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3,705,914

PESTICIDAL CARBAMATE DERIVATIVES OF NAPHTHAQUINONES

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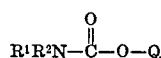
2 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to naphthaquinonyl and anthraquinonyl carbamates and processes for preparing them. The invention also relates to pesticidal compositions containing the above carbamates.

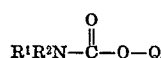
This invention relates to organic compounds, processes for preparing them and pesticidal compositions containing them. More particularly this invention relates to new substituted quinones and pesticidal compositions containing them.

According to the present invention we provide a compound having the general formula:



wherein R^1 represents an atom of hydrogen or a hydrocarbyl group; R^2 represents a hydrocarbyl group; and Q represents a naphthaquinonyl or anthraquinonyl radical.

In a preferred aspect the invention provides a compound having the formula:

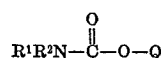


wherein R^1 represents an atom of hydrogen or an alkyl group; and R^2 represents an alkyl group; and Q represents either

- (i) a 1,4-naphthaquinon-2-yl radical optionally substituted with one or more alkyl groups of halogen atoms, or
- (ii) a 9,10-anthraquinon-1-yl radical.

When R^1 and R^2 represent alkyl groups, and when Q represents a 1,4-naphthaquinon-2-yl radical bearing substituent alkyl groups, the said alkyl groups are preferably lower alkyl groups comprising from 1 to 6 carbon atoms, for example, methyl, ethyl and n-butyl groups.

In a more preferred aspect therefore, the invention provides a compound having the formula:



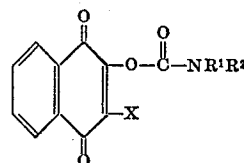
wherein R^1 represents an atom of hydrogen or an alkyl group comprising from 1 to 6 carbon atoms; R^2 represents an alkyl group comprising from 1 to 6 carbon atoms; and Q represents either

- (i) a 1,4-naphthaquinon-2-yl radical optionally substituted with one or more alkyl groups comprising from 1 to 6 carbon atoms, or halogen atoms, or
- (ii) a 9,10-anthraquinon-1-yl radical.

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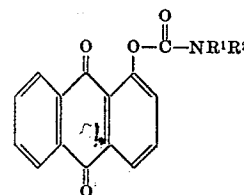
In a yet further preferred aspect the invention provides a quinone derivative having either

(i) the formula:



wherein R^1 represents an atom of hydrogen or an alkyl group comprising from 1 to 6 carbon atoms; R^2 represents an alkyl comprising from 1 to 6 carbon atoms; and X represents an alkyl group comprising from 1 to 6 carbon atoms, or a halogen atom: or

(ii) the formula:



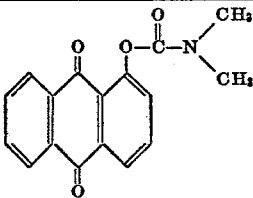
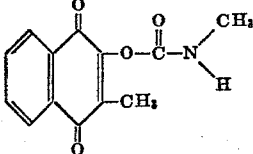
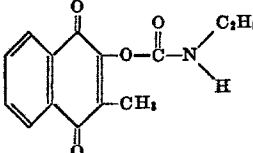
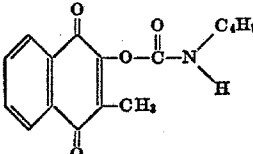
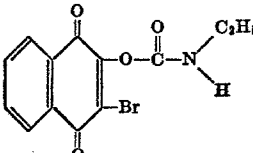
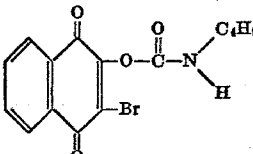
wherein R^1 and R^2 represent alkyl groups comprising from 1 to 6 carbon atoms.

Specific compounds according to the present invention are those whose structure formulae are displayed in Table 1 hereinafter, together with the melting point (expressed in degrees centigrade) for each compound.

TABLE 1

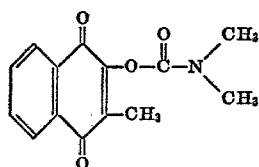
Compound No.	Structural formula	Melting point, ° C.
1.....		91
2.....		187-189
3.....		197
4.....		112-113

TABLE 1—Continued

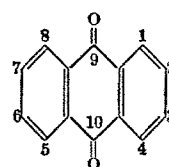
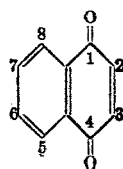
Compound No.	Structural formula	Melting point, °C.
5.....		199-201
6.....		
7.....		
8.....		
9.....		
10.....		

A particularly useful compound pesticidally is the compound No. 1 in Table 1 above.

In a particular aspect therefore the invention provides the compound having the formula:

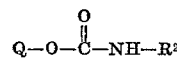


The numbering of the ring atoms of the naphthaquinone (I) and anthraquinone (II) rings is as shown in the formulas I and II:



(II)

The compounds of the invention may be prepared by a number of different methods. For example, compounds of the invention having the structure:

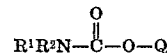


wherein Q represents a 1,4-naphthaquinonyl radical joined to the adjacent oxygen atom at any of the carbon atoms occupying the positions numbered 2, 3, 5, 6, 7 or 8 in the naphthaquinone ring and optionally substituted at the remaining positions, or a 9,10 anthraquinonyl radical joined to the adjacent oxygen atom at any of the carbon atoms occupying the positions numbered from 1 to 8 in the anthraquinonyl ring; and R^2 is a hydrocarbonyl group, may be obtained by reacting the corresponding quinone bearing an hydroxyl group at the appropriate position, with an isocyanate of the formula:

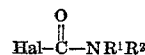


wherein R^2 has the meaning recited.

Compounds of the invention having the formula:



wherein Q, R^1 and R^2 have any of the meanings as hereinbefore defined may be obtained by reacting the corresponding quinone bearing an hydroxyl group at the appropriate position, with a carbamoyl halide having the formula:



wherein Hal represents an atom of chlorine, bromine or iodine, and R^1 and R^2 have any of the meanings recited above.

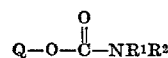
The compounds of this invention may also be prepared by reacting a quinonyl chloroformate having the formula:



wherein Q and X have any of the meanings recited above, with an amine having the formula:



wherein R^1 and R^2 have any of the meanings recited above, to yield a compound of the invention having the formula:



wherein Q, R^1 and R^2 have any of the meanings recited above.

The above reactions may be carried out in the presence of a solvent and optionally in the presence of a base.

The quinonyl chloroformate used in the above reactions may be prepared by reacting the corresponding quinone, bearing an hydroxyl group, with phosgene, in a suitable solvent and optionally in the presence of a base.

Suitable solvents for all the above reactions are non-hydroxylic solvents, such as ethers, e.g. diethyl ether, dioxan; ketones, e.g. acetone, cyclohexanone; esters, e.g. ethyl acetate; and hydrocarbons, e.g. benzene and cyclohexane. Other suitable solvents are aprotic nitrogen-containing solvents, e.g. pyridine, dimethylformamide.

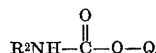
Suitable bases for the above reactions are aprotic nitrogen-containing compounds, e.g. pyridine, triethylamine, N-

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methylmorpholine; and the salts of weak inorganic acids, e.g. carbonic acid, with metals, particularly the alkali and alkaline earth metals. Especially useful bases for the reactions are sodium and potassium carbonates.

The reactions are conveniently carried out at temperatures in the range in which the solvent is in the liquid state, i.e. between its melting point and its boiling point under the ambient pressure. The compounds of this invention are usefully prepared at temperatures in the range 0° C. to 150° C., and preferably in the range 10° C. to 100° C.

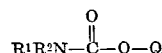
In another aspect therefore the invention provides a process for preparing a compound having the formula:



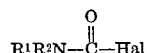
wherein Q represents a quinonyl radical, and R² is a hydrocarbon group in which a quinone bearing a hydroxyl group at the appropriate position is reacted with an isocyanate of the formula:



In another further aspect the invention provides a process for preparing a compound having the formula:



wherein Q, R¹ and R² have any of the meanings as hereinbefore defined, in which a quinone bearing a hydroxyl group at the appropriate position is reacted with a carbamoyl halide having the formula:



where Hal represents an atom of chlorine, bromine or iodine.

In a preferred aspect the invention provides a process as described hereinabove carried out in the presence of a solvent or diluent, and a base.

The invention compounds and compositions comprising them are very toxic to arachnid and insect pests, including for example, the following.

Tetranychus telarius (red spider mites)
Aedes aegypti (yellow fever mosquitoes)

In particular the invention compound No. 1 of Table 1, and compositions comprising it, are very useful in the control of red spider mites, and gives outstanding control of strains which have become resistant to the toxicants normally used against them. This compound is also very advantageous in use because of its remarkably low toxicity to mammals, thus rendering it safer in use than many of the red spider controlling agents presently available. This is illustrated in Table 2 below where the acute oral LD₅₀ toxicity value for rats of compound No. 1 of Table 1 is compared with those of several acaricides presently used in the control of red spider mites. The compounds, are named with their British Standard common names, and the toxicity data was obtained from "The Pesticide Manual" (1st edition, 1968) edited by H. Martin, and published by the British Crop Protection Council.

TABLE 2

Compound:	Acute oral toxicity to rats, 65
No. 1 of Table 1 -----	>4000
Dicofol -----	684
Binapacryl -----	120
Azinphos-methyl -----	16
Dinobuton -----	140
Demeton methyl -----	65
Carbophenothion -----	32
Parathion -----	3.6
Methodathion -----	25
Dioxathion -----	23

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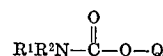
Further advantages of the compound No. 1 of Table 1 are the rapidity of its action when compared with some other acaricides, and its specificity of action. At the rates used in the control of red spider there appears to be no adverse effects on beneficial insects.

Compounds of the present invention and compositions comprising them are also toxic to nematode pests, including for example, *Meloidogyne incognita* (root knot nematodes) and possess activity against a wide variety of fungal diseases including, for example, the following specific diseases:

Puccinia recondita (rust) on wheat
Phytophthora infestans (late blight) on tomatoes
Sphaerotheca fuliginea (powdery mildew) on cucumber
15 *Podosphaera leucotricha* (powdery mildew) on apple
Uncinula necator (powdery mildew) on vine
Piricularia oryzae (blast) on rice
Plasmopara viticola (downy mildew) on vine
Venturia inaequalis (scab) on apple
20 *Rhizoctonia solani* (sore shin) on cotton
Fusarium culmorum (blight) on wheat
Pythium ultimum (damping off) on peas

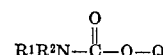
A particularly useful feature of the activity of the invention compounds is their ability to act as systemic pesticides, that is to say, their ability to move in a plant to combat a infestation or infection thereon remote from a site of initial application of a compound. Thus a compound of the invention, or a composition containing the same, may be applied to the soil surrounding the roots of a plant and taken up by the plant through its roots to combat pests on the plant.

The invention further consists in pesticidal compositions comprising as an active ingredient a compound having the formula:



wherein R¹ represents an atom of hydrogen or a hydrocarbyl group; R² represents a hydrocarbyl group; and Q represents a naphthaquinonyl or anthraquinonyl radical.

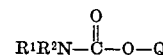
In a preferred aspect the invention consists in pesticidal compositions comprising as an active ingredient a compound having the formula:



wherein R¹ represents an atom of hydrogen or an alkyl group; R² represents an alkyl group; and Q represents either

- (i) a 1,4-naphthaquinonyl-2-yl radical optionally substituted with one or more alkyl groups or halogen atoms, or
(ii) a 9,10-anthraquinon-1-yl radical

In a more preferred aspect the invention consists in pesticidal compositions comprising as an active ingredient a compound having the formula:



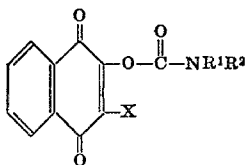
wherein R¹ represents an atom of hydrogen or an alkyl group comprising from 1 to 6 carbon atoms; R² represents an alkyl group comprising from 1 to 6 carbon atoms; and Q represents either

- (i) a 1,4-naphthaquinon-2-yl radical optionally substituted with one or more alkyl groups, comprising from 1 to 6 carbon atoms, or halogen atoms, or
75 (ii) a 9,10-anthraquinon-1-yl radical.

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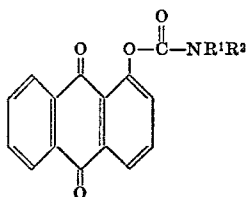
In a yet further preferred aspect the invention consists in pesticidal compositions comprising as an active ingredient a quinone derivative having either

(i) the formula:



wherein R¹ represents an atom of hydrogen or an alkyl group comprising from 1 to 6 carbon atoms; R² represents an alkyl comprising from 1 to 6 carbon atoms; and X represents an alkyl group comprising from 1 to 6 carbon atoms, or a halogen atom; or

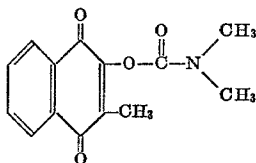
(ii) the formula:



wherein R¹ and R² represent alkyl groups comprising from 1 to 6 carbon atoms.

A particularly useful pesticidal composition is one which comprises as an active ingredient compound No. 1 of Table 1 hereinbefore.

In a further particular aspect therefore this invention provides a pesticidal composition comprising as an active ingredient the compound having the formula:



In use, the invention compounds, or compositions containing them may be applied in a variety of ways. Thus their application can suitably be directed onto the foliage of the plant or to infected and/or infested areas thereof, alternatively the soil surrounding the plant can be treated with the invention compounds or compositions containing them. If desired the seeds themselves can be similarly treated.

According to a further feature therefore we provide a method of combating undesired pests on plants which comprises applying to the locus of the plant a compound, or composition containing the same, as hereinbefore defined.

In a further aspect the invention provides a method of combating pests on plants which comprises applying to the plants or to seeds thereof a compound or composition as hereinbefore defined. The invention further includes a method of treating agricultural soil which comprises applying to the soil a compound or a composition as hereinbefore defined.

In a yet further aspect the invention includes a method of combating pests which comprises applying to the pests or to a pest habitat a compound or composition as hereinbefore defined.

The compounds and compositions of the invention may be used for agricultural or horticultural purposes and the compound or type of composition used in any instance will depend upon the particular purpose for which it is to be used.

Compositions comprising the invention compounds may be in the form of dusting powders or granules wherein the active ingredient is mixed with a solid diluent or carrier.

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Suitable solid diluents or carriers may be, for example, kaolinite (china clay), montmorillonite, attapulgite, talc, pumice, silica, calcium carbonate, gypsum, powdered magnesia, fuller's earth, Hewitt's earth and diatomaceous earth. Compositions for dressing seed, for example, may comprise an agent assisting the adhesion of the composition to the seed, for example, a mineral oil.

The composition may also be in the form of dispersible powders or grains comprising, in addition to the active ingredient, a wetting agent to facilitate the dispersion of the powder or grains in liquids. Such powders or grains may include fillers, suspending agents and the like.

The compositions may also be in the form of liquid preparations to be used as dips or sprays which are generally aqueous dispersions or emulsions containing the active ingredient in the presence of one or more wetting agents, dispersing agents, emulsifying agents or suspending agents.

Wetting agents, dispersing agents and emulsifying agents may be of the cationic, anionic, or non-ionic type. Suitable agents of the cationic type include, for example, quaternary ammonium compounds, for example, cetyltrimethylammonium bromide. Suitable agents of the anionic type include, for example, soaps, salts of aliphatic monoesters of sulphuric acid, for example sodium lauryl sulphate, salts of sulphonated aromatic compounds, for example sodium dodecylbenzenesulphonate, sodium, calcium or ammonium lignosulphonate, butylnaphthalene sulphonate; and a mixture of the sodium salts of diisopropyl- and triisopropyl-naphthalene sulphonic acids.

Suitable agents of the non-ionic type include, for example, the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol or cetyl alcohol, or with alkyl phenols such as octylphenol, nonylphenol and octylcresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, the condensation products of the said partial esters with ethylene oxide, the lecithins, and block copolymers of ethylene oxide and propylene oxide.

Suitable suspending agents are, for example, bentonite, pyrogenic silica, and hydrophilic colloids, for example polyvinylpyrrolidone and sodium carboxymethyl-cellulose, and the vegetable gums, for example gum acacia and gum tragacanth.

The aqueous solutions dispersions or emulsions may be prepared by dissolving the active ingredient or ingredients in an organic solvent which may contain one or more wetting, dispersing or emulsifying agents and then adding the mixture so obtained to water which may likewise contain one or more wetting, dispersing or emulsifying agents. Suitable organic solvents are ethylene dichloride, isopropyl alcohol, propylene glycol, diacetone alcohol, toluene, kerosene, methylnaphthalene, xylenes and trichloroethylene.

The compounds of the invention may also be formulated into compositions comprising capsules or microcapsules containing either the active ingredients itself, or a composition containing the active ingredient, and prepared by any of the known encapsulation or microencapsulation techniques.

The compositions to be used as sprays may also be in the form of aerosols wherein the formulation is held in a container under pressure in the presence of a propellant such as fluorotrichloromethane or dichlorodifluoromethane.

By the inclusion of suitable additives, for example, for improving the distribution, adhesive power and resistance to rain on treated surfaces, the different compositions can be better adapted for the various uses for which they are intended.

The compounds of this invention may also be conveniently formulated by admixing them with fertilizers. A preferred composition of this type comprises granules of fertilizer material incorporating, for example coated with, a compound of the invention. The fertilizer material may, for example, comprise nitrogen or phosphate-containing substances.

In yet a further aspect of the invention, therefore, we provide a pesticidal composition comprising a compound of the invention as hereinbefore defined, in admixture with a fertilizer material.

The compositions which are to be used in the form of aqueous dispersions or emulsions are generally supplied in the form of a concentrate containing a high proportion of the active ingredient or ingredients, the said concentrate to be diluted with water before use.

These concentrates are often required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water in order to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. The concentrates may conveniently contain from 10-85% by weight of the active ingredient or ingredients and generally from 25-60% by weight of the active ingredient or ingredients. When diluted to form aqueous preparations, such preparations may contain varying amounts of the active ingredient or ingredients depending upon the purpose for which they are to be used, but an aqueous preparation containing between 0.001% and 1.0% by weight of active ingredient or ingredients may be used.

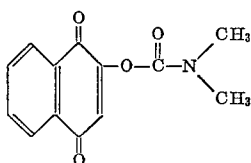
It is to be understood that the pesticidal compositions of this invention may comprise, in addition to a compound of the invention, one or more other compounds having biological activity.

As an example of such a composition the invention provides a composition comprising in addition to a compound of the invention, the compound O,O-dimethyl-O-4(2-diethylamino-6-methylpyrimidinyl) thiophosphate, also known by the British Standards common name pirimiphos-methyl.

The invention is illustrated, but not limited, by the following Examples.

EXAMPLE 1

This example illustrates the preparation of 2-methyl-1,4-naphthaquinon-3-yl dimethylcarbamate (compound No. 1 of Table 1), having the structure:



To a solution of 2-hydroxy-3-methyl-1,4-naphthaquinone (2.5 g.) in pyridine (30 cc.) was added dimethylcarbamoyl chloride (1.5 cc.). After keeping at 75° C. for 4 hours, the pyridine was removed by evaporation at reduced pressure, and the residue distributed between water (100 cc.) and chloroform (100 cc.). The chloroform layer was separated, and washed successively with 4% aqueous hydrochloric acid (2× 100 cc.), water (1× 200 cc.), 4% aqueous sodium hydroxide solution (3× 100 cc.) and water (2× 100 cc.). The chloroform solution was then dried over anhydrous sodium sulphate, filtered, and the filtrate evaporated to a solid residue which on recrystallisation from alcohol yielded 2-methyl-1,4-naphthaquinon-3-yl dimethylcarbamate as a buff crystalline solid having a melting point of 91° C.

EXAMPLE 2

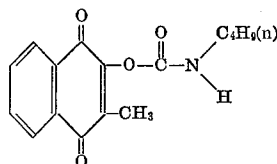
By a procedure similar to that illustrated in Example 1 above, but using the appropriate reactants, the preparation of the following compounds was effected.

2-bromo-1,4-naphthaquinon-3-yl dimethylcarbamate (compound No. 4, Table 1)

9,10-anthraquinon-1-yl dimethylcarbamate (compound No. 5, Table 1).

EXAMPLE 3

This example illustrates the preparation of 3-methyl-1,4-naphthaquinon-2-yl n-butylcarbamate (compound No. 8 of Table 1), having the structure:



To a solution of 2-hydroxy-3-methyl-1,4-naphthaquinone (2.0 g.) in dimethylformamide (40 cc.) in a 100 cc. conical flask, was added N-methylmorpholine (3 drops) and n-butyl isocyanate (1.5 cc.) at 15° C. The flask was then corked and kept at the ambient temperature for 5 days, after which the contents were poured into cold water (250 cc.) and stirred briskly for 2 minutes. The precipitated solid was collected by filtration, washed with cold water, and finally air dried to yield 3-methyl-1,4-naphthaquinon-3-yl n-butylcarbamate, as a yellow microcrystalline solid, having a melting point of 120-2° C.

EXAMPLE 4

By a procedure similar to that illustrated in Example 3 above, but using the appropriate reactants, the preparation of the following compounds was effected:

1,4-naphthaquinon-2-yl methylcarbamate (compound No. 2, Table 1)

3-bromo-1,4-naphthaquinon-2-yl methylcarbamate (compound No. 3, Table 1)

3-methyl-1,4-naphthaquinon-2-yl methylcarbamate (compound No. 6, Table 1)

3-methyl-1,4-naphthaquinon-2-yl ethylcarbamate (compound No. 7, Table 1)

3-bromo-1,4-naphthaquinon-2-yl ethylcarbamate (compound No. 9, Table 1)

3-bromo-1,4-naphthaquinon-2-yl n-butylcarbamate (compound No. 10, Table 1)

EXAMPLE 5

This example illustrates an atomisable fluid comprising a mixture consisting of 25% by weight of compound No. 1 of Table 1 and 75% by weight of xylene.

EXAMPLE 6

This example illustrates a dusting powder which may be applied directly to plants or other surfaces and comprises 1% by weight of compound No. 1 of Table 1 and 99% by weight of talc.

EXAMPLE 7

25 parts by weight of the product described in Example 1, 65 parts by weight of xylene, and 10 parts of an alkyl aryl polyether alcohol ("Triton" X-100; "Triton" is a trademark) were mixed in a suitable mixer. There was thus obtained an emulsion concentrate which can be mixed with water to produce an emulsion suitable for use in agricultural applications.

EXAMPLE 8

5 parts by weight of the product described in Example 1 were thoroughly mixed in a suitable mixer with 95 parts by weight of talc. There was thus obtained a dusting powder.

EXAMPLE 9

10 parts by weight of the product described in Example 1, 10 parts of an ethylene oxide-octylphenol condensate ("Lissapol" NX; "Lissapol" is a trademark) and 80 parts by weight of diacetone alcohol were thoroughly mixed. There was thus obtained a concentrate which, on mixing with water, gave an aqueous dispersion suitable for application as a spray in the control of pests.

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EXAMPLE 10

This example illustrates a concentrated liquid formulation in the form of an emulsion. The ingredients listed below were mixed together in the stated proportions and the whole stirred until the constituents were dispersed.

	Percent wt.
Compound No. 4 (Table 1) -----	20
"Lubrol" L ("Lubrol" is a trademark) -----	17
Calcium dodecylbenzenesulphonate -----	3
Ethylene dichloride -----	45
"Aromasol" H ("Aromasol" is a trademark) -----	15
	100

EXAMPLE 11

The ingredients listed below were ground together in the proportions stated to produce a powdered mixture readily dispersible in liquids.

	Percent wt.
Compound No. 5 (Table 1) -----	50
Dispersol T ("Dispersol" is a trademark) -----	5
China clay -----	45
	100

EXAMPLE 12

A composition in the form of grains readily dispersible in a liquid (for example water) was prepared by grinding together the first four of the ingredients listed below in the presence of water and then the sodium acetate was mixed in. The admixture was dried and passed through a British Standard mesh sieve, size 44-100 to obtain the desired size of grains.

	Percent wt.
Compound No. 10 (Table 1) -----	50
Dispersol T -----	12.5
Calcium lignosulphonate -----	5
Sodium dodecylbenzenesulphonate -----	12.5
Sodium acetate -----	20
	100

EXAMPLE 13

A composition suitable for use as a seed dressing was prepared by mixing all three of the ingredients set out below in the proportions stated.

	Percent wt.
Compound No. 1 (Table 1) -----	80
Mineral oil -----	2
China clay -----	18
	100

EXAMPLE 14

A granular composition was prepared by dissolving the active ingredient in a solvent, spraying the solution obtained onto the granules of pumice and allowing the solvent to evaporate.

	Percent wt.
Compound No. 5 (Table 1) -----	5
Pumice granules -----	95
	100

EXAMPLE 15

An aqueous dispersion formulation was prepared by mixing and grinding the ingredients recited below in the proportions stated.

	Percent wt.
Compound No. 10 (Table 1) -----	40
Calcium lignosulphonate -----	10
Water -----	50
	100

The following constitutes an explanation of the compositions or substances represented by the various trade-

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marks and tradenames referred to in the foregoing examples.

"Lubrol" L is a condensate of 1 mole of nonyl phenol with 13 molar proportions of ethylene oxide.

"Aromasol" H is a solvent mixture of alkylbenzenes.

"Dispersol" T is a mixture of sodium sulphate and a condensate of formaldehyde with the sodium salt of naphthalene sulphonate.

"Lubrol" APN 5 is a condensate of 1 mole of nonyl phenol with 5½ moles of naphthalene oxide.

"Lissapol" NX is a condensate of 1 mole of nonyl phenol with 8 moles of ethylene oxide.

"Triton" X-100 is an alkyl aryl polyether alcohol.

EXAMPLE 16

The toxicity of a number of the compounds of this invention towards a variety of insect and other invertebrate pests was investigated and the tests conducted and results obtained are set out below. The compounds of the invention were in each case used in the form of a liquid preparation containing 0.1% (1000 parts per million (p.p.m.)) by weight of the compound. The preparations were made by dissolving each of the compounds in a mixture of solvents consisting of 4 parts by volume of acetone and 1 part by volume of diacetone alcohol. The solutions were then diluted with water containing 0.01% by weight of a wetting agents sold under the trade name of "Lissapol" NX until the liquid preparations contained the required concentrations of the compound ("Lissapol" is a trademark). In the case of the preparations used in the tests against *Aedes aegypti* and *Meloidogyne incognita*, these were further diluted until they contained 100 p.p.m. of the compound under test.

The test procedure adopted with regard to each test species basically the same and comprised supporting a number of the insects on some medium which may be a host plant or some foodstuff on which the insect feeds, and treating either or both the insect and the medium with the preparations. The mortality of the insects was then assessed at periods varying from one to three days after the treatment.

In the chemosterilant test with *Tetranychus telarius* the procedure was as follows: 3 days after spraying French bean plants infested with the pest, any living adults were removed from the plants and transferred to fresh untreated plants. After a further period of 3 days the adults were again removed, and any eggs laid on the plants transferred to transparent adhesive tape, and after a yet further period of three days the viability of the eggs was assessed.

In Table 3A below, the columns indicate, from left to right, the specific name and the common name of the species under test, the host plant or medium on which it was supported and the number of days which elapsed after treatment before assessing the mortality of the pest, or other effects, for example, if feeding had been discouraged (time interval T).

TABLE 3A

Species	Common name	Support medium/food	Time interval T (days)
<i>Tetranychus telarius</i> ----	Red spider mite (adults).	French bean...	3
Do-----	Red spider mite (egg)-----do-----		3
Do-----	Red spider mite (chemosterilant effect).	do-----	
<i>Aedes aegypti</i> -----	Mosquito (adults)-----	Plywood-----	1
<i>Meloidogyne incognita</i> ---	Root knot nematode---	Water-----	1

The actual results obtained are given in Table 3B. The assessment is expressed in integers which range from 0 to 3.

0 represents less than 30% kill

1 represents from 30-49% kill

2 represents from 50-90% kill

3 represents over 90% kill

TABLE 3B

Species	Compound No. of Table 1			
	1	6	8	9
<i>Tetranychus telarius</i> (adults).....	3	0	2	0
<i>Tetranychus telarius</i> (egg).....	1	0	0	0
<i>Tetranychus telarius</i> (chemosterilant test).....	0	0	2	0
<i>Aedes aegypti</i> (adult).....	0	3	0	3
<i>Meloidogyne incognita</i>	3	0	3	0

TABLE 4

Compound No. (Table 1)	<i>Puccinia recondita</i> (Rust)		<i>Phytophthora infestans</i> (Late blight)		<i>Sphaerotheca fuliginea</i> (Powdery mildew)		ESA	<i>Podosphaera leucotricha</i> (Powdery mildew)		<i>Uncinula necator</i> (Powdery mildew)		<i>Plasmopara viticola</i> (Downy mildew)		<i>Piricularia oryzae</i> (Blast)		<i>Venturia inaequalis</i> (Scab)	
	PSA	PRD	PSA	PRD	PSA	PRD		PSA	PRD	PSA	PRD	PSA	PRD	PSA	PRD	PSA	PRD
1.....	0	0	0	-----	3	3	-----	3	3	3	3	3	0	0	0	0	-----
2.....	0	1	-----	0	0	0	-----	0	0	-----	-----	2	0	-----	0	0	-----
3.....	3	0	3	-----	2	0	0	2	0	-----	-----	3	0	3	0	-----	-----
4.....	3	0	3	0	0	0	0	0	1	-----	-----	3	0	0	2	-----	-----
5.....	1	0	1	0	3	0	-----	0	3	-----	-----	2	0	0	1	-----	-----
6.....	1	-----	0	-----	-----	-----	-----	0	-----	0	-----	-----	-----	0	-----	-----	-----
7.....	0	-----	0	-----	0	-----	-----	0	-----	0	-----	-----	-----	0	-----	1	-----
8.....	1	-----	0	-----	-----	-----	-----	0	-----	2	-----	-----	-----	0	-----	0	-----
9.....	0	-----	3	-----	0	-----	-----	0	-----	3	-----	-----	-----	0	-----	3	-----
10.....	0	-----	-----	-----	-----	-----	-----	0	-----	-----	-----	-----	-----	0	-----	-----	-----

EXAMPLE 17

Compositions according to the invention were made up in the following manner and tested in different ways against various foliar-borne fungal diseases. The procedure adopted for each test is described below.

An aqueous solution or suspension containing 500 parts per million (p.p.m.) of the compound under test and suitable either for drenching the soil surrounding growing plants, or for spraying onto the leaves of cucumber, vine, or apple plants is obtained by adding water to a solution of the compound (200 mg.) in acetone (1 ml.) until the total volume of the mixture is 400 ml. An aqueous solution or suspension suitable for spraying onto the leaves of wheat, barley, or rice plants is prepared similarly, but instead of water a 0.1% volume/volume aqueous solution of the polyoxyethylenesorbitan monolaurate wetting agent, "Tween" 20, is used ("Tween" is a trademark).

A. Spray-applied Protectant Test (P.S.A.)

A suspension or solution containing 500 p.p.m. of the active compound was sprayed directly onto the leaves of plants, a wetting agent being used when the plant was wheat, barley or rice. After 24 hours the plant was inoculated with the fungus under test and after a suitable period of time (time interval A—see table below) depending upon the particular plant and fungus, the extent of infection was assessed visually.

(B) Drench-applied Protectant Test (P.R.D.)

A suspension or solution containing 500 p.p.m. of the active compound was applied to the soil surrounding the plant under test, and 48 hours later the plant was inoculated with the fungus. The extent of infection was assessed visually after a period of time (time interval B—see table below) depending upon the plant and the fungus.

(C) Spray-applied Eradicant Test (E.S.A.)

The plants were inoculated with the fungus under test, and 24 hours later the liquid preparation containing 500 p.p.m. of the active compound was sprayed onto the leaves of the plants as described under A above. After a further period of time (time interval C—see table below), again depending upon the particular plant and fungus, the extent of infection was assessed visually.

Disease and plant	Time interval A and B (days)	Time interval C (days)
<i>Puccinia recondita</i> (wheat).....	10	-----
<i>Phytophthora infestans</i> (tomato).....	3	-----
<i>Sphaerotheca fuliginea</i> (cucumber).....	7	9
<i>Podosphaera leucotricha</i> (apple).....	10	6
<i>Uncinula necator</i> (vine).....	10	9
<i>Plasmopara viticola</i> (vine).....	7	-----
<i>Piricularia oryzae</i> (rice).....	7	6
<i>Venturia inaequalis</i> (apple).....	21	20

The results of the tests are set out in the table below, the amount of disease being expressed as a grading giving the percentage amount of disease:

5 Grading:	Percentage amount of disease
0 -----	61 to 100
1 -----	26 to 60
2 -----	6 to 25
3 -----	0 to 5

EXAMPLE 18

Compounds of the invention were also tested against various soil-borne fungal diseases by the procedures set out below.

Test against *Fusarium culmorum*—procedure

The culture *Fusarium culmorum* was maintained on 2% malt agar test tube slopes at 20° C. Thirteen to seventeen days prior to testing the chemical, the culture was transferred to soil cornmeals, which consisted of 400 grams of 5% maize meal in John Innes seed compost contained in a ½ pint bottle. The cornmeals were plugged with cotton wool and sterilized in an autoclave for 2 hours, before inoculation. Two days prior to testing the chemical, the seeds and the soil were prepared. The soil was prepared by mixing the cornmeals with John Innes seed compost at the rate of 2 cornmeals to 3 buckets of compost (2 gallon capacity buckets). The seeds were prepared by rolling 10 grams of wheat seeds in a 25% china clay formulation of the chemical (where the chemical was a powder) or a 12.5% china clay formulation (where the chemical was a liquid) at the rate of 1000 p.p.m. weight/weight, e.g. 40 milligrams of 25% formulation on 10 grams of seeds. To test the chemical approximately 100 grams of the mixed soil was placed in a fibre pot, twenty seeds were placed on the surface and a further approximate 100 grams were placed on top of the seeds. This was repeated 3 times making four replicates in all. The pots were maintained in the greenhouse between 16° C. and 20° C. After 10 days the number of germinated seeds was recorded and after 17 days the roots were uncovered and the number healthy recorded. These recordings were compared with untreated seeds and seeds treated with mercury (Agrosan) and calculations were made to obtain a grading for disease control, and the results given in Table 5 following.

Test against *Pythium ultimum*—procedure

The culture *Pythium ultimum* was maintained on 2% malt agar test tube slopes at 20° C. Thirteen to seventeen days prior to testing the chemical, the culture was transferred to soil cornmeals which consisted of 400 grams of 5% maize meal in John Innes seed compost contained in a ½ pint bottle. The cornmeals were plugged with cotton wool and sterilized in an autoclave for 2 hours before inoculation. Two days prior to testing the chemical, the seeds and the soil were prepared. The soil was prepared by mixing the cornmeals with John Innes seed compost at the rate of 2 cornmeals to 3½ buckets of compost (2 gallon capacity buckets). The seeds were prepared by rolling 25 grams of peas in a 25% china clay formulation of the chemical (where the chemical was a powder) or a 12.5% china clay formulation (where the chemical was

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a liquid) at the rate of 500 p.p.m. weight/weight, e.g. 50 milligrams of 25% formulation on 25 grams seed. To test the chemical approximately 100 grams of the mixed soil were placed in a fibre pot, 10 seeds were placed on the surface and a further approximate 100 grams were placed on top of the seeds. This was repeated five times making six replicates in all. The pots were maintained in the greenhouse between 16° C. and 20° C. After 10 days the number of germinated seeds was recorded and after 17 days the roots, if any, were uncovered and recorded as being healthy or unhealthy. These recordings were compared with untreated seeds and seeds treated with thiram and drazoxalon and calculations were made to obtain a grading for disease control, and the results given in Table 5 below.

Test against *Rhizoctonia solani*—procedure

The culture *Rhizoctonia solani* was maintained on soil cornmeals which consisted of 400 grams of 5% maize meal in John Innes seed compost contained in a ½ pint bottle. The cornmeals were plugged with cotton wool and sterilized in an autoclave for 2 hours before inoculation. Nine days prior to testing the chemical, the soil was prepared by mixing the cornmeals with John Innes seed compost at the rate of 1 cornmeal to 1½ buckets of compost (2 gallon capacity buckets). Four days before testing the chemical, it was mixed with 400 grams of soil in a quart bottle at the rate of 100 p.p.m. weight/weight. Approximately 100 grams of John Innes seed compost was placed in a fibre pot, eight cotton seeds were placed on the surface, and 100 grams of the mixed soil was placed on top of the seeds. This was repeated three times, making four replicates in all. After 13 days the seedlings were assessed for disease. These assessments were compared with untreated seeds and seeds treated with pentachloronitrobenzene (PCNB), and calculations were made to obtain a grading for disease control, and the results given in Table 5 below.

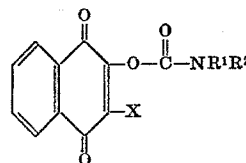
TABLE 5

Compound No. (Table 1)	<i>Fusarium culmorum</i>	<i>Pythium ultimum</i>	<i>Rhizoctonia solani</i>
2-----	3	0	0
3-----	0	3	0
4-----	3	1	2
5-----	0	0	2
6-----	3	0	0
10-----	2	0	0

16

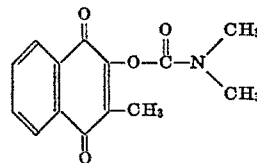
We claim:

1. A quinone derivative having the formula:



wherein R¹ represents an atom of hydrogen or an alkyl group having from 1 to 6 carbon atoms; R² represents an alkyl group having for 1 to 6 carbon atoms; and X represents an alkyl group having from 1 to 6 carbon atoms or a halogen atom.

2. The compound according to claim 1 and having the formula:



References Cited

- Chem. Abstracts, 61:14598a.
Chem. Abstracts, 63:5572g.
Chem Abstracts, 67:21734r.
Migrdichian, Organic Synthesis, vol. 1, 1957, pp. 319-320.

VIVIAN GARNER, Primary Examiner

U.S. Cl. X.R.

260—377; 424—200, 300