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N-OXY- AND THIOALKYLCARBONYLOXYALKYLPYRROLE INSECTICIDAL, ACARICIDAL AND MOLLUSCICIDAL AGENTS

Insects, acarina and mollusks destroy growing and harvested crops. In the United States alone, agronomic crops must compete with thousands of insect and acarid species. Accordingly, there is ongoing research to create new and more effective insecticides, acaricides and molluscicides for the control of insects, acarina and mollusks and for the protection of plants from attack by insects, acarina and mollusks. There is also ongoing research to create new insecticides and acaricides to overcome the resistance observed with several classes of insecticidal and acaricidal agents.

The present invention describes N-oxy- and thioalkylcarbonyloxyalkylpyrrole compounds which are useful as insecticidal, acaricidal and molluscicidal agents for the control of insects, acarina and mollusks and for the protection of plants from attack by insects, acarina and mollusks.

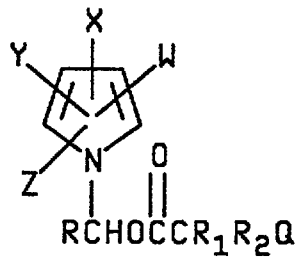
This invention also relates to compositions containing those compounds and methods for using those compounds and compositions. Advantageously, it has been found that the N-oxy- and thioalkylcarbonyloxyalkylpyrrole compounds of the present invention, and compositions containing them, are effective insecticidal, acaricidal and molluscicidal agents for the control of insects, acarina and mollusks and for the

protection of plants from attack by insects, acarina and mollusks. The compounds of the present invention are especially useful for the control of tobacco budworms.

Advantageously, the present invention provides a method for controlling insects, acarina and mollusks by contacting said insects, acarina and mollusks, their breeding grounds, food supply or habitat with an insecticidally, acaricidally or molluscicidally effective amount of a formula I, N-oxy- or thioalkylcarbonyloxyalkylpyrrole compound.

The present invention also provides a method for protecting growing plants from attack by insects, acarina and mollusks by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally, acaricidally or molluscicidally effective amount of a formula I, N-oxy- or thioalkylcarbonyloxyalkylpyrrole compound.

The N-oxy- and thioalkylcarbonyloxyalkylpyrrole compounds of the present invention have the following structural formula I:



(I)

wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen,
C_1-C_4 alkyl optionally substituted with one or more halogen atoms, or
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF_3, CN, NO_2, $S(O)_mCF_2R_4$ or
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is halogen, CF_3 or
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF_3;

R is hydrogen or C_1-C_4 alkyl;

R_1 and R_2 are each independently hydrogen,
C_1-C_6 alkyl optionally substituted with one or more halogen atoms,
C_1-C_6 alkoxy optionally substituted with one

or more halogen atoms,
C_1-C_6 alkylthio optionally substituted with one or more halogen atoms, or
phenyl optionally substituted with one or more halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms, or

when R_1 and R_2 are taken together with the atom to which they are attached may form a C_3-C_6 cycloalkyl group optionally substituted with one to three C_1-C_4 alkyl groups, C_2-C_6 alkenyl groups or phenyl groups, or R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or $S(O)_p$;

p is an integer of 0, 1 or 2;

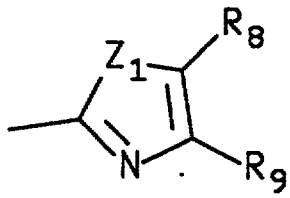
R_3 is hydrogen,
C_1-C_6 alkyl,
C_1-C_6 alkenyl,
C_2-C_6 alkynyl,
phenyl optionally substituted with one or more halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted

with one or more halogen atoms,

$C(O)R_7$ provided p is 0,

$C(O)A_1$ provided p is 0,

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl,

C_2-C_6 alkenyl,

C_2-C_6 alkynyl, or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

n is an integer of 1, 2 or 3;

R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or

when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-;

A_1 is OR_{10} or $NR_{11}R_{12}$;

R_{10} is C_1-C_6 alkyl or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

R_{11} and R_{12} are each independently hydrogen or C_1-C_4 alkyl; and

R_{13} is C_1-C_4 alkyl.

Preferred formula I compounds of the invention are those wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen or C_1-C_4 alkyl;

X is Cl, Br, CF_3 or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF_3 or

phenyl optionally substituted with one or more

halogen atoms

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted

with one or more halogen atoms;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms, or

R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,

phenyl optionaly substituted with one or more halogen atoms,

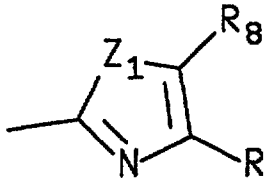
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl;

n is an integer of 1, 2 or 3;

R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or

when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-; and

R_{13} is C_1-C_4 alkyl.

More preferred insecticidal, acaricidal and molluscicidal compounds of this invention are those wherein

W is CN;

X is phenyl optionally substituted with one or more
- halogen atoms,
- NO_2 groups,
- CN groups,
- C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
- C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl or Br;

Z is Cl, Br or CF_3;

R is hydrogen;

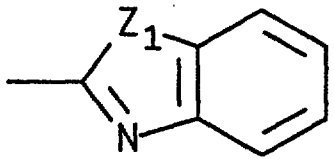
R_1 and R_2 are each independently
- hydrogen or
- C_1-C_6 alkyl, or
- R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or S;

R_3 is
- C_1-C_6 alkyl,
- phenyl optionally substituted with one or more
  - halogen atoms,
  - NO_2 groups,
  - CN groups,
  - C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
  - C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

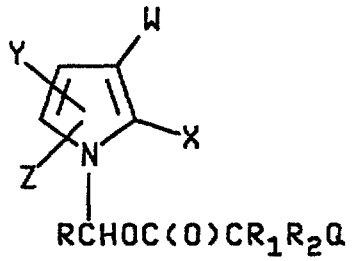
Z_1 is O or S;

R_7 is C_1-C_6 alkyl;

n is an integer of 1, 2 or 3; and

R_{13} is C_1-C_4 alkyl.

Most preferred compounds of this invention which are especially effective insecticidal, acaricidal and molluscicidal agents are those having the structural formula II:



(II)

wherein

W is CN;

X is phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl or Br;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen or

C_1-C_6 alkyl, or

R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,

phenyl optionally substituted with one or more

halogen atoms,

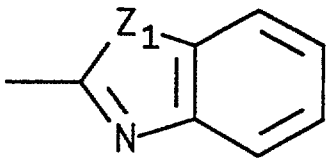
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl;

n is an integer of 1, 2 or 3; and

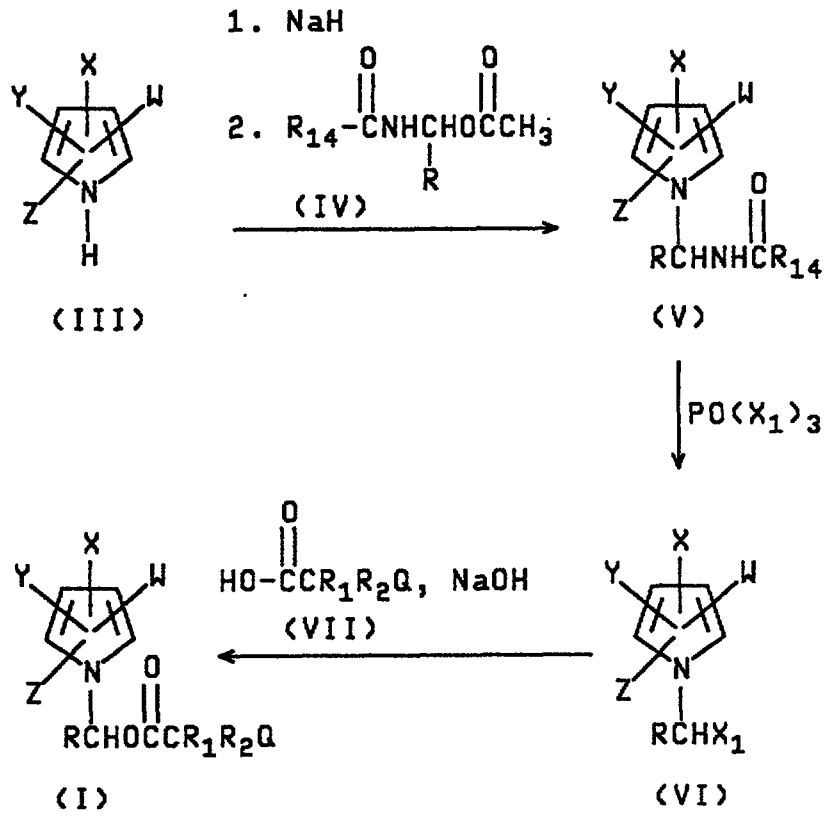
R_{13} is C_1-C_4 alkyl.

Exemplary of halogen hereinabove are fluorine, chlorine, bromine and iodine.

Advantageously, it has been found that the formula I compounds of the present invention are especially useful for the control of tobacco budworms, southern armyworms and two-spotted spider mites.

Formula I compounds may be prepared as shown in Flow Diagram I.

FLOW DIAGRAM I



wherein

R_{14} is C_1-C_6 alkyl optionally substituted with one to three halogen atoms,

phenyl optionally substituted with one or two halogen, CN, NO_2, C_1-C_4 alkyl, C_1-C_4 alkoxy or CF_3 groups,

2- or 3-thienyl or

2- or 3-furyl;

X_1 is Cl or Br; and
W, X, Y, Z, R, R_1, R_2 and Q are as described hereinabove for formula I.

The appropriately substituted pyrrole of formula III is reacted with an alkylating agent of formula IV in the presence of an alkali metal hydride or an alkali metal C_1-C_6 alkoxide to form an N-alkanoylaminomethyl or N-aroylaminomethylpyrrole of formula V, said formula V aminomethylpyrrole is then reacted with an excess of phosphorous oxychloride or phosphorus oxybromide to form a 1-halomethylpyrrole of formula VI. Said 1-halomethylpyrrole is reacted with a carboxylic acid of formula VII in the presence of an alkali metal hydroxide, such as sodium or potassium hydroxide, to form desired N-oxy- and thioalkylcarbonyloxyalkylpyrrole compounds of formula I.

The N-oxy- and thioalkylcarbonyloxyalkylpyrrole compounds of the present invention are effective for controlling insects, acarina and mollusks. Those compounds are also effective for protecting growing or harvested crops from attack by insects, acarina and mollusks.

Insects controlled by the formula I compounds of this invention include Lepidoptera such as tobacco budworms, cabbage loopers, cotton boll worms, beet armyworms, southern armyworms and diamondback moths; Homoptera such as aphids, leaf hoppers, plant hoppers and white flies; Thysanoptera such as thrips; Coleoptera such as boll weevils, Colorado potato beetles, southern corn rootworms and mustard beetles; and Orthoptera such as locusts, crickets, grasshoppers and cockroaches. Acarina controlled by the compounds of this invention include mites such as two-spotted spider mites, carmine spider mites, banks grass mites, strawberry mites, citrus rust mites and leprosis mites.

Mollusks controlled by the compounds of this invention include gastropoda such as snails, slugs, cowries and limpets. Advantageously, it has been found that the compounds of the present invention are especially effective against tobacco budworms, southern armyworms, two-spotted spider mites and slugs.

In practice, generally about 10 ppm to 10,000 ppm and preferably about 100 ppm to about 5,000 ppm of a formula I compound, dispersed in water or another liquid carrier, is effective when applied to the plants, the crops or the soil in which said crops are growing to protect said crops from attack by insects, acarina and mollusks.

The formula I compounds of this invention are also effective for controlling insects, acarina and mollusks, when applied to the foliage of plants and/or to the soil or water in which said plants are growing in sufficient amount to provide a rate of from about 0.100 kg/ha to 4.0 kg/ha of active ingredient.

While the compounds of this invention are effective for controlling insects, acarina and mollusks when employed alone, they may also be used in combination with other biological chemicals, including other insecticides, acaricides and molluscicides. For example, the formula I compounds of this invention may be used effectively in conjunction or combination with pyrethroids, phosphates, carbamates, cyclodienes, endotoxin of bacillus thuringiensis (Bt), formamidines, phenol tin compounds, chlorinated hydrocarbons, benzoylphenyl ureas and the like.

The compounds of this invention may be formulated as emulsifiable concentrates, flowable concentrates or wettable powders which are diluted with water or other suitable polar solvent, generally <u>in situ</u>, and then applied as a dilute spray. Said

compounds may also be formulated in dry compacted granules, granular formulations, dusts, dust concentrates, suspension concentrates, microemulsions and the like all of which lend themselves to seed, soil, water and/or foliage applications to provide the requisite plant protection. Such formulations include the compounds of the invention admixed with inert, solid or liquid diluents.

For example, wettable powders, dusts, and dust concentrate formulations can be prepared by grinding and blending together about 25% to about 85% by weight of formula I compounds and about 75% to about 15% by weight of a solid diluent such as bentonite, diatomaceous earth, kaolin, attapulgite, or the like, about 1% to 5% by weight of a dispersing agent such as sodium lignosulfonate, and about 1% to 5% by weight of a nonionic surfactant, such as octylphenoxy polyethoxy ethanol, nonylphenoxy polyethoxy ethanol or the like.

A typical emulsifiable concentrate can be prepared by dissolving about 15% to about 70% by weight of a formula I compound in about 85% to about 30% by weight of a solvent such as isophorone, toluene, butyl cellosolve, methyl acetate, propylene glycol monomethyl ether, or the like and dispersing therein about 1% to 5% by weight of a nonionic surfactant such as an alkylphenoxy polyethoxy alcohol.

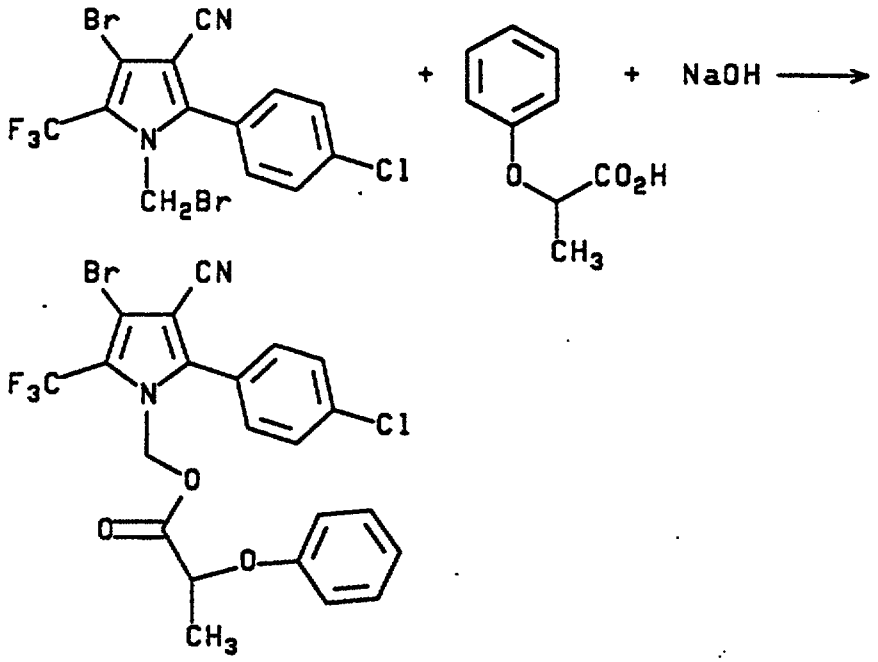
An especially effective method for controlling terrestrial gastropods with the formula I compounds of the invention, is to proffer the active molluscicidal material in the form of a bait formulation. These bait formulations can be widely varied but generally contain about 1% to 20% by weight of the active ingredient, about 40% to 50% by weight of solid edible nutritive substance, about 5% to 10% by weight of a carbohydrate source such as sugar, molasses, corn

syrup or the like and the remainder of the formulation, i.e. about 30% to 50% by weight of water or other consumable liquid.

In order to facilitate a further understanding of the invention, the following examples are presented to illustrate more specific details thereof. The invention is not to be limited thereby except as defined in the claims.

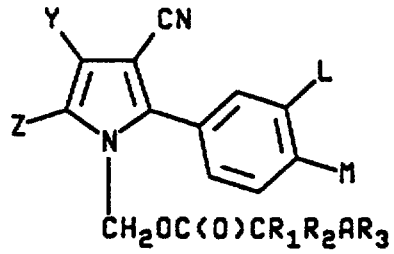
EXAMPLE 1

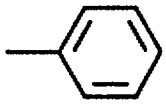
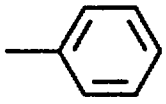
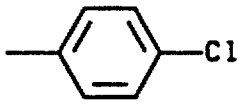
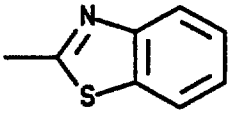
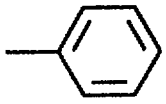
Preparation of [3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenoxypropionate

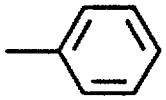
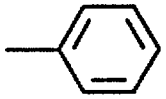
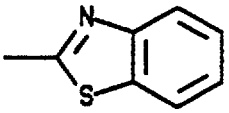


4-Bromo-1-(bromomethyl)-2-(p-chlorophenyl)-5-(trifluormethyl)pyrrole-3-carbonitrile (2.5 g, 5.7 mmol) is added to a mixture of 2-phenoxypropionic acid (1.9 g, 11.4 mmol) and sodium hydroxide (0.46 g, 11.4 mmol) in N,N-dimethylformamide. The reaction mixture is stirred for one hour at 50°C and diluted with a 3:2 ethyl acetate/water mixture. The organic phase is separated, dried over $MgSO_4$ and concentrated <u>in vacuo</u> to obtain a tan oil. The oil is crystallized from 2-propanol to give the title product as a yellow solid (2.7 g, mp 101°-103°C).

Using essentially the same procedure, but employing the appropriately substituted 1-(halomethyl)-pyrrole and carboxylic acid, the following compounds are obtained:

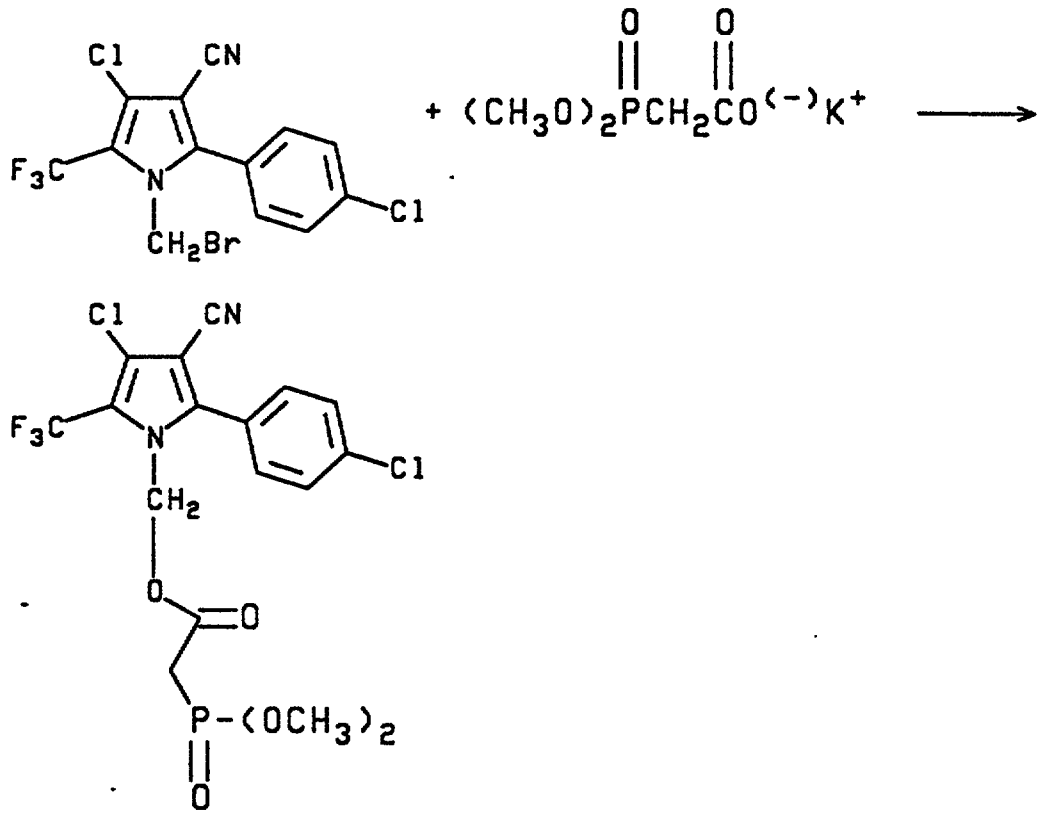


L	M	Y	Z	R_1	R_2	R_3	A	mp°C
H	Cl	Br	CF_3	H	H		O	117 - 118
H	Cl	Br	CF_3	H	H	CH_3	O	100 - 101
H	Cl	Br	CF_3	H	H		S	oil
H	Cl	Br	CF_3	H	H		O	132 - 134
H	Cl	Br	CF_3	H	H		O	165.5 - 168
H	Cl	Br	CF_3		=CH-CH=CH-		S	110 - 111.5
H	Cl	Br	CF_3		=CH-CH=CH-		O	101 - 102
Cl	Cl	Cl	Cl	H	H		S	79.5 - 82

L	M	Y	Z	R_1	R_2	R_3	A	mp°C
Cl	Cl	Cl	Cl	H	H		O	103.5 - 105
Cl	Cl	Cl	Cl	H	CH_3		O	112 - 115
H	Cl	Br	CF_3	H	H	$-(CH_2CH_2O)_3CH_3$	O	oil
H	CF_3	Cl	Cl	H	H		O	195 - 197
H	CF_3	Cl	Cl		=CH-CH=CH-		O	125 - 128
H	Cl	Br	CF_3	H	$-CH_2-CH_2-CH_2-$		O	121 - 123
H	CF_3	Cl	Cl	H	$-CH_2-CH_2-CH_2-$		O	104 - 106.5
H	CF_3	Cl	Cl	H	$-CH_2-CH_2-CH_2-$		S	84 - 86.5

EXAMPLE 2

Preparation of [3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (dimethylphosphono)acetate



A solution of potassium (dimethylphosphono)-acetate (0.69 g, 4 mmol) in N,N-dimethylformamide is treated with 1-(bromomethyl)-4-chloro-2-(p-chlorophenyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (0.79 g, 2 mmol), stirred at room temperature for one hour, diluted with water and extracted with ethyl acetate. The combined organic extracts are washed sequentially with water and brine, dried over anhydrous $MgSO_4$ and concentrated <u>in vacuo</u> to obtain a brown oil. The oil is chromatographed using silica gel and a 1:1 hexanes/ethyl acetate mixture to give the title product as a viscous yellow oil (0.41 g) which is identified by ^{13}C and ^{19}FNMR spectral analyses.

EXAMPLE 3

Insecticide and acaricide evaluations

The following tests show the efficacy of the compounds as insecticides and acaricides. The evaluations are conducted with solutions of test compounds dissolved or dispersed in 50/50 acetone/water mixtures. The test compound is technical material dissolved or dispersed in said acetone/water mixtures in sufficient amounts to provide the concentrations set forth in Table I below.

All concentrations reported herein are in terms of active ingredient. All tests are conducted in a laboratory maintained at about 27°C. The rating system employed is as follows:

Rating System

0 = no effect	5 = 56-65% kill
1 = 10-25% kill	6 = 66-75% kill
2 = 26-35% kill	7 = 76-85% kill
3 = 36-45% kill	8 = 86-99% kill
4 = 46-55% kill	9 = 100% kill
	- = no evaluation

The test species of insects used in the present evaluations along with specific test procedures are described below.

Spodoptera eridania 3rd instar larvae, southern armyworm

A sieva lima bean leaf expanded to 7 to 8 cm in length is dipped in the test suspension with agitation for 3 seconds and placed in a hood to dry. The leaf is then placed in a 100x10 mm petri dish containing a damp filter paper on the bottom and 10 3rd

instar caterpillars. The dish is maintained for 5 days before observations are made of mortality, reduced feeding or an interference with normal moulting.

Tetranychus urticae (OP-resistant strain), 2-spotted spider mite

Sieva lima bean plants with primary leaves expanded to 7 to 8 cm are selected and cut back to one plant per pot. A small piece is cut from a leaf taken from the main colony and placed on each leaf of the test plants. This is done about 2 hours before treatment to allow the mites to move over to the test plant and to lay eggs. The size of the cut piece is varied to obtain about 100 mites per leaf. At the time of the treatment, the piece of leaf used to transfer the mites is removed and discarded. The mite-infested plants are dipped in the test formulation for 3 seconds with agitation and set in the hood to dry. Plants are kept for 2 days before estimates of adult kill are made.

Empoasca abrupta, adults, western potato leafhopper

A Sieva lima bean leaf about 5 cm long is dipped in the test formulation for 3 seconds with agitation and placed in a hood to dry. The leaf is placed in a 100x10 mm petri dish containing a moist filter paper on the bottom. About 10 adult leafhoppers are added to each dish and the treatments are kept for 3 days before mortality counts are made.

Heliothis virenscens, 3rd instar tobacco budworm

Cotton cotyledons are dipped in the test formulation and allowed to dry in a hood. When dry, each is cut into quarters and ten sections placed individually in 30 mL plastic medicine cups containing a 5 to 7 mm long piece of damp dental wick. One 3rd

instar caterpillar is added to each cup and a cardboard lid placed on the cup. Treatments are maintained for 3 days before mortality counts and estimates of reduction in feeding damage are made.

Diabrotic undecimpunctata howardi, third instar southern corn rootworm

One cc of fine talc is placed in a 30 mL wide-mouth screw-top glass jar. One mL of the appropriate acetone test solution is pipetted onto the talc so as to provide 1.25 and 0.25 mg of active ingredient per jar. The jars are set under a gentle air flow until the acetone is evaporated. The dried talc is loosened, 1 cc of millet seed is added to serve as food for the insects and 25 mL of moist soil is added to each jar. The jars are capped and the contents throroughly mixed on a Vortex Mixer. Following this, ten 3rd-instar rootworms are added to each jar and the jars are loosely capped to allow air exchange for the larvae. The treatments are held for 6 days before mortality counts are made. Missing larvae are presumed dead, since they decompose rapidly and can not be found. The concentrations used in this test correspond approximately to 50 and 10 kg/ha, respectively.

The data obtained for the above described evaluations are reported in Table I.

TABLE I

Insecticide And Acaricide Evaluations

Compound	Armyworm (ppm)			OP-Resistant Mites (ppm)		Leaf-hopper (ppm)		Tobacco Budworm (ppm)			Southern Corn Rootworm (kg/ha)	
	1000	100	10	300	100	100	10	1000	100	10	50	10
[4-Bromo-2-(p-chlorophenyl)-3-cyano-5-(trifluoromethyl)pyrrol-1-yl]methyl phenoxyacetate	9	9	9	9	9	9	8.5	9	9	8.5	9	7
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl methyl carbonate	9	9	9	9	9	9	9	9	9	9	9	6
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]-methyl (phenylthio)acetate	9	9	9	9	9	9	9	9	9	7	4.5	0
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]-methyl (p-chlorophenoxy)-acetate	9	9	9	9	9	9	4	9	9	9	9	6

TABLE I (Continued)

Compound	Armyworm (ppm)			OP-Resistant Mites (ppm)		Leaf-hopper (ppm)		Tobacco Budworm (ppm)			Southern Corn Rootworm (kg/ha)	
	1000	100	10	300	100	100	10	1000	100	10	50	10
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenoxypropionate	9	9	9	9	8	9	6	9	9	8.5	9	0
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-(benzothiazol-2-yloxy)acetate	9	9	9	0	-	2	-	9	9	6	0	-
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-thiophenecarboxylate	9	9	9	0	-	9	6.5	9	9	8.5	9	8
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-furoate	9	9	9	9	9	9	8	9	9	8.5	8.5	9

TABLE I (Continued)

Compound	Armyworm (ppm)			OP-Resistant Mites (ppm)		Leaf-hopper (ppm)		Tobacco Budworm (ppm)			Southern Corn Rootworm (kg/ha)	
	1000	100	10	300	100	100	10	1000	100	10	50	10
[2,3-Dichloro-4-cyano-5-(3,4-dichlorophenyl)-pyrrol-1-yl]methyl (phenylthio)acetate	9	9	9	5	-	4	0	9	9	0	0	-
[2,3-Dichloro-5-(3,4-dichlorophenyl)-4-cyanopyrrol-1-yl]methyl 2-phenoxyacetate	9	9	9	9	0	6	0	9	9	0	0	-
[2,3-Dichloro-5-(3,4-dichlorophenyl)-4-cyano-pyrrol-1-yl]methyl 2-methyl-2-phenoxypropionate	9	4.5	0	0	0	0	0	9	6.5	0	0	-
[3-Bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl {2-[2-(2-methoxyethoxy)ethoxy]-ethoxy}acetate	9	9	9	9	0	9	9	9	9	7.5	9	6

TABLE I (Continued)

Compound	Armyworm (ppm)			OP-Resistant Mites (ppm)		Leaf-hopper (ppm)		Tobacco Budworm (ppm)			Southern Corn Rootworm (kg/ha)	
	1000	100	10	300	100	100	10	1000	100	10	50	10
[2,3-Dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)-pyrrol-1-yl]methyl 2-(benzothiazol-2-yl-oxy)acetate	9	9	0	0	-	4.7	0	9	6	0	0	-
[3,4-Dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoromethyl-p-tolyl)-pyrrol-1-yl]methyl 2-furoate	9	9	9	7	9	9	0	9	9	4	5.5	0
[3-Bromo-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl tetrahydro-2-furoate	9	9	9	9	9	9	3	9	9	6	0	-

TABLE I (Continued)

Compound	Armyworm (ppm)			OP-Resistant Mites (ppm)		Leaf-hopper (ppm)		Tobacco Budworm (ppm)			Southern Corn Rootworm (kg/ha)	
	1000	100	10	300	100	100	10	1000	100	10	50	10
[2,3-Dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl tetrahydro-2-furoate	9	9	9	0	-	9	9	9	9	3	0	-
[2,3-Dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)-pyrrol-1-yl]methyl 2-thiophenecarboxylate	9	9	9	0	-	9	3	-	9	4	0	-
[3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (dimethylphosphono)acetate	-	9	9	-	7	9	8	-	9	9	9	9

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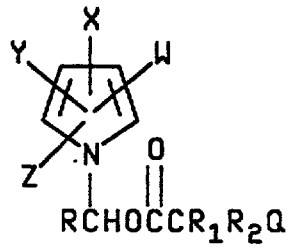
WE CLAIM:

1. A compound characterized by the structural formula



wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen,

C_1-C_4 alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF_3, CN, NO_2, $S(O)_mCF_2R_4$ or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted

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with one or more halogen atoms;

Y is halogen, CF_3 or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF_3;

R is hydrogen or C_1-C_4 alkyl;

R_1 and R_2 are each independently hydrogen,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms,

C_1-C_6 alkoxy optionally substituted with one or more halogen atoms,

C_1-C_6 alkylthio optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one mor more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms, or

when R_1 and R_2 are taken together with the atom to which they are attached may form a C_3-C_6 cycloalkyl group optionally substituted with one to three C_1-C_4 alkyl groups, C_2-C_6 alkenyl groups or phenyl groups, or R_1 or R_2 may be taken together

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with R_3 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Q is AR_3 or $P(O)(OR_{13})_2$;

A is O or $S(O)_p$;

p is an integer of 0, 1 or 2;

R_3 is hydrogen,

C_1-C_6 alkyl,

C_1-C_6 alkenyl,

C_2-C_6 alkynyl,

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

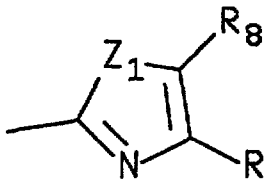
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,

$C(O)R_7$ provided p is 0,

$C(O)A_1$ provided p is 0,

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl,

C_2-C_6 alkenyl,

C_2-C_6 alkynyl, or

phenyl optionally substituted with one or more

halogen atoms,

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NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

n is an integer of 1, 2 or 3;

R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or
when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-;

A_1 is OR_{10} or $NR_{11}R_{12}$;

R_{10} is C_1-C_6 alkyl or
phenyl optionally substituted with one or more halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

R_{11} and R_{12} are each independently hydrogen or C_1-C_4 alkyl; and

R_{13} is C_1-C_4 alkyl.

2. The compound according to claim 1 wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen or C_1-C_4

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alkyl;

X is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

Y is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted
with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted
with one or more halogen atoms;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen,
C_1-C_6 alkyl optionally substituted with one
or more halogen atoms, or
R_1 or R_2 may be taken together with R_3 and
the atoms to which they are attached to form
a 5- to 6-membered heterocyclic ring;

Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,
phenyl optionaly substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,

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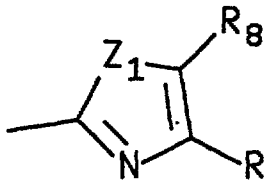
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl;

n is an integer of 1, 2 or 3;

R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or

when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-; and

R_{13} is C_1-C_4 alkyl.

3. The compound according to claim 2 wherein

W is CN;

X is phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl or Br;

Z is Cl, Br or CF_3;

R is hydrogen;

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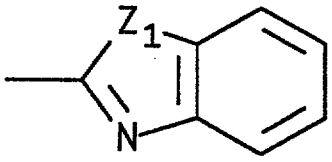
R_1 and R_2 are each independently hydrogen or
C_1-C_6 alkyl, or
R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

Q is AR_3 or $P(OR_{13})_2$;
A is O or S;
R_3 is C_1-C_6 alkyl,
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,
$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5-membered heterocyclic ring;
Z_1 is O or S;
R_7 is C_1-C_6 alkyl;
n is an integer of 1, 2 or 3; and
R_{13} is C_1-C_4 alkyl.

4. The compound according to claim 3 wherein the compound has the structural formula

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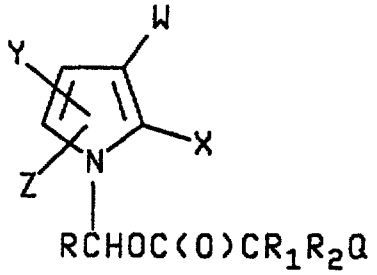
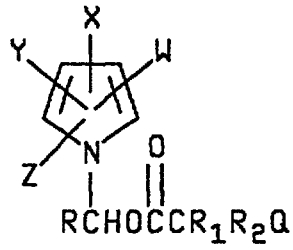


5. The compound selected from the group consisting of [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-methyl)pyrrol-1-yl]methyl methyl carbonate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-furoate; [4-bromo-2-(p-chlorophenyl)-3-cyano-5-(trifluoromethyl) pyrrol-1-yl]methyl phenoxyacetate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-methyl)pyrrol-1-yl]methyl(p-chlorophenoxy)acetate; and [3-bromo-5-(p-chlorophenyl)4-cyano-2-(trifluoromethyl) pyrrol-1-yl]methyl(phenylthio)acetate.

6. A method for controlling insects, acarina and mollusks which is characterized by contacting said insects, acarina and mollusks, their breeding ground, food supply or habitat with an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

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R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen,

C_1-C_4 alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF_3, CN, NO_2, $S(O)_mCF_2R_4$ or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is halogen, CF_3 or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF_3;

R is hydrogen or C_1-C_4 alkyl;

R_1 and R_2 are each independently hydrogen,

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C_1-C_6 alkyl optionally substituted with one or more halogen atoms,

C_1-C_6 alkoxy optionally substituted with one or more halogen atoms,

C_1-C_6 alkylthio optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one mor more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms, or

when R_1 and R_2 are taken together with the atom to which they are attached may form a C_3-C_6 cycloalkyl group optionally substituted with one to three C_1-C_4 alkyl groups, C_2-C_6 alkenyl groups or phenyl groups, or R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or $S(O)_p$;

p is an integer of 0, 1 or 2;

R_3 is hydrogen,

C_1-C_6 alkyl,

C_1-C_6 alkenyl,

C_2-C_6 alkynyl,

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

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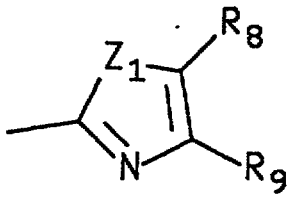
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,

$C(O)R_7$ provided p is 0,

$C(O)A_1$ provided p is 0,

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl,

C_2-C_6 alkenyl,

C_2-C_6 alkynyl, or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

n is an integer of 1, 2 or 3;

R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or

when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-;

A_1 is OR_{10} or $NR_{11}R_{12}$;

R_{10} is C_1-C_6 alkyl or

phenyl optionally substituted with one or

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more halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

R_{11} and R_{12} are each independently hydrogen or C_1-C_4 alkyl; and

R_{13} is C_1-C_4 alkyl.

7. The method according to claim 6 wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $C(=S)NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen or C_1-C_4 alkyl;

X is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms
NO_2 groups,

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CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms, or

R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,

phenyl optionaly substituted with one or more halogen atoms,

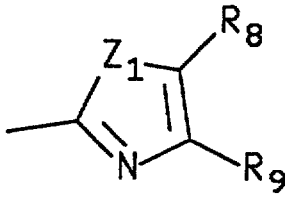
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Z_1 is O or S;

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R_7 is C_1-C_6 alkyl;
n is an integer of 1, 2 or 3;
R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or
when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-; and
R_{13} is C_1-C_4 alkyl.

8. The method according to claim 7 wherein the compound is selected from the group consisting of [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl methyl carbonate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-furoate;
[4-bromo-2-(p-chlorophenyl)-3-cyano-5-(trifluoromethyl)pyrrol-1-yl]methyl phenoxyacetate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (p-chlorophenoxy)acetate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (phenylthio)acetate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenoxypropionate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-thiophenecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl {2-[2-(2-methoxyethoxy)-ethoxy]ethoxy}acetate;
[3,4-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoromethyl-p-tolyl)pyrrol-1-yl]methyl 2-furoate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl tetrahydro-2-furoate; and
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (dimethylphosphono)acetate.

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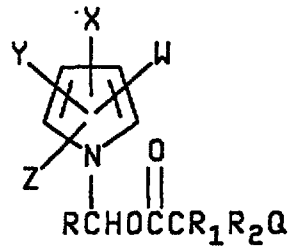
9. A method for protecting growing plants from attack by insects, acarina and mollusks which is characterized by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein W, X, Y, Z, R, R_1, R_2 and Q are as described in claim 6.

10. The method according to claim 9 wherein

W is CN;

X is phenyl optionally substituted with one or more
- halogen atoms,
- NO_2 groups,
- CN groups,
- C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
- C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl or Br;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen or
- C_1-C_6 alkyl, or
- R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

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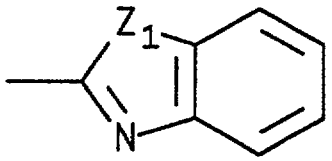
Q is AR_3 or $P(=O)(OR_{13})_2$;
A is O or S;
R_3 is C_1-C_6 alkyl,
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,
$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5-membered heterocyclic ring;
Z_1 is O or S;
R_7 is C_1-C_6 alkyl;
n is an integer of 1, 2 or 3; and
R_{13} is C_1-C_4 alkyl.

11. The method according to claim 9 wherein the compound is selected from the group consisting of [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl methyl carbonate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-furoate;
[4-bromo-2-(p-chlorophenyl)-3-cyano-5-(trifluoromethyl)pyrrol-1-yl]methyl phenoxyacetate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (p-chlorophenoxy)acetate;

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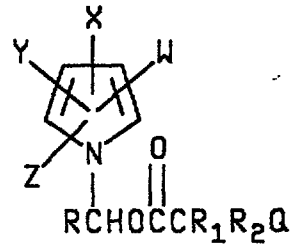
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (phenylthio)acetate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenoxypropionate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-thiophenecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl {2-[2-(2-methoxyethoxy)-ethoxy]ethoxy}acetate;
[3,4-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-methyl-p-tolyl)pyrrol-1-yl]methyl 2-furoate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl tetrahydro-2-furoate; and
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (dimethylphosphono)acetate.

12. A composition for controlling insects, acarina and mollusks which is characterized by an agronomically acceptable carrier and an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein W, X, Y, Z, R, R_1, R_2 and Q are as described in claim 1.

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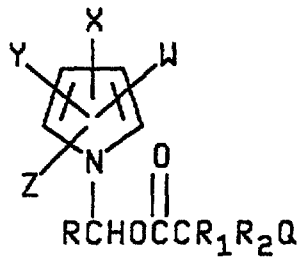
N-OXY- AND THIOALKYLCARBONYLOXYALKYLPYRROLE INSECTICIDAL, ACARICIDAL AND MOLLUSCICIDAL AGENTS

ABSTRACT OF THE INVENTION

There are provided N-oxy- and thioalkylcarbonyloxyalkylpyrrole compounds of formula I



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and their use for the control of insects, acarina and mollusks. Further provided are compositions and methods comprising those compounds for the protection of plants from attack by insects, acarina and mollusks.

N-OXY- AND THIOALKYLCARBONYLOXYALKYLPYRROLE INSECTICIDAL, ACARICIDAL AND MOLLUSCICIDAL AGENTS

Insects, acarina and mollusks destroy growing and harvested crops. In the United States alone, agronomic crops must compete with thousands of insect and acarid species. Accordingly, there is ongoing research to create new and more effective insecticides, acaricides and molluscicides for the control of insects, acarina and mollusks and for the protection of plants from attack by insects, acarina and mollusks. There is also ongoing research to create new insecticides and acaricides to overcome the resistance observed with several classes of insecticidal and acaricidal agents.

EP-A-0 426 948, EP-A-0 372 263, EP-A-0 484 614 and EP-A-0 372 982 disclose pyrrole compounds having insecticidal, acaricidal and nematicidal effects.

Chemical Abstracts, Vol. 91, 1979, abstract No. 193167v, discloses pyrrole compounds having acaricidal and insecticidal effects.

EP-A-0 545 103 is a document under Art. 54(3) EPC disclosing 1-(substituted)thioalkylpyrrole.

The present invention describes N-oxy- and thioalkylcarbonyloxyalkylpyrrole compounds which are useful as insecticidal, acaricidal and molluscicidal agents for the control of insects, acarina and mollusks and for the protection of plants from attack by insects, acarina and mollusks.

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This invention also relates to compositions containing those compounds and methods for using those compounds and compositions. Advantageously, it has been found that the N-oxy- and thioalkylcarbonyloxy-alkylpyrrole compounds of the present invention, and compositions containing them, are effective insecticidal, acaricidal and molluscicidal agents for the control of insects, acarina and mollusks and for the

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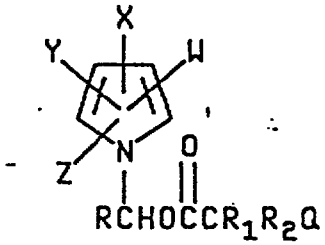
Claims

1. A compound characterized by the structural formula



wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen,

C_1-C_4 alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF_3, CN, NO_2, $S(O)_mCF_2R_4$ or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted

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with one or more halogen atoms;

Y is halogen, CF_3 or

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF_3;

R is hydrogen or C_1-C_4 alkyl;

R_1 and R_2 are each independently hydrogen,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms,

C_1-C_6 alkoxy optionally substituted with one or more halogen atoms,

C_1-C_6 alkylthio optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one mor more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms, or

when R_1 and R_2 are taken together with the atom to which they are attached may form a C_3-C_6 cycloalkyl group optionally substituted with one to three C_1-C_4 alkyl groups, C_2-C_6 alkenyl groups or phenyl groups, or R_1 or R_2 may be taken together

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with R_3 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Q is AR_3 or $P(OR_{13})_2$;

A is O or $S(O)_p$;

p is an integer of 0, 1 or 2;

R_3 is hydrogen,

C_1-C_6 alkyl,

C_1-C_6 alkenyl,

C_2-C_6 alkynyl,

phenyl optionally substituted with one or more

halogen atoms,

NO_2 groups,

CN groups,

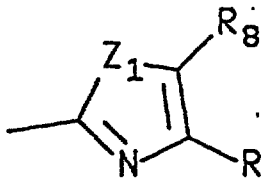
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,

$C(O)R_7$ provided p is 0,

$C(O)A_1$ provided p is 0,

$(CH_2CH_2O)_nR_7$, or



; or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 4- to 7-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl,

C_2-C_6 alkenyl,

C_2-C_6 alkynyl, or

phenyl optionally substituted with one or more

halogen atoms,

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NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

n is an integer of 1, 2 or 3;

R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or
when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-;

A_1 is OR_{10} or $NR_{11}R_{12}$;

R_{10} is C_1-C_6 alkyl or
phenyl optionally substituted with one or more halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

R_{11} and R_{12} are each independently hydrogen or C_1-C_4 alkyl; and

R_{13} is C_1-C_4 alkyl.

2. The compound according to claim 1 wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen or C_1-C_4

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alkyl;

X is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen,
C_1-C_6 alkyl optionally substituted with one or more halogen atoms, or
R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Q is AR_3 or $P(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,
phenyl optionaly substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,

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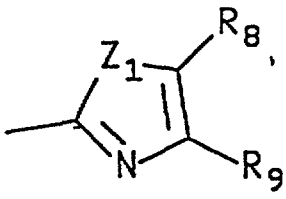
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl;

n is an integer of 1, 2 or 3;

R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or

when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-; and

R_{13} is C_1-C_4 alkyl.

3. The compound according to claim 2 wherein

W is CN;

X is phenyl optionally substituted with one or more halogen atoms,

NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl or Br;

Z is Cl, Br or CF_3;

R is hydrogen;

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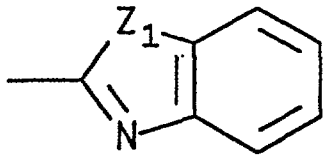
R_1 and R_2 are each independently hydrogen or
C_1-C_6 alkyl, or
R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

Q is AR_3 or $P(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,
$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl;

n is an integer of 1, 2 or 3; and

R_{13} is C_1-C_4 alkyl.

4. The compound according to claim 3 wherein the compound has the structural formula

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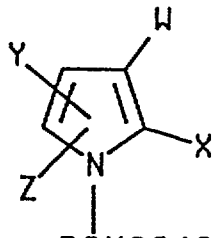

$RCHOC(O)CR_1R_2Q$

5. The compound according to claim 1 selected from the group consisting of [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-methyl)pyrrol-1-yl]methyl methyl carbonate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-furoate; [4-bromo-2-(p-chlorophenyl)-3-cyano-5-(trifluoromethyl) pyrrol-1-yl]methyl phenoxyacetate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-methyl)pyrrol-1-yl]methyl(p-chlorophenoxy)acetate; and [3-bromo-5-(p-chlorophenyl)4-cyano-2-(trifluoromethyl) pyrrol-1-yl]methyl(phenylthio)acetate.

6. A method for controlling insects, acarina and mollusks which is characterized by contacting said insects, acarina and mollusks, their breeding ground, food supply or habitat with an insecticidally, acaricidally or molluscicidally effective amount of a compound according to claim 1.

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7. The method according to claim 6 wherein

W is CN, NO_2, $S(O)_mCF_2R_4$ or $\overset{S}{\overset{\|}{C}}NR_5R_6$;

R_4 is hydrogen, F, Cl, Br, CF_2H, CCl_2H, CClFH, CF_3 or CCl_3;

m is an integer of 0, 1 or 2;

R_5 and R_6 are each independently hydrogen or C_1-C_4 alkyl;

X is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms,
NO_2 groups,
CN groups,
C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF_3 or
phenyl optionally substituted with one or more
halogen atoms
NO_2 groups,

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CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen,

C_1-C_6 alkyl optionally substituted with one or more halogen atoms, or

R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Q is AR_3 or $P(O)(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,

phenyl optionaly substituted with one or more halogen atoms,

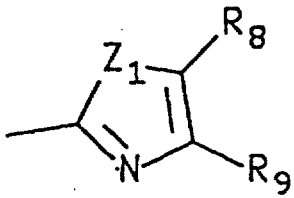
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5- to 6-membered heterocyclic ring;

Z_1 is O or S;

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R_7 is C_1-C_6 alkyl;
n is an integer of 1, 2 or 3;
R_8 and R_9 are each independently hydrogen or C_1-C_4 alkyl, or
when taken together may form a ring wherein R_8R_9 is represented by -CH=CH-CH=CH-; and
R_{13} is C_1-C_4 alkyl.

8. The method according to claim 7 wherein the compound is selected from the group consisting of [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl methyl carbonate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-furoate; [4-bromo-2-(p-chlorophenyl)-3-cyano-5-(trifluoromethyl)pyrrol-1-yl]methyl phenoxyacetate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (p-chlorophenoxy)acetate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (phenylthio)acetate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenoxypropionate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-thiophenecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (2-[2-(2-methoxyethoxy)-ethoxy]ethoxy}acetate; [3,4-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoromethyl-p-tolyl)pyrrol-1-yl]methyl 2-furoate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl tetrahydro-2-furoate; and [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (dimethylphosphono)acetate.

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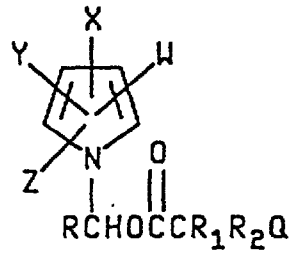
9. A method for protecting growing plants from attack by insects, acarina and mollusks which is characterized by applying to the foliage of said plants or to the soil or water in which they are growing an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein W, X, Y, Z, R, R_1, R_2 and Q are as described in claim 6.

10. The method according to claim 9 wherein

W is CN;

X is phenyl optionally substituted with one or more
- halogen atoms,
- NO_2 groups,
- CN groups,
- C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or
- C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl or Br;

Z is Cl, Br or CF_3;

R is hydrogen;

R_1 and R_2 are each independently hydrogen or
- C_1-C_6 alkyl; or
- R_1 or R_2 may be taken together with R_3 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

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Q is AR_3 or $\overset{O}{\overset{\|}{P}}(OR_{13})_2$;

A is O or S;

R_3 is C_1-C_6 alkyl,

phenyl optionally substituted with one or more

halogen atoms,

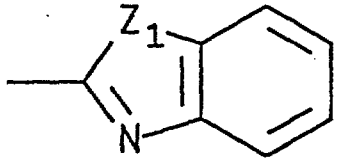
NO_2 groups,

CN groups,

C_1-C_4 alkyl groups optionally substituted with one or more halogen atoms, or

C_1-C_4 alkoxy groups optionally substituted with one or more halogen atoms,

$(CH_2CH_2O)_nR_7$, or



, or

R_3 may be taken together with either R_1 or R_2 and the atoms to which they are attached to form a 5-membered heterocyclic ring;

Z_1 is O or S;

R_7 is C_1-C_6 alkyl;

n is an integer of 1, 2 or 3; and

R_{13} is C_1-C_4 alkyl.

11. The method according to claim 9 wherein the compound is selected from the group consisting of [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl methyl carbonate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-furoate; [4-bromo-2-(p-chlorophenyl)-3-cyano-5-(trifluoromethyl)pyrrol-1-yl]methyl phenoxyacetate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (p-chlorophenoxy)acetate;

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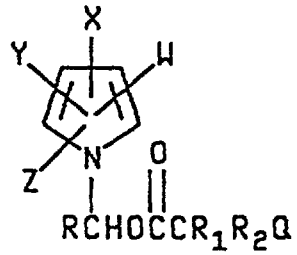
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (phenylthio)acetate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenoxypropionate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-thiophenecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (2-[2-(2-methoxyethoxy)-ethoxy]ethoxy)acetate;
[3,4-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-methyl-p-tolyl)pyrrol-1-yl]methyl 2-furoate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl tetrahydro-2-furoate; and
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl (dimethylphosphono)acetate.

12. A composition for controlling insects, acarina and mollusks which is characterized by an agronomically acceptable carrier and an insecticidally, acaricidally or molluscicidally effective amount of a compound having the structural formula



wherein W, X, Y, Z, R, R_1, R_2 and Q are as described in claim 1.

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