Oxford, 1989.

In the following Examples, all percentages are by weight and all formulations are worked up in conventional ways. Compound numbers refer to compounds in Index Table A.

Example A

Wettable Powder

Compound 1	65.0%
dodecylphenol polyethylene glycol ether	2.0%
sodium ligninsulfonate	4.0%
sodium silicoaluminate	6.0%
montmorillonite (calcined)	23.0%.

Example B

Granule

Compound 1	10.0%
attapulgite granules (low volative	

matter, 0.71/0.30 mm; U.S.S. No. 25-50 sieves)	90.0%.

Example C

Extruded Pellet

Compound 1	25.0%
anhydrous sodium sulfate	10.0%
crude calcium ligninsulfonate	5.0%
sodium alkylnaphthalenesulfonate	1.0%
calcium/magnesium bentonite	59.0%.

Example D

Emulsifiable Concentrate

Compound 1	20.0%
blend of oil soluble sulfonates and polyoxyethylene ethers	10.0%
isophorone	70.0%.

The compounds of this invention exhibit activity against a wide spectrum of foliar-feeding, fruit-feeding, seed-feeding, aquatic and soil-inhabiting arthropods (term "arthropod" includes insects, mites and nematodes) which are pests of growing and stored agronomic crops, forestry, greenhouse crops, ornamentals, nursery crops, stored food and fiber products, livestock, household, and public and animal health. Those skilled in the art will appreciate that not all compounds are equally effective against all pests. Nevertheless, all of the compounds of this invention display activity against pests that include: eggs, larvae and adults of the Order Lepidoptera; eggs, foliar-feeding, fruit-feeding, root-feeding, seed-feeding larvae and adults of the Order Coleoptera; eggs, immatures and adults of the Orders Hemiptera and Homoptera; eggs, larvae, nymphs and adults of the Order Acari; eggs, immatures and adults of the Orders Thysanoptera, Orthoptera and Dermaptera; eggs, immatures and adults of the Order Diptera; and eggs, junveniles and adults of the Phylum Nemata. The compounds of this invention are also active against pests of the Orders Hymenoptera, Isoptera, Phthiraptera, Siphonoptera, Blattaria, Thysanaura and Pscoptera; pests belonging to the Class Arachnida and Phylum Platyhelminthes. The compounds are particularly active against southern corn rootworm (*Diabrotica undecimpunctata howardi*), aster leafhopper (*Mascrosteles fascifrons*), boll weevil (*Anthonomus grandis*), two-spotted spider mite (*Tetranychus urticae*), fall armyworm (*Spodoptera*

frugiperda), black bean aphid (*Aphis fabae*), tobacco budworm (*Heliothis virescens*), rice water weevil (*Lissorhoptrus oryzophilus*), rice leaf beetle (*Oulema oryzae*), whitebacked planthopper (*Sogatella furcifera*), green leafhopper (*Nephotettix cincticeps*), brown planthopper (*Nilaparvata lugens*), small brown planthopper (*Laodelphax striatellus*), rice stem borer (*Chilo suppressalis*), rice leafroller (*Cnaphalocrocis medinalis*), black rice stink bug (*Scotinophara lurida*), rice stink bug (*Lagynotomus elongatus*), rice bug (*Leptocorisa chinensis*), slender rice bug (*Cletus puntiger*), and southern green stink bug (*Nezara viridula*). See WO 90/10623 and WO 92/00673 for more detailed pest descriptions.

Compounds of this invention can also be mixed with one or more other insecticides, fungicides, nematocides, bactericides, acaricides, semiochemicals, repellants, attractants, pheromones, feeding stimulants or other biologically active compounds to form a multi-component pesticide giving an even broader spectrum of agricultural protection. Examples of other agricultural protectants with which compounds of this invention can be formulated are: insecticides such as avermectin B, monocrotophos, carbofuran, tetrachlorvinphos, malathion, parathion—methyl, methomyl, chlordimeform, diazinon, deltamethrin, oxamyl, fenvalerate, esfenvalerate, permethrin, profenofos, sulprofos, triflumuron, diflubenzuron, methoprene, buprofezin, thiodicarb, acephate, azinphosmethyl, chlorpyrifos, dimethoate, fipronil, flufenprox, fonophos, isofenphos, methidathion, methamidophos, phosmet, phosphamidon, phosalone, pirimicarb, phorate, terbufos, trichlorfon, methoxychlor, bifenthrin, biphenate, cyfluthrin, fenpropathrin, fluvalinate, flucythrinate, tralomethrin, metaldehyde and rotenone; fungicides such as carbendazim, thiuram, dodine, maneb, chloroneb, benomyl, cymoxanil, fenpropidine, fenpropimorph, triadimefon, captan, thiophanate-methyl, thiabendazole, phosethyl-Al, chlorothalonil, dichloran, metalaxyl, captafol, iprodione, oxadixyl, vinclozolin, kasugamycin, myclobutanil, tebuconazole, difenoconazole, diniconazole, fluquinconazole, ipconazole, metconazole, penconazole, propiconazole, uniconzole, flutriafol, prochloraz, pyrifenox, fenarimol, triadimenol, diclobutrazol, copper oxychloride, furalaxyl, folpet, flusilazol, blasticidin S, diclomezine, edifenphos, isoprothiolane, iprobenfos, mepronil, neo-asozin, pencycuron, probenazole, pyroquilon, tricyclazole, validamycin, and flutolanil; nematocides such as aldoxycarb, fenamiphos and fosthietan; bactericides such as oxytetracyline, streptomycin and tribasic copper sulfate; acaricides such as binapacryl, oxythioquinox,

chlorobenzilate, dicofol, dienochlor, cyhexatin, hexythiazox, amitraz, propargite, tebufenpyrad and fenbutatin oxide; and biological agents such as Bacillus thuringiensis and baculovirus.

In certain instances, combinations with other arthropodicides having a similiar spectrum of control but a different mode of action will be particularly advantageous for resistance management.

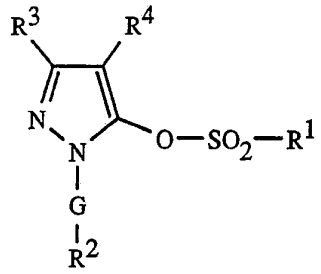
Arthropod pests are controlled and protection of agronomic crops, animal and human health is achieved by applying one or more of the compounds of this invention, in an effective amount, to the environment of the pests including the agronomic and/or nonagronomic locus of infestation, to the area to be protected, or directly on the pests to be controlled. A preferred method of application is by spraying. Alternatively, granular formulations of these compounds can be applied to the plant foliage or the soil. Other methods of application include direct and residual sprays, aerial sprays, systemic uptake, baits, eartags, boluses, foggers, fumigants, aerosols, and many others. The compounds can be incorporated into baits that are consumed by the arthropods or in devices such as traps and the like.

The compounds of this invention can be applied in their pure state, but most often application will be of a formulation comprising one or more compounds with suitable carriers, diluents, and surfactants and possibly in combination with a food depending on the contemplated end use. A preferred method of application involves spraying a water dispersion or refined oil solution of the compounds. Combinations with spray oils, spray oil concentrations, spreader stickers, adjuvants, and synergists and other solvents such as piperonyl butoxide often enhance compound efficacy.

The rate of application required for effective control will depend on such factors as the species of arthropod to be controlled, the pest's life cycle, life stage, its size, location, time of year, host crop or animal, feeding behavior, mating behavior, ambient moisture, temperature, and the like. Under normal circumstances, application rates of about 0.01 to 2 kg of active ingredient per hectare are sufficient to control pests in agronomic ecosystems, but as little as 0.001 kg/hectare may be sufficient or as much as 8 kg hectare may be required. For nonagronomic applications, effective use rates will range from about 1.0 to 50 mg/square meter but as little as 0.1 mg/square meter may be sufficient or as much as 150 mg/square meter may be required.

The following Tests demonstrate the control efficacy of compounds of this invention on specific pests. The pest control protection afforded by the compounds is not limited, however, to these species. See Index Tables A and B for compound descriptions.

Index Table A



Compound	G	R^1	R^2	R^3	R^4	m.p. (°C)
1	SO_2	CH_3	CH_3	CH_3	H	129-130
2	SO_2	CH_3	nPr	CH_3	H	oil[a]
3	SO_2	CH_3	iBu	CH_3	H	oil[b]
4	CO	CH_3	N(H)iPr	CH_3	H	oil[c]
5	SO_2	CH_3	nPr	CH_3	CH_3	oil[d]
6	SO_2	CH_3	nBu	CH_3	H	oil[e]
7	SO_2	CH_3	$N(CH_3)_2$	CH_3	H	oil[f]
9	SO_2	CH_3	nPr	CH_3OCH_2	H	oil[g]
10	CO	CH_3	C_2H_5	CH_3	H	74.5-77.5
12	SO_2	CH_3	nPr	C_2H_5	H	oil[h]
14	CO	CH_3	C_2H_5	CH_3	H	51-53
16	SO_2	CH_3	CH_2Ph	CH_3	H	119-122
17	SO_2	CH_3	nPr	CH_3	Br	oil[i]
18	CO	CH_3	N(H)iPr	$CH_3S(O)_2NH$	H	139-142
19	C=S	CH_3	$N(H)C_2H_5$	CH_3	H	47-49
20	CO	CH_3	N(H)iPr	NH_2	H	oil[j]
35	SO_2	CH_3	nPr	$C(O)OC_2H_5$	H	89-90
47	SO_2	CH_3	nPr	Ph	H	80-82
51	CO	CH_3	N(H)iPr	Ph	H	141-144

a ^1H NMR reported in Example 1

b ^1H NMR ($CDCl_3$) δ 1.10 (d,6), 2.31 (s,3), 2.33 (m,1) 3.33 (s,3), 3.35 (m,2) 6.12 (s,1)

c ^1H NMR ($CDCl_3$) δ 1.27 (d,6), 2.24 (s,3), 3.38 (s,3), 4.02 (m,1), 6.07 (s,1), 6.9 (br,1)

d ^1H NMR ($CDCl_3$) δ 1.05 (t,3), 1.82 (q,2), 2.02 (s,3), 2.24 (s,3), 3.38 (m,2), 3.40 (s,3)

[e] ^{1}H NMR ($CDCl_3$) δ 0.93 (t,3), 1.44 (m,2), 1.78 (m,2), 2.31 (s,3), 3.33 (s,3), 3.42 (m,2), 6.12 (s,1)

[f] ^{1}H NMR ($CDCl_3$) δ 2.28 (s,3), 3.00 (s,6), 3.29 (s,3), 6.08 (s,1)

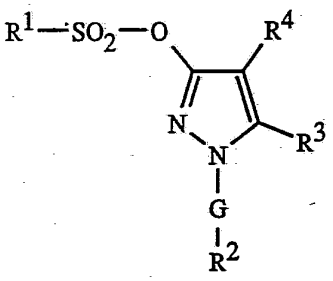
[g] ^{1}H NMR ($CDCl_3$) δ 1.15 (t,3), 2.02 (m,2), 3.36 (s,3), 3.42 (s,3), 3.46 (m,2), 4.45 (s,2), 6.33 (s,1)

[h] ^{1}H NMR ($CDCl_3$) δ 1.05 (t,3), 1.14 (t,3), 2.00 (m,2), 2.66 (q,2), 3.39 (s,3), 3.45 (m,2), 6.14 (s,1)

[i] ^{1}H NMR ($CDCl_3$) δ 1.17 (t,3), 2.11 (m,2), 2.32 (s,3), 3.81 (s,3), 3.58 (m,2)

[j] ^{1}H NMR ($CDCl_3$) 1.24 (d,6), 3.85 (s,3), 3.89 (br,2), 4.02 (m,1), 5.71 (s,1), 6.76 (br,1)

Index Table B



Cmpd[r]	G	R^1	R^2	R^3	R^4	m.p. (°C)
8	CO	CH_3	N(H)iPr	NH_2	H	142-144
11	CO	CH_3	N(H)iPr	H	H	90-91
13	SO_2	CH_3	nPr	NH_2	H	72-73
15	CO	CH_3	C_2H_5	CH_3	H	50-51
21	SO_2	CH_3	nPr	CH_3	H	85-86
22	SO_2	CH_3	CH_3	H	H	93-96
23	C=S	CH_3	N(H)iPr	NH_2	H	101-102
24	SO_2	CH_3	nPr	H	H	oil[k]
25	SO_2	CH_3	nPr	H	CH_3	62-64
26	CO	CH_3	N(H)iPr	CH_3	H	140-141
27	SO_2	nPr	nPr	CF_3	H	40-43
28	SO_2	CH_3	nPr	CF_3	H	55-57
29	SO_2	CH_3	iPr	CH_3	H	28-30
30	SO_2	CH_3	nBu	CH_3	H	oil[l]
31	SO_2	CH_3	C_2H_5	CH_3	H	36-39
32	SO_2	CH_3	nPr	SCH_3	H	66-67
33	SO_2	CH_2Cl	nPr	CH_3	H	56-57

	34	SO_2	CH_3	nPr	$C(O)OC_2H_5$	H	116-119
	36	SO_2	CH_3	iBu	CH_3	H	oil[m]
	37	CO	CH_3	N(H)sBu	H	H	67-68
	38	SO_2	CH_3	iBu	H	H	oil[n]
	39	SO_2	CH_3	CH_2Ph	CH_3	H	128-129
	40	SO_2	CH_3	nPr	CH_3	CH_3	94-96
	41	SO_2	CH_3	CH_3	H	Br	137-138
	42	SO_2	CH_3	nPr	C_2H_5	H	67-68
	43	SO_2	CH_3	iPr	H	H	45-46
	44	SO_2	CH_3	$CH_2CH_2C(F)=CF_2$	CH_3	H	oil[o]
	45	SO_2	CH_3	iBu	SCH_3	H	oil[p]
	46	SO_2	CH_3	nPr	Ph	H	75-78
	48	SO_2	CH_3	nPr	cPr	H	55-56
	49	CO	CH_3	$N(H)cPrCH_3$	H	H	90-91
	50	CO	CH_3	N(H)iPr	Ph	H	137-138
	52	SO_2	CH_3	$CH_2CH_2C(F)=CF_2$	H	H	oil[q]

r cmpd = Compound

k ^{1}H NMR ($CDCl_3$) δ 1.04 (t,3), 1.78 (m,2), 3.37 (s,3) 3.44 (m,2), 6.37 (d,1), 7.99 (d,1)

l ^{1}H NMR (CDCl3) δ 0.93 (t,3), 1.40 (m,2), 1.70 (m,2), 3.34 (s,3), 3.43 (m,2), 6.08 (s,1)

m ^{1}H NMR ($CDCl_3$) δ 1.08 (d,6), 2.11 (m,1), 2.55 (s,3), 3.32 (d,2), 3.34 (s,3), 6.08 (s,1)

n ^{1}H NMR ($CDCl_3$) δ 1.08 (d,6), 2.11 (m,2), 3.32 (d,2), 3.34 (s,3), 6.37 (s,1), 8.00 (s,1)

o ^{1}H NMR ($CDCl_3$) δ 2.32 (s,3), 2.83 (m,2), 3.34 (s,3), 3.67 (m,2), 6.15 (s,1)

p ^{1}H NMR ($CDCl_3$) δ 1.09 (d,6), 2.23 (m,1), 2.51 (s,3), 3.31 (d,2), 3.36 (s,3), 6.05 (s,1)

q ^{1}H NMR ($CDCl_3$) δ 3.83 (m,2), 3.37 (s,3), 3.73 (m,2), 6.32 (s,1), 7.76 (s,1)

TEST A

Fall Armyworm

Test units, each consisting of a H.I.S. (high impact sytrene) tray with 16 cells were prepared. In 12 of the cells is placed wet filter paper and approximately 8 cm^2 of lima leaf, in the other 4 cells is a 0.5 cm layer of wheat germ diet. Fifteen to twenty third instar larvae of fall armyworm (*Spodoptera frugiperda*) were placed in a 8 ounce (230 mL) plastic cup. Solutions of each of

the test compounds in 75/25 acetone/distilled water solvent were sprayed into the tray and cup. Spraying was accomplished by passing the tray and cup, on a conveyor belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds of active ingredient per acre (about 0.55 kg/ha) at 30 psi (207 kPa). The insects were transferred into the tray (one insect per cell). The trays were covered and held at 27°C and 50% relative humidity for 48 h after which time readings were taken on the 12 cells with lima leaves. The 4 remaining cells were read at 7 days for a delayed toxicity reading. Of the compounds tested, the following gave mortality levels of 80% or higher: 24.

TEST B

Southern Corn Rootworm

Units consisting of an 8-ounce (230 mL) plastic cup containing 1 one-inch square of a soybean-wheatgerm diet were prepared. The test units were sprayed as described in TEST A with individual solutions of the test compounds. After the spray on the cups had dried, five second-instar larvae of the southern corn rootworm (*Diabrotica undecimpunctata howardi*) were placed into each cup. The cups were then covered and held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 17*, 21*, 22, 24, 25, 26, 29*, 30*, 31*, 32, 33, 36, 37, 38*, 39, 40, 41, 42, 43*, 44, 45*.

* Compound sprayed at a rate of 0.13 kg/ha.

TEST C

Boll Weevil

Five adult boll weevils (*Anthonomus grandis*) were placed into each of a series of 9-ounce (260 mL) cups. The test units were sprayed as described in TEST A with individual solutions of the below-listed compounds. Each cup was then covered with a vented lid and held at 27°C. and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 11, 13, 22, 24, 25, 32, 36, 38, 41, 43*, 45*.

* Compound sprayed at a rate of 0.13 kg/ha.

TEST D

Aster Leafhopper

Test units were prepared from a series of 12-ounce (350 mL) cups, each containing oat (*Avena sativa*) seedlings in a 1-inch (2.5 cm) layer of sterilized soil and a 1/2 inch layer of sand. The test units were sprayed as described in TEST A with individual solutions of the compounds. After the oats had dried from the spraying, between 10 and 15 adult aster leafhoppers (*Mascrosteles fascifrons*) were aspirated into each of the cups covered and vented lids. The cups were held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following gave mortality levels of 80% or higher: 1, 2, 3, 4, 7, 10, 21*, 22, 24, 25, 29*, 30, 31*, 32, 33, 36, 37, 38*, 40, 42, 43*, 44, 45*.

* Compound sprayed at a rate of 0.13 kg/ha.

TEST E

Black Bean Aphid

Individual nasturtium leaves were infested with 10 to 15 aphids (all stages of *Aphis fabae*) and sprayed with their undersides facing up as described in TEST A. The leaves were then set in 3/8-inch (0.94 cm) diameter vials containing 4 mL of sugar water solution and covered with a clear plastic 1-ounce (29 mL) portion cup to prevent escape of aphids that drop from the leaves. The test units were held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following resulted in greater than or equal to 80% mortality at 1000 ppm: 22, 25, 32, 33, 36, 38, 41, 42, 45*.

* Compound sprayed at a rate of 0.13 kg/ha.

TEST F

Two-Spotted Spider Mite

One inch squares (2.54 cm) of kidney bean leaves that had been infested on the undersides with 25 to 30 adult mites (*Tetranychus urticae*) were sprayed with their undersides facing up on a hydraulic sprayer with a solution of the test compound (acetone/distilled water 75/25 solvent). Spraying was accomplished by passing the leaves, on a conveyer belt, directly beneath a flat fan hydraulic nozzle which discharged the spray at a rate of 0.5 pounds of active ingredient per acre (about 0.55 kg/ha) at 30 psi (207 kPa). The leaf squares were then placed

underside-up on a square of wet cotton in a petri dish and the perimeter of the leaf square was tamped down onto the cotton with forceps so that the mites cannot escape onto the untreated leaf surface. The test units were held at 27°C and 50% relative humidity for 48 h, after which time mortality readings were taken. Of the compounds tested, the following resulted in greater than or equal to 80% mortality: 4, 22, 24, 25, 36, 38*, 41, 43*.

* Compound sprayed at a rate of 0.13 kg/ha.

TEST G

Contact Activity Against Green Leafhopper Nymphs

Three rice (*Oryza sativa*) seedlings, 1.5 leaf stage and about 10 cm tall, are transplanted into a 1/2 oz. (14 mL) plastic cup containing Kumiai Brown artificial soil. Seven milliliters of distilled water is then added to the cup. The test chemical is prepared by first dissolving the chemical in acetone and then adding water to produce a final test concentration of 75:25 (acetone:water). Four plastic cups, each cup serving as a replicate, are then placed on a spray chamber turntable. The cups are sprayed for 45 seconds with 50 mL of the chemical solution at a pressure of 2.0 kg/cm^2 with air atomizing spray nozzles. The turntable completes 7.5 rotations during the 45 second spray interval. After chemical application, treated cups are held in a vented enclosure to dry for about 2 h. After drying, the cups are placed into conical shaped test units and the surface of the soil covered with 2 to 3 mm of quartz sand. Eight to ten 3rd-instar nymphs of the green leafhopper (*Nephotettix cincticeps*) are transferred into the test units using an aspirator. The test units are held at 27°C and 65% relative humidity. Counts of the number of live and dead nymphs are taken at 24 and 48 h post-infestation. Insects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 2, 3, 4, 5, 7, 9, 11, 12, 13, 17, 21, 22, 24, 25.

TEST H

Contact Activity Against Brown Planthopper Nymphs

Three rice (*Oryza sativa*) seedlings, 1.5 leaf stage and about 10 cm tall are transplanted into a 1/2 oz. (14 mL) plastic cup containing Kumiai Brown artificial soil. Seven milliliters of distilled water is then added to the cup. The test chemical is prepared by first dissolving the chemical in acetone and then adding water to produce a final test concentration of 75:25 (acetone:water). Four plastic

cups, each cup serving as a replicate, are then placed on a spray chamber turntable. The cups are sprayed for 45 seconds with 50 mL of the chemical solution at a pressure of 2.0 kg/cm^2 with air atomizing spray nozzles. The turntable completes 7.5 rotations during the 45 second spray interval. After chemical application, treated cups are held in a vented enclosure to dry for about 2 h. After drying, the cups are placed into conical shaped test units and the surface of the soil covered with 2 to 3 mm of quartz sand. Eight to ten 3rd-instar nymphs of the brown planthopper (*Nilaparvata lugens*) are transferred into the test units using an aspirator. The test units are held at 27°C and 65% relative humidity. counts of the number of live and dead nymphs are taken at 24 and 48 h post-infestation. Insects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 2, 3, 4, 5, 7, 8, 11, 12, 13, 17, 21, 22, 23, 24, 25, 26.

TEST I

Solution Systemic Activity Against Green Leafhopper Nymphs

The test chemical is added directly into 10 mL of distilled water and dissolved completely. This chemical solution is poured into a conical shaped test unit. Three rice seedlings are then positioned in the unit by a notched sponge disk. The sponge disk allows complete immersion of the seedling root systems in the chemical solution, while the aerial portion of the plant is isolated above the solution. The sponge also prevents the test nymphs from accidentally contacting the test solution. A 7 to 10 mm space, between the surface of the chemical solution and the bottom of the sponge disk, prevents accidental chemical contamination of the sponge. The rice seedlings are allowed to absorb the chemical from the solution for 24 h in a growth chamber held at 27°C and 65% relative humidity. Eight to ten 3rd-instar nymphs of the green leafhopper (*Nephotettix cincticeps*) are transferred into the test units using an aspirator. The infested units are held under the same temperature and humidity conditions described above. Counts of the number of live and dead nymphs are taken at 24 and 48 h post-infestation. Inspects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 2, 3, 5, 7, 11, 12, 13, 17, 21.

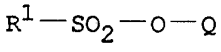
TEST J

Solution Systemic Activity Against Brown Planthopper Nymphs

The test chemical is added directly into 10 mL of distilled water and dissolved completely. This chemical solution is poured into a conical shaped test unit. Three rice seedlings are then positioned in the unit by a notched sponge disk. The sponge disk allows complete immersion of the seedling root systems in the chemical solution, while the aerial portion of the plant is isolated above the solution. The sponge also prevents the test nymphs from accidentally contacting the test solution. A 7 to 10 mm space, between the surface of the chemical solution and the bottom of the sponge disk, prevents accidental chemical contamination of the sponge. The rice seedlings are allowed to absorb the chemical from the solution for 24 h in a growth chamber held at 27°C and 65% relative humidity. Eight to ten 3rd-instar nymphs of the brown planthopper (*Nilaparvata lugens*) are transferred into the test units using an aspirator. The infested units are held under the same temperature and humidity conditions described above. Counts of the number of live and dead nymphs are taken at 24 and 48 h post-infestation. Inspects which cannot walk are classified as dead. Of the compounds tested, the following gave mortality levels of 80% or higher at 48 h at 100 ppm: 2, 3, 5, 7, 11, 12, 13, 21.

CLAIMS:

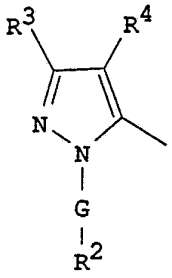
1. A compound of the formula



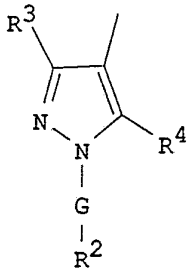
I

wherein:

Q is selected from the group

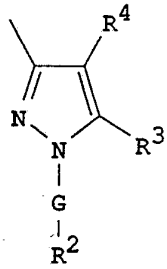


Q-1



and

Q-2



;

Q-3

G is selected from the group S, S(=O), $S(=O)_2$, C=S and C=O;

R^1 is selected from the group C_1–C_3 alkyl and C_1-C_3 haloalkyl;

R^2 is selected from the group C_1–C_6 alkyl, C_3-C_6 cycloalkyl, C_2–C_6 alkenyl and C_2–C_6 alkynyl each of which can be optionally substituted with R^5; or R^2 is selected from the group C_1–C_6 haloalkyl, $N(R^7)R^8$, C_3-C_6 cyclohaloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_4-C_7 cycloalkylalkyl and C_4–C_7 cycloalkylalkyl substituted with R^6;

R^3 and R^4 are independently selected from the group H, C_1–C_6 haloalkyl, C_1-C_6 alkoxy, C_1-C_6 haloalkoxy, C_1–C_6 alkylthio, C_1–C_6 haloalkylthio, C_3-C_6 cyclohaloalkyl, C_2–C_6 haloalkenyl, C_2–C_6 haloalkynyl, C_4-C_7 cycloalkylalkyl, C_1-C_6 alkylsulfinyl, C_1–C_6 haloalkylsulfinyl, C_1-C_6 alkylsulfonyl, C_1–C_6 haloalkylsulfonyl, C_2-C_6 alkoxycarbonyl, C_2–C_6 alkylcarbonyl, formyl, halogen, OH, NO_2, $N(R^{14})R^{15}$, $C(O)N(R^{14})R^{15}$, CN and phenyl optionally substituted with W; C_1-C_6 alkyl; C_3-C_6 cycloalkyl; C_2-C_6 alkenyl; C_2–C_6 alkynyl; wherein each of C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_2-C_6 alkenyl and C_2-C_6 alkynyl can be optionally substituted with R^{13};

R^5 and R^{13} are independently selected from the group CN, SCN, NO_2, OR^9, SR^9, $S(O)R^9$, SO_2R^9, $OC(O)R^9$, OSO_2R^9, $Si(R^9)(R^{10})(R^{11})$, CO_2R^9, $C(O)N(R^9)R^{10}$, $C(O)R^9$, $N(R^9)R^{10}$ and phenyl optionally substituted with R^{12};

R^6 is selected from the group halogen, CN and C_1-C_2 alkyl;

R^7 is selected from the group C_1-C_6 alkyl optionally substituted with R^{16}, C_3-C_6 cycloalkyl optionally substituted with R^{19}, and C_4-C_7 cycloalkylalkyl optionally substituted with R^{19};

R^8 is selected from the group H, CN, C_1-C_6 haloalkyl and C_1–C_6 alkyl optionally substituted with CN;

R^7 and R^8 can be taken together to form $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$ or $-CH_2CH_2-O-CH_2CH_2-$;

R^9, R^{10} and R^{11} are independently selected from the group C_1-C_3 alkyl and C_1–C_3 haloalkyl;

R^{12} and W are independently selected from the group halogen, C_1–C_2 alkyl, C_1-C_2 haloalkyl, C_1–C_2 alkoxy, C_1–C_2 haloalkoxy, C_1-C_2 alkylthio, C_1-C_2 haloalkylthio, C_1-C_2 alkylsulfinyl, C_1-C_2 haloakylsulfinyl, C_1-C_2 alkylsulfonyl, C_1-C_2 haloalkylsulfonyl, NO_2 and CN;

R^{14} and R^{15} are independently selected from the group H, C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkylcarbonyl, C_2-C_6 alkoxycarbonyl, C_1-C_6 alkylsulfonyl and $C(O)N(R^{17})R^{18}$; or

R^{14} and R^{15} can be taken together to form $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$ or $-CH_2CH_2-O-CH_2CH_2-$;

R^{16} is selected from the group 1 to 5 halogens, CN, C_1-C_2 alkoxy, C_1-C_2 alkylthio, C_1-C_2 alkylsulfonyl and C_3-C_6 trialkylsilyl;

R^{17} and R^{18} are independently selected from the group H and C_1-C_3 alkyl; and

R^{19} is selected from the group 1 to 5 halogens, C_1-C_3 alkyl, CN, C_1-C_2 alkoxy, C_1-C_2 alkylthio, C_1-C_2 alkylsulfonyl and C_3-C_6 trialkylsilyl.

2. A compound according to Claim 1 wherein:

G is selected from the group $S(=O)_2$ and C=O

R^1 is selected from the group CH_3 and $ClCH_2$;

R^2 is selected from the group C_1-C_6 alkyl, C_1-C_6 haloalkyl, C_2-C_6 alkenyl, C_2-C_6 haloalkenyl and $N(R^7)R^8$;

R^3 and R^4 are independently selected from the group H, C_1-C_2 alkyl, C_1-C_2 haloalkyl, C_1-C_2 alkoxy, $N(R^{14})R^{15}$ and halogen; and

R^{14} and R^{15} are independently selected from the group H and C_1-C_6 alkyl.

3. A compound according to Claim 2 wherein Q is Q-1.

4. A compound according to Claim 2 wherein Q is Q-2.

5. A compound according to Claim 2 wherein Q is Q-3.

6. An arthropodicidal composition comprising an arthropodicidally effective amount of a compound according to any one of Claims 1 to 5 and a carrier therefor.

7. A method for controlling arthropods comprising applying to them or to their environment an arthropodicidally effective amount of a compound according to any one of Claims 1 to 5.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/01271

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 C07D231/20; C07D231/18; A01N43/50

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	C07D

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
A	EP,A,0 182 603 (NIPPON KAYAKU KABUSHIKI KAISHA) 28 May 1986 see page 49 - page 51; claims ---	1-7
A	EP,A,0 220 857 (NIPPON KAYAKU KABUSHIKI KAISHA) 6 May 1987 see page 61 - page 65; claims ---	1-7
A	GB,A,629 482 (DUPONT DE NEMOURS) 21 September 1949 see page 1 - page 2 ---	1-5
A	GB,A,631 269 (DUPONT DE NEMOURS) 31 October 1949 see page 1 - page 2 ---	1-5

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° Special categories of cited documents :[10]

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

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

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

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

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

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

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

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

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
11 MAY 1993	- 8. 06. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	LUYTEN H.W.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP,A,0 100 476 (BAYER) 15 February 1984 see claims	1-7
A	EP,A,0 245 944 (NIPPON KAYAKU KABUSHIKI KAISHA) 19 November 1987 cited in the application see page 62 - page 63; claims & US,A,4 791 127 (KATO SHOICHI ET. AL.)	1-7
A	PESTICIDE SCIENCE vol. 29, no. 1, 1990, BARKING ,UK pages 95 - 100 NIELS JACOBSON ET. AL. cited in the application	1-7

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9301271
SA 70165

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 11/05/93

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		JP-A- 61118367	05-06-86
		US-A- 4652574	24-03-87
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		JP-A- 62081377	14-04-87
		EP-A- 0245944	19-11-87
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