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N-SUBSTITUTED CARBONYLOXYALKYLPYRROLE
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-substituted carbonyloxyalkylpyrrole 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.

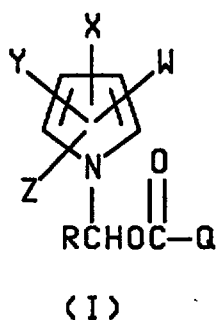
This invention also relates to compositions containing those compounds and methods for using those compounds and compositions. Advantageously, it has been found that the N-substituted carbonyloxyalkylpyrrole compounds of the present invention, and compositions containing them, are effective insecticidal, 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.

5 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-substituted carbonyloxyalkylpyrrole
10 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
15 growing an insecticidally, acaricidally or molluscicidally effective amount of a formula I, N-substituted carbonyloxyalkylpyrrole compound.

The N-substituted carbonyloxyalkylpyrrole compounds of the present invention have the following
20 structural formula I:



30 wherein

S
||

W is CN, NO₂, S(O)_nCF₂R₁ or CNR₂R₃;
R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

n is an integer of 0, 1 or 2;

R₂ and R₃ are each independently hydrogen,

C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or

5 phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

10 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or

15 phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

20 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is halogen, CF₃ or

25 phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

30 C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is hydrogen, halogen or CF₃;

R is hydrogen or C₁-C₄ alkyl;

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups,

35 C₂-C₆ alkenyl groups, or

phenyl groups optionally substituted with one
or more halogen atoms,
NO₂ groups,
CN groups,
5 C₁-C₄ alkyl groups optionally substituted with one or more halogen
atoms, or
C₁-C₄ alkoxy groups optionally substituted with one or more halogen
atoms,
10 CR₄R₅C(O)R₆, or
CR₄R₅C(O)A;
R₄ and R₅ are each independently hydrogen,
C₁-C₆ alkyl optionally substituted with one
15 or more halogen atoms,
C₁-C₆ alkoxy optionally substituted with one
or more halogen atoms,
C₁-C₆ alkylthio optionally substituted with
one or more halogen atoms,
20 phenyl optionally substituted with one or
more halogen atoms,
CN groups,
NO₂ groups,
C₁-C₄ alkyl groups optionally substituted with one or more halogen
25 atoms, or
C₁-C₄ alkoxy groups optionally substituted with one or more halogen
atoms, or
30 when R₄ and R₅ are taken together with the
atom to which they are attached may form a
C₃-C₆ cycloalkyl group optionally substituted
with one to three C₁-C₄ alkyl groups, C₂-C₆
alkenyl groups or phenyl groups;
35 R₆ is C₁-C₄ alkyl or
phenyl optionally substituted with one or more

halogen atoms,
CN groups,
NO₂ groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

A is OR₆ or NR₇R₈; and

R₇ and R₈ are each independently hydrogen or C₁-C₄
alkyl.

Preferred N-substituted carbonyloxyalkyl-
pyrrole compounds of the present invention are those
wherein

W is CN, NO₂, S(O)_nCF₂R₁ or $\begin{array}{c} \text{S} \\ || \\ \text{CNR}_2\text{R}_3 \end{array}$;
R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or
CCl₃;

n is an integer of 0, 1 or 2;

R₂ and R₃ are each independently hydrogen,
C₁-C₄ alkyl optionally substituted with one or
more halogen atoms, or
phenyl optionally substituted with one or more
halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or
phenyl optionally substituted with one or more
halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted

with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
Y is halogen, CF₃ or
5 phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
10 with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
Z is hydrogen, halogen or CF₃;
R is hydrogen or C₁-C₄ alkyl; and
15 Q is C₃-C₆ cycloalkyl optionally substituted with one
or more C₁-C₆ alkyl groups,
C₂-C₆ alkenyl groups, or
phenyl groups optionally substituted with one
or more halogen atoms,
20 NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substi-
tuted with one or more halogen
atoms, or
25 C₁-C₄ alkoxy groups optionally substi-
tuted with one or more halogen
atoms.

More preferred formula I insecticidal,
acaricidal and molluscicidal agents are those wherein

30
$$\begin{array}{c} \text{S} \\ || \\ \text{W} \end{array}$$

W is CN, NO₂, S(O)_nCF₂R₁ or CNR₂R₃;
R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or
CCl₃;
n is an integer of 0, 1 or 2;
35 R₂ and R₃ are each independently hydrogen or

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

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; and

Q is C_3-C_6 cycloalkyl optionally substituted with one or more C_1-C_6 alkyl groups,

C_2-C_6 alkenyl groups, or

phenyl groups 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.

Most preferred N-substituted carbonyloxy-alkylpyrrole compounds of this invention which are especially effective insecticidal, acaricidal and molluscicidal agents are those wherein

5 W is CN;

X is Cl, Br or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

10 CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

15 Y is Cl, Br or CF₃;

Z is Cl or Br; and

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups,

C₂-C₆ alkenyl groups, or

20 phenyl groups optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

25 C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

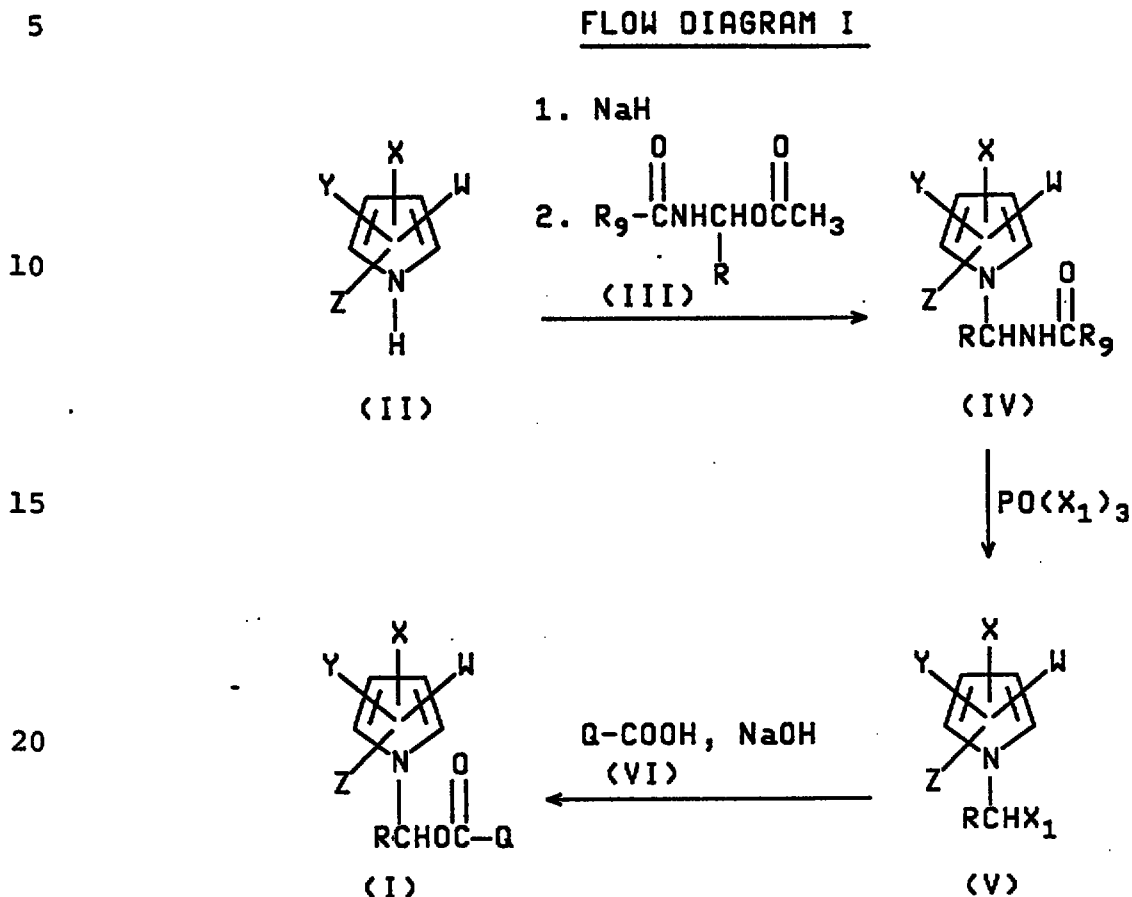
C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

30 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, two-spotted spider mites and slugs.

35

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



wherein

R_9 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-furfuryl;

X_1 is Cl or Br; and

W, X, Y, Z, R and Q are as described hereinabove for formula I.

The appropriately substituted pyrrole of formula II is reacted with an alkylating agent of formula III in the presence of an alkali metal hydride or an alkali metal C₁-C₆ alkoxide to form an N-alka-
5 noylaminomethyl or N-aroylaminomethylpyrrole of formula IV, said formula IV aminomethylpyrrole is then reacted with an excess of phosphorus oxychloride or phosphorus oxybromide to form a 1-halomethylpyrrole of formula V. Said 1-halomethylpyrrole is reacted with a carboxylic
10 acid of formula VI in the presence of an alkali metal hydroxide, such as sodium or potassium hydroxide, to form desired N-substituted carbonyloxyalkylpyrrole compounds of formula I.

The N-substituted carbonyloxyalkylpyrrole
15 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
20 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
25 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
30 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
35 limpets. Advantageously, it has been found that the

compounds of the present invention are especially effective against tobacco budworm eggs and third-instar larvae, southern armyworms, two-spotted spider mites and slugs.

5 In practice generally about 10 ppm to 10,000 ppm and preferably 100 ppm to about 5,000 ppm of a formula I N-substituted carbonyloxyalkylpyrrole compound, dispersed in water or another liquid carrier, is effective when applied to the plants, the crops or the
10 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
15 to the soil or water in which said plants are growing in sufficient amount to provide a rate of from about 0.1 kg/ha to 4.0 kg/ha of active ingredient.

 While the compounds of this invention are effective for controlling insects, acarina and mollusks
20 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
25 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
30 formulated as emulsifiable concentrates, flowable concentrates, or wettable powders which are diluted with water or other suitable polar solvent, generally in situ, and then applied as a dilute spray. Said compounds may also be formulated in dry compacted granules, granular formulations, dusts, dust concentrates,
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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 an N-substituted carbonyloxyalkylpyrrole 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.

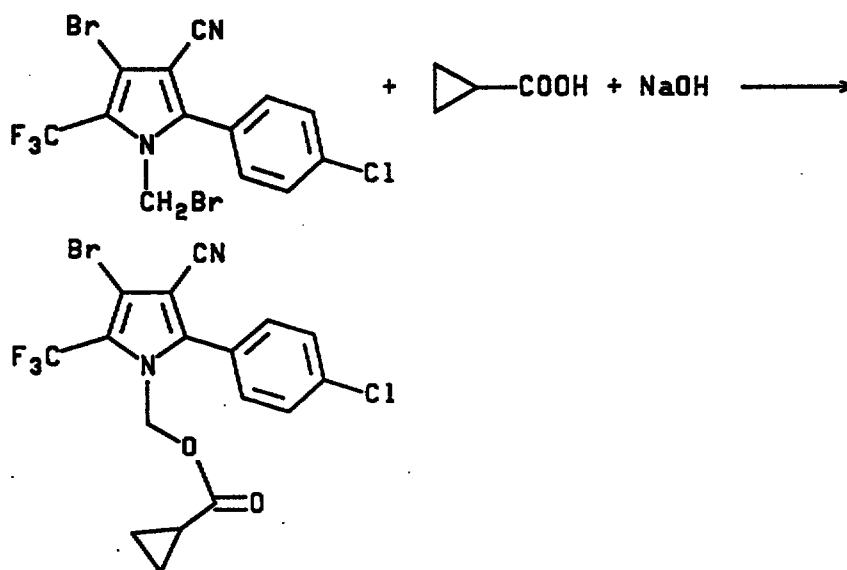
An especially effective method for controlling terrestrial gastropods with the formula I compounds of the invention, is to proffer the active molluscicidal material in the form of a bait formulation. These bait formulations can be widely varied but generally contain about 1% to 20% by weight of the active ingredient, about 40% to 50% by weight of a 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 cyclopropane-carboxylate

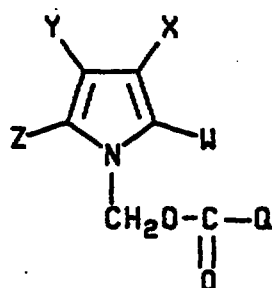


4-Bromo-1-(bromomethyl)-2-(p-chlorophenyl)-5-(trifluoromethyl)pyrrole-3-carbonitrile (2.21 g, 4.99 mmol) is added to a mixture of cyclopropanecarboxylic acid (0.52 g, 6.04 mmol) and sodium hydroxide (0.24 g, 6.0 mmol) in N,N-dimethylformamide. The reaction mixture is stirred overnight at room temperature, diluted with water and extracted with ethyl acetate. The combined organic extracts are washed sequentially with water and brine, dried over MgSO_4 and concentrated

in vacuo to obtain a brown oil. The oil is triturated with hexanes to obtain an off white solid. Recrystallization of the solid from 2-propanol gives the title product as tan needles (1.3 g, mp 122°-123°C).

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

5



10

15

<u>W</u>	<u>X</u>	<u>Y</u>	<u>Z</u>	<u>Q</u>	<u>mp°C</u>
	CN	Br	CF ₃		120.0 - 121.5

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	CN	Cl	CF ₃		104 - 105
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	CN	Cl	Cl		87 - 89
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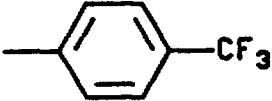
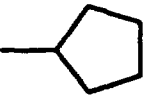
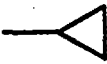
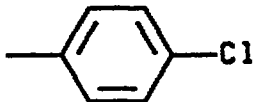
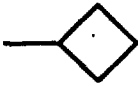
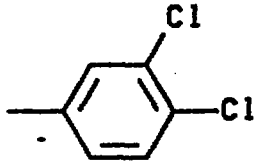
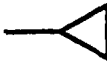
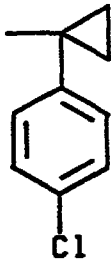
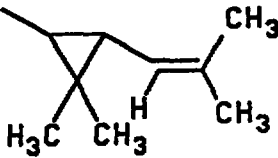
	CN	Br	CF ₃		90 - 91
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	CN	Br	CF ₃		124 - 125
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	CN	Br	CF ₃		51 - 56
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	W	X	Y	Z	Q	mp°C
5		CN	Cl	Cl		121 - 122
10	Br	CN	Br	Br		105 - 106
15		CN	Cl	CF ₃		105 - 106
20		Br	CN	Cl		96 - 97
25		CN	Cl	CF ₃		156 - 158
30		CN	Cl	CF ₃		oil

EXAMPLE 2

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 and acarina used in the present evaluations along with specific test procedures are described below.

Spodoptera eridania 3rd instar larvae, southern army-worm

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 any interference with normal moulting.

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

10 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
15 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.

20 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
25 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 virescens, 3rd instar tobacco budworm

30 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
35 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.

5 *Heliothis virescens*, tobacco budworm egg

 Tobacco budworm eggs are collected on cheesecloth in the rearing colony. This cheesecloth is cut into 10 mm to 20 mm squares containing about 50-100 eggs per square. Each square is dipped in the test formulation and placed on a separate cotton cotyledon, previously dipped in the test formulation. The treatments are dried, transferred into an 8 ounce Dixie® cup (240 mL, 6 cm high, top diameter 9.5 cm, bottom diameter 8 cm) containing a 5 cm length of damp cotton dental wick and covered with a clear plastic lid. Treatments are maintained for three days before mortality counts are made.

20 *Diabrotic undecimpunctata howardi*, 3rd 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 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 thoroughly 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

concentration used in this test corresponds to approximately 50 kg/ha.

5

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

TABLE I

Insecticide and Acaricide Evaluations

Compound	Southern Armyworm			OP. Res.			Tobacco Budworm			S. Corn	
	1,000	100	10	300	100	10	Egg (ppm)	Larvae (ppm)	Rootworm (kg/ha)		
[3-Bromo-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate	9	9	9	9	9	9	0	9	8	9	
[3-Chloro-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate	9	9	9	9	9	9	7	9	9	9	21
[2,3-Dichloro-4-cyano-5-(alpha,alpha,alpha-tri-fluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate	9	9	9	9	9	9	0	9	6	0	
[3-Bromo-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate	9	9	9	9	9	9	8	9	9	9	

TABLE I (Continued)

Compound	Southern Armyworm			OP. Res.			Leafhopper			Tobacco Budworm		S. Corn	
	1,000	100	10	300	100	100	100	100	10	Egg (ppm)	Larvae (ppm)	Egg (kg/ha)	Rootworm (kg/ha)
[3-Bromo-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate	9	9	9	9	9	9	9	9	8	0	9	7.5	9
[3-Bromo-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate	9	9	9	9	9	9	9	9	-	0	9	9	9
[3-Bromo-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate	9	9	9	5	-	-	-	-	-	0	9	6.5	0
[2,3-Dichloro-4-cyano-5-(alpha, alpha, alpha-tri-fluoro-p-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate	9	9	9	9	8	-	-	-	-	0	9	4	9

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TABLE I (Continued)

Compound	Southern Armyworm			OP. Res.			Leafhopper			Tobacco Budworm		S. Corn	
	1,000	100	10	300	100	100	(ppm)	100	10	Egg (ppm)	Larvae (ppm)	Egg (ppm)	Rootworm (kg/ha)
(2,3,5-Tribromo-4-cyano-pyrrol-1-yl)methyl cyclopropanecarboxylate	9	5	0	9	0	0	3.5	0	0	9	0	0	0
[3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate	9	9	9	9	0	0	4.5	9	9	8	9	9	9
[3-Bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)pyrrol-1-yl]methyl cyclopropanecarboxylate	9	9	7	9	8	8	-	-	-	0	9	0	5.7
[3-Chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-(p-chlorophenyl)cyclopropanecarboxylate	9	9	9	9	0	0	-	-	-	0	9	7	7.5

1
23
1

TABLE I (Continued)

Compound	Southern Armyworm		OP. Res.		Leafhopper		Tobacco Budworm		S. Corn	
	(ppm)		(ppm)		(ppm)		(ppm)		(kg/ha)	
	1,000	100	10	300	100	100	1,000	100	10	50
[3-Chloro-5-(p-chloro-phenyl)-4-cyano-2-(tri-fluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)-cyclopropanecarboxylate	9	-	-	0	-	-	-	-	-	0

EXAMPLE 3

Evaluation of (2,3,5-Tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate for the control of slugs, species *Arion subfuscus*

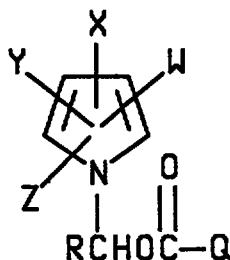
The test compound is weighed and diluted in acetone to achieve the desired concentration, and 1.0 mL of each test solution is added to 0.65 g of unprocessed bran. The acetone is then removed by evaporation. The bait composition is prepared by mixing the above-said treated unprocessed bran with 0.35 mL of a 12% molasses solution. The thus-prepared bait composition is placed into the lid of a 1 oz jar which is then placed onto the bottom of an 8 oz waxed paper cup which has been lined with wet filter paper. Each cup is then infested with 8 slugs. A control cup which contains 0% test compound in the bait composition is also prepared and infested. Test treatments are examined daily for 6 days and feeding and mortality rates are recorded. The data obtained are reported below.

<u>Compound</u>	<u>% Mortality of <i>Arion subfuscus</i> (% Bait)</u>		
	<u>5.0%</u>	<u>1.0%</u>	<u>0.15%</u>
(2,3,5-Tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate	75	100	88



WE CLAIM:

1. A compound characterized by the structural formula



wherein

W is CN, NO₂, S(O)_nCF₂R₁ or $\text{C}(=\text{S})\text{NR}_2\text{R}_3$;
 R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;

n is an integer of 0, 1 or 2;

R₂ and R₃ are each independently hydrogen,

C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ 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;

Q is C_3-C_6 cycloalkyl optionally substituted with one
or more C_1-C_6 alkyl groups,

C_2-C_6 alkenyl groups, or

phenyl groups optionally substituted with one
or more halogen atoms,

NO_2 groups,

CN groups,

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

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

$CR_4R_5C(O)R_6$, or

$CR_4R_5C(O)A$;

R_4 and R_5 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,





phenyl optionally substituted with one or more halogen atoms,
CN groups,
NO₂ groups,
C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms, or

when R₄ and R₅ are taken together with the atom to which they are attached may form a C₃-C₆ cycloalkyl group optionally substituted with one to three C₁-C₄ alkyl groups, C₂-C₆ alkenyl groups or phenyl groups;

R₆ is C₁-C₄ alkyl or phenyl optionally substituted with one or more halogen atoms,
CN groups,
NO₂ groups,
C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

A is OR₆ or NR₇R₈; and

R₇ and R₈ are each independently hydrogen or C₁-C₄ alkyl.

2. The compound according to claim 1

wherein

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups,
C₂-C₆ alkenyl groups, or
phenyl groups optionally substituted with one or more halogen atoms,
NO₂ groups,





CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

3. The compound according to claim 3

wherein

R₂ and R₃ are each independently hydrogen or C₁-C₄ alkyl optionally substituted with one or more halogen atoms;

X is Cl, Br, CF₃ or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF₃ or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF₃; and

R is hydrogen.

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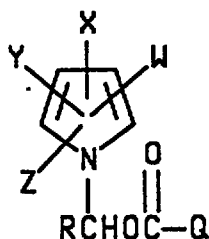
4. The compound according to claim 3
wherein
W is CN;
X is Cl, Br or
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
Y is Cl, Br, or CF₃; and
Z is Cl or Br.

5. The compound selected from the group
consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-
(trifluoro-methyl)pyrrol-1-yl]methyl cyclopropanecar-
boxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl 1-methylcyclopropane-
carboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl 1-phenylcyclopropane-
carboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-tri-
fluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropane-
carboxylate; and
(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclo-
propanecarboxylate.





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 , $\text{S}(\text{O})_n\text{CF}_2\text{R}_1$ or CNR_2R_3 ;
R₁ is hydrogen, F, Cl, Br, CF_2H , CCl_2H , CClFH , CF_3 or CCl_3 ;
n is an integer of 0, 1 or 2;
R₂ and R₃ are each independently hydrogen, $\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms, or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, $\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or $\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;
X is halogen, CF_3 , CN, NO_2 , $\text{S}(\text{O})_n\text{CF}_2\text{R}_1$ or 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;

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;

Q is C_3-C_6 cycloalkyl optionally substituted with one
or more C_1-C_6 alkyl groups,
 C_2-C_6 alkenyl groups, or
phenyl groups optionally substituted with one
or more halogen atoms,

NO_2 groups,

CN groups,

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

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

$CR_4R_5C(O)R_6$, or

$CR_4R_5C(O)A$;

R_4 and R_5 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,
phenyl optionally substituted with one or
more halogen atoms,
CN groups,
 NO_2 groups,
 C_1-C_4 alkyl groups optionally substi-
tuted with one or more halogen
atoms, or
 C_1-C_4 alkoxy groups optionally sub-
stituted with one or more halogen
atoms, or

when R_4 and R_5 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;

R_6 is C_1-C_4 alkyl or
phenyl optionally substituted with one or more
halogen atoms,
CN groups,
 NO_2 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;

A is OR_6 or NR_7R_8 ; and

R_7 and R_8 are each independently hydrogen or C_1-C_4
alkyl.

7. The method according to claim 6 wherein
the compound is selected from the group consisting of
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;



[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluorop-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluorop-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate;
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;
[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
and [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

8. 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

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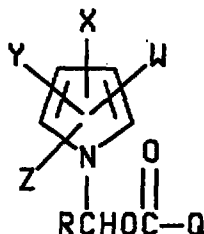




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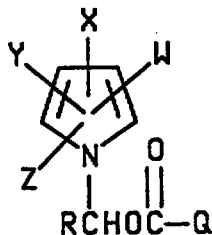


wherein W, X, Y, Z, R and Q are as described in claim 6.

9. The method according to claim 8 wherein the compound is selected from the group consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate; [2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate; [2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate; (2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate; [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;

[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)-pyrrol-1-yl]methyl cyclopropanecarboxylate;
 [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
 and [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

10. A composition for controlling insects, acarina and mollusks 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 and Q are as described in claim 1.

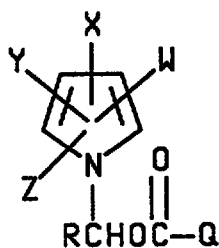
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N-SUBSTITUTED CARBONYLOXYALKYLPYRROLE
INSECTICIDAL, ACARICIDAL AND MOLLUSCICIDAL AGENTS

ABSTRACT OF THE INVENTION

There are provided N-substituted carbonyl-oxyalkylpyrrole compounds of formula I

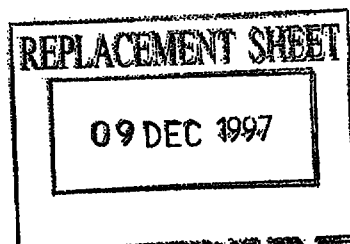


and their use for the control of insects, acarina and mollusks. Further provided are compositions and methods comprising those compounds for the protection of plants from attack by insects, acarina and mollusks.

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- 1 -



N-SUBSTITUTED CARBONYLOXYALKYLPYRROLE
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.

Insert

(A)



The present invention describes N-substituted carbonyloxyalkylpyrrole 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-substituted carbonyloxyalkylpyrrole 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

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REPLACEMENT SHEET

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Insert

A

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

EP-A-0 372 263 discloses pyrrole compounds having insecticidal, acaricidal and molluscicidal effects.

Chemical Abstracts, vol. 91, 1979, abstracts no. 193167v discloses pyrrole-1-yl-methyl-cyclopropanecarboxylate compounds with acaricidal and insecticidal activity.

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

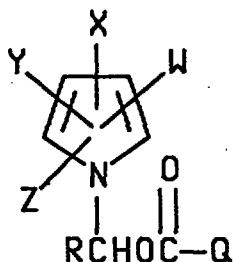


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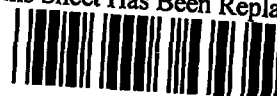
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CLAIMS

1. A compound characterized by the structural formula



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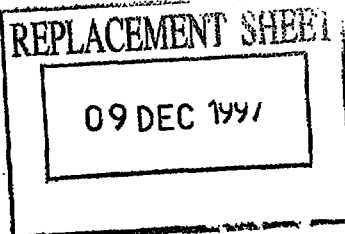


wherein

W is CN , NO_2 , $\text{S(O)}_n\text{CF}_2\text{R}_1$ or CNR_2R_3 ;
 R_1 is hydrogen, F, Cl, Br, CF_2H , CCl_2H , CClFH , CF_3 or CCl_3 ;
 n is an integer of 0, 1 or 2;
 R_2 and R_3 are each independently hydrogen, $\text{C}_1\text{-C}_4$ alkyl optionally substituted with one or more halogen atoms, or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, $\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or $\text{C}_1\text{-C}_4$ alkoxy groups optionally substituted with one or more halogen atoms;
 X is halogen, CF_3 , CN , NO_2 , $\text{S(O)}_n\text{CF}_2\text{R}_1$ or phenyl optionally substituted with one or more halogen atoms, NO_2 groups, CN groups, $\text{C}_1\text{-C}_4$ alkyl groups optionally substituted with one or more halogen atoms, or



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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;

Q is C_3-C_6 cycloalkyl optionally substituted with one
or more C_1-C_6 alkyl groups,

C_2-C_6 alkenyl groups, or

phenyl groups optionally substituted with one
or more halogen atoms,

NO_2 groups,

CN groups,

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

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

$CR_4R_5C(O)R_6$, or

$CR_4R_5C(O)A$;

R_4 and R_5 are each independently hydrogen,

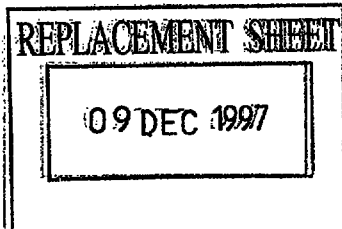
C_1-C_6 alkyl optionally substituted with one
or more halogen atoms,

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,

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phenyl optionally substituted with one or more halogen atoms, CN groups, NO₂ groups, C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms, or

when R₄ and R₅ are taken together with the atom to which they are attached may form a C₃-C₆ cycloalkyl group optionally substituted with one to three C₁-C₄ alkyl groups, C₂-C₆ alkenyl groups or phenyl groups;

R₆ is C₁-C₄ alkyl or phenyl optionally substituted with one or more halogen atoms, CN groups, NO₂ groups, C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

A is OR₆ or NR₇R₈; and

R₇ and R₈ are each independently hydrogen or C₁-C₄ alkyl.

2. The compound according to claim 1

wherein

Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups, C₂-C₆ alkenyl groups, or phenyl groups optionally substituted with one or more halogen atoms, NO₂ groups,



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CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms.

3. The compound according to claim 3

wherein

R₂ and R₃ are each independently hydrogen or C₁-C₄ alkyl optionally substituted with one or more halogen atoms;

X is Cl, Br, CF₃ or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Y is Cl, Br, CF₃ or

phenyl optionally substituted with one or more halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or

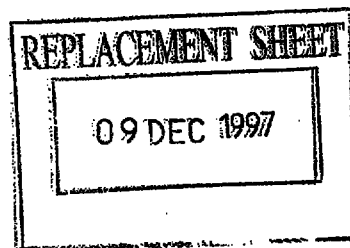
C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

Z is Cl, Br or CF₃; and

R is hydrogen.

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4. The compound according to claim 3

wherein

W is CN;

X is Cl, Br or

phenyl optionally substituted with one or more
halogen atoms,

NO₂ groups,

CN groups,

C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or

C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;

Y is Cl, Br, or CF₃; and

Z is Cl or Br.

according to claim 1

5. ^A ~~that~~ compound selected from the group
consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-
(trifluoro-methyl)pyrrol-1-yl]methyl cyclopropanecar-
boxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl 1-methylcyclopropane-
carboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;

[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl 1-phenylcyclopropane-
carboxylate;

[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-tri-
fluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropane-
carboxylate; and

(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclo-
propanecarboxylate.

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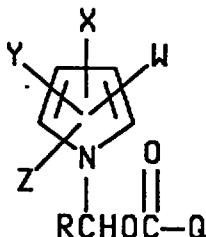




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6. A method for controlling insects, acarina and mollusks which is characterized by contacting said insects, acarina and mollusks their breeding ground, food supply or habitat with an insecticidally, acaricidally or molluscicidally effective amount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

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wherein

W is CN, NO₂, S(O)_nCF₂R₁ or CNR₂R₃;
R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;
n is an integer of 0, 1 or 2;
R₂ and R₃ are each independently hydrogen, C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or phenyl optionally substituted with one or more halogen atoms, NO₂ groups, CN groups, C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;
X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or phenyl optionally substituted with one or more halogen atoms, NO₂ 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;

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;

Q is C_3-C_6 cycloalkyl optionally substituted with one
or more C_1-C_6 alkyl groups,

C_2-C_6 alkenyl groups, or

phenyl groups optionally substituted with one
or more halogen atoms,

NO_2 groups,

CN groups,

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

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

$CR_4R_5C(O)R_6$, or

$CR_4R_5C(O)A$;

R_4 and R_5 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,

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

CN groups,

NO_2 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_4 and R_5 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;

R_6 is C_1-C_4 alkyl or phenyl optionally substituted with one or more halogen atoms,

CN groups,

NO_2 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;

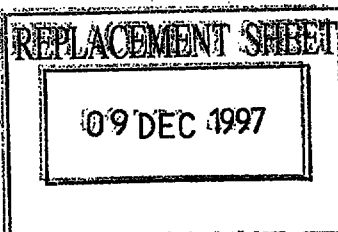
A is OR_6 or NR_7R_8 ; and

R_7 and R_8 are each independently hydrogen or C_1-C_4 alkyl.

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7. The method according to claim 6 wherein the compound is selected from the group consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;

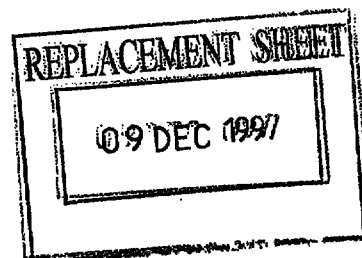
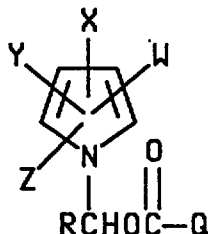


[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate;
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;
[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
and [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

8. 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

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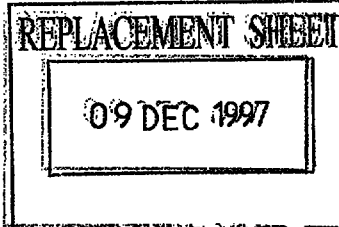
wherein W, X, Y, Z, R and Q are as described in claim 6.

9. The method according to claim 8 wherein the compound is selected from the group consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate; [2,3-dichloro-4-cyano-5-(alpha, alpha, alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate; [2,3-dichloro-4-cyano-5-(alpha, alpha, alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate; (2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate; [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;



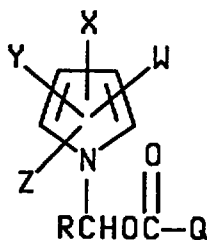


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[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)-pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
and [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

10. A composition for controlling insects, acarina and mollusks 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 and Q are as described in claim 1.

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☒ Description : paged ... to paged ...

☒ Claim(s) : paged ... to paged ...

☐ Drawing(s) : paged ... to paged ...

☐ Abstract : paged ... to paged ...

DATE OF RECEIPT 7/10/98

N-SUBSTITUTED CARBONYLOXYALKYLPYRROLE INSECTICIDAL, ACARICIDAL
AND MOLLUSCICIDAL AGENTS

5 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
10 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 over
15 come the resistance observed with several classes of
insecticidal and acaricidal agents.

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

20 EP-A-0 372 263 discloses pyrrole compounds having
insecticidal, acaricidal and molluscicidal effects.

Chemical Abstracts, vol. 91, 1979, abstracts no.
25 193167v discloses pyrrole-1-yl-methyl-cyclopropane-
carboxylate compounds with acaricidal and insecticidal
activity.

EP-A-0 545 103 is a document under Article 54(3) EPC
30 disclosing 1-(substituted)-thioalkylpyrroles.

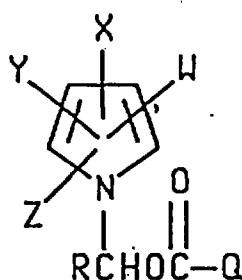
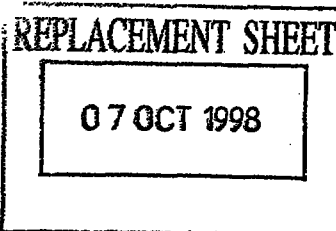
The present invention describes N-substituted
carbonyloxyalkylpyrrole compounds which are useful as
insecticidal, acaricidal and molluscicidal agents for the
35 control of insects, acarina and mollusks and for the
protection of plants from attack by insects, acarina and
mollusks.

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



Claims

1. A compound characterized by the structural formula



wherein

S
 $\parallel$

W is CN, NO₂, S(O)_nCF₂R₁ or CNR₂R₃;
R₁ is hydrogen, F, Cl, Br, CF₂H, CCl₂H, CClFH, CF₃ or CCl₃;
n is an integer of 0, 1 or 2;
R₂ and R₃ are each independently hydrogen, C₁-C₄ alkyl optionally substituted with one or more halogen atoms, or phenyl optionally substituted with one or more halogen atoms, NO₂ groups, CN groups, C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;
X is halogen, CF₃, CN, NO₂, S(O)_nCF₂R₁ or phenyl optionally substituted with one or more halogen atoms, NO₂ groups, CN groups, C₁-C₄ 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;

Q is C_3-C_6 cycloalkyl optionally substituted with one
or more C_1-C_6 alkyl groups,

C_2-C_6 alkenyl groups, or

phenyl groups optionally substituted with one
or more halogen atoms,

NO_2 groups,

CN groups,

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

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

$CR_4R_5C(O)R_6$, or

$CR_4R_5C(O)A$;

R_4 and R_5 are each independently hydrogen,

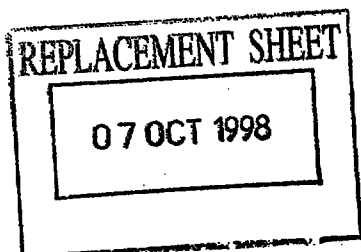
C_1-C_6 alkyl optionally substituted with one
or more halogen atoms,

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,

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phenyl optionally substituted with one or more halogen atoms,
CN groups,
NO₂ groups,
C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms, or

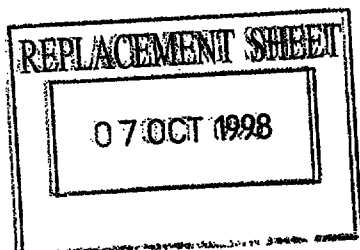
when R₄ and R₅ are taken together with the atom to which they are attached may form a C₃-C₆ cycloalkyl group optionally substituted with one to three C₁-C₄ alkyl groups, C₂-C₆ alkenyl groups or phenyl groups;

R₆ is C₁-C₄ alkyl or
phenyl optionally substituted with one or more halogen atoms,
CN groups,
NO₂ groups,
C₁-C₄ alkyl groups optionally substituted with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted with one or more halogen atoms;

A is OR₆ or NR₇R₈; and

R₇ and R₈ are each independently hydrogen or C₁-C₄ alkyl.

2. The compound according to claim 1
wherein
Q is C₃-C₆ cycloalkyl optionally substituted with one or more C₁-C₆ alkyl groups,
C₂-C₆ alkenyl groups, or
phenyl groups optionally substituted with one or more halogen atoms,
NO₂ 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.

3. The compound according to claim 3

wherein

R_2 and R_3 are each independently hydrogen or C_1-C_4 alkyl optionally substituted with one or more halogen atoms;

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 ; and

R is hydrogen.



4. The compound according to claim 3
wherein
W is CN;
X is Cl, Br or
phenyl optionally substituted with one or more
halogen atoms,
NO₂ groups,
CN groups,
C₁-C₄ alkyl groups optionally substituted
with one or more halogen atoms, or
C₁-C₄ alkoxy groups optionally substituted
with one or more halogen atoms;
Y is Cl, Br, or CF₃; and
Z is Cl or Br.

5. A compound according to claim 1 selected from the group
consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-
(trifluoro-methyl)pyrrol-1-yl]methyl cyclopropanecar-
boxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl 1-methylcyclopropane-
carboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoro-
methyl)pyrrol-1-yl]methyl 1-phenylcyclopropane-
carboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-tri-
fluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropane-
carboxylate; and
(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclo-
propanecarboxylate.

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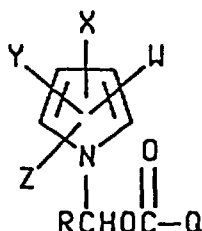
6. A method for controlling insects, acarina and mollusks which is characterized by contacting said insects, acarina and mollusks their breeding ground, food supply or habitat with an insecticidally, acaricidally or molluscicidally effective amount of a compound according to claim 1.

7. The method according to claim 6 wherein the compound is selected from the group consisting of
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;
[3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate;
[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-trifluoro-p-tolyl)pyrrol-1-yl]methyl cyclohexanecarboxylate;
(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate;
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;
[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;



[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; and [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

8. 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



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

9. The method according to claim 8 wherein the compound is selected from the group consisting of [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-methylcyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclohexanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 1-phenylcyclopropanecarboxylate; [2,3-dichloro-4-cyano-5-(alpha, alpha, alpha-trifluorop-tolyl)pyrrol-1-yl]methyl cyclopropanecarboxylate; [3-bromo-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2-phenylcyclopropanecarboxylate;



[2,3-dichloro-4-cyano-5-(alpha,alpha,alpha-tri-fluoro-p-tolyl)pyrrol-1-yl]methyl cyclohexane-carboxylate;

(2,3,5-tribromo-4-cyanopyrrol-1-yl)methyl cyclopropanecarboxylate;

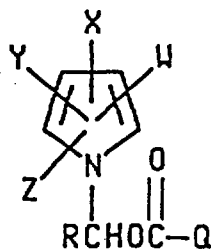
[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclobutanecarboxylate;

[3-bromo-5-chloro-4-cyano-2-(3,4-dichlorophenyl)-pyrrol-1-yl]methyl cyclopropanecarboxylate;

[3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl cyclopropanecarboxylate;

and [3-chloro-5-(p-chlorophenyl)-4-cyano-2-(trifluoromethyl)pyrrol-1-yl]methyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate.

10. A composition for controlling insects, acarina and mollusks 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 and Q are as described in claim 1.

