

PATENT SPECIFICATION

(11) 1 296 389

NO DRAWINGS

- (21) Application No. 60498/69 (22) Filed 11 Dec. 1969
 (31) Convention Application No. P 18 17 069.9
 (32) Filed 21 Dec. 1968 in
 (33) Germany (DT)
 (45) Complete Specification published 15 Nov. 1972
 (51) International Classification C07D 91/62 // A01N 9/14
 (52) Index at acceptance
 C2C 172—192—282 215 247 256 25Y 311 313 314 31Y
 339 396 397 464 465 551 614 694 695 791 79Y QM



(54) 1,3,4-THIADIAZOLES

(71) We, SCHERING AKTIEN-GESELLSCHAFT, a Body Corporate organised according to the laws of Germany, of Berlin and Bergkamen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

- 10 The present invention is concerned with new 1,3,4-thiadiazoles which are substituted in the 2- and 5-position, and with their use as soil and seed fungicides and as nematocides, as well as with processes for their manufacture.
 15 Substances based on 1,2,4-thiadiazole and having a fungicidal activity have been known (cf. United States Patent Specifications 3,260,588 and 3,260,725). 5 - Ethoxy - 3 - trichloromethyl - 1,2,4 - thiadiazole, which is distinguished by its special fungicidal activity,
 20 has however only a specific activity against Pythium.

The present invention provides compounds of the general formula



in which R_1 represents a lower halogenoalkyl group, as hereinafter defined, especially a halogenomethyl group,

- 30 R_2 represents an aliphatic hydrocarbon group which preferably contains up to 8 carbon atoms, and
 n represents 1 or 2.

- 35 The new 1,3,4-thiadiazoles of the present invention are especially active fungicides against harmful fungi occurring in the soil, on seeds and other parts of plants. As compared with the aforesaid 5 - ethoxy - 3 - trichloromethyl - 1,2,4 - thiadiazole, the new compounds are specifically active not only against
 40 Pythium but also against Rhizoctonia, Fusarium and other fungi and pests.

When used in a fungicidally active does the compounds of the present invention are barely poisonous so that they can be confidently applied to seeds or used in combination therewith. Since in addition they display good plant compatibility, any damage to useful plants caused by their use can be substantially prevented.

The compounds are active against *inter alia*, Pythium, Rhizoctonia, Fusarium, Tilletia, Helminthosporium as well as against Venturia, Plasmopara, Botrytis and other fungi causing damage to plants.

Moreover, it has been observed that the compounds display a nematocidal and bactericidal activity. Compounds in which R_1 represents a trifluoromethyl group display especially in the vapour or gaseous phase an excellent fungicidal activity at 1 ppm referred to the air volume.

Particularly active are, for example, the following compounds

- 2 - trifluoromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole, 65
- 2 - dichloromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole, 65
- 2 - trichloromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole, 65
- 2 - dichloromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole, 70
- 2 - trichloromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole, 70
- 2 - trichloromethyl - 5 - propylsulphonyl-1,3,4-thiadiazole, 75
- 2 - dichloromethyl - 5 - propylsulphonyl-1,3,4-thiadiazole, 75
- 2 - dichloromethyl - 5 - ethylsulphonyl-1,3,4-thiadiazole, 80
- 2 - trifluoromethyl - 5 - ethylsulphonyl-1,3,4-thiadiazole, 80
- 2 - trifluoromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole, 85
- 2 - trifluoromethyl - 5 - ethylsulphonyl-1,3,4-thiadiazole, 85
- 2 - trifluoromethyl - 5 - isopropylsulphonyl-1,3,4-thiadiazole and

2 - trifluoromethyl - 5 - isopropylsulphonyl-1,3,4-thiadiazole.

By the broad spectrum of their fungicidal activity the compounds of the present invention surpass not only the aforesaid known 1,2,4-thiadiazole derivative but over and above this also agents based on zinc ethylene-bis-dithiocarbamate, 1,4-dichloro-2,5-dimethoxybenzene, pentachloronitrobenzene and N-(trichloromethylthio) - cyclohex - 4 - ene - 1,2-dicarboximide. They are thus able to ensure a reliable control of the above-named fungi.

Since, moreover, the new compounds are only slightly toxic towards warm-blooded animals—the acute oral toxicity (LD₅₀) for the rat for, for example, 2 - trichloromethyl - 5-methylsulphonyl - 1,3,4 - thiadiazole is 717 mg/kg—there is relatively no risk associated with their use.

The new compounds can therefore be used in agriculture and in horticulture for general soil treatment, for the treatment of seeds or for treating seed furrows. The effect achieved by such a treatment extends not only to destructive fungi that attack from the soil but also to those which are transmitted by seeds and act as parasites on the parts of the plants that are above the ground. Surprisingly, some of the fungicidal compounds of the present invention display systemic properties. Moreover, their use at the same time controls nematodes living in the soil and destroys bacteria.

The active substances can be used by themselves, or in mixtures containing them, or if desired in combination with other plant protective agents or pesticides, for example with insecticides, when the simultaneous control of these or other pests is desired. It is also possible to apply them in admixture with synergistically active substances.

Accordingly, the present invention also provides fungicidal preparations which comprise the new 1,3,4-thiadiazoles in admixture or conjunction with a suitable carrier.

The new compounds are advantageously used in the form of, for example, powders, spraying agents, granulates, solutions, emulsions or suspensions, with the addition of solid and/or liquid diluents and/or vehicles and, if desired, adhesives, wetting agents, emulsifiers and/or dispersants.

Suitable liquid vehicles are, for example, water, mineral oils or other organic solvents, for example xylene, chlorobenzene, chloroform, 1,3-dichloropropene, cyclohexanone, ether, ethyl acetate, dimethylformamide, dimethylsulphoxide, ethylene dibromide and 1,2-dichloro-3-bromopropane.

Suitable solid vehicles are, for example, lime, attaclay and other clays, kaolin, chalk, talcum as well as natural or synthetic silicic acid and others.

As surface-active substances there may be mentioned, for example, salts of ligninsul-

phonic acids, salts of alkylated benzenesulphonic acids, sulphonated acid amides and their salts, polyethoxylated amines and alcohols.

If the new active substances are to be used for seed dressing, it is possible to admix dye-stuffs, for example new fuchsin, with them in order to impart a distinctly visible coloration to the dressed seeds.

The proportion of the active substance(s) in the preparations may vary within wide limits, the exact concentration of active substance incorporated in the preparation depending mainly on the quantity in which the preparation is to be used in treating, for example, the soil or the seeds. For example, the preparations may contain 10 to 80, preferably about 10 to 50, per cent by weight of active substance and about 99 to 20 per cent by weight of liquid or solid vehicle(s) and, if desired, up to 20 per cent by weight of surface-active substances. The various forms of the preparation are manufactured in a known manner, for example by way of grinding or mixing operations. It is worth noting that the active substances can be used with excellent results in dry dressings having a low content of active substance.

To assist the germination of seeds the preparations are applied in a known manner either before seeding directly to the seeds or are introduced during seeding into the seed furrows. When treating the soil as such it is advantageous to introduce the preparation into the top soil layers to a depth of about 20 cm, for example by tilling with a rotary hoe.

Accordingly, the present invention also provides a method of controlling fungi and/or nematocides and/or bacteria, wherein a crop area is treated with a 1,3,4-thiadiazole of the present invention.

The present invention further provides a method of controlling fungi and/or nematocides and/or bacteria, wherein seeds are treated with a 1,3,4-thiadiazole of the present invention.

In addition, the present invention provides a method of controlling fungi and/or nematocides and/or bacteria, wherein a living plant is treated with a 1,3,4-thiadiazole of the present invention.

It is to be understood in the description and claims herein that the "lower halogeno-alkyl group" represented by R₁ is an alkyl group containing up to 7 carbon atoms which is mono-, di- or polyfluorinated, -chlorinated or -brominated, or, alternatively, an alkyl group containing up to 7 carbon atoms which is substituted by two or more different halogen atoms selected from fluorine, chlorine and bromine atoms. Among the compounds of the present invention are especially valuable those in which R₁ represents a mono-, di- or trihalogenomethyl group, for example a monochloro-

methyl, dichloromethyl, trichloromethyl, monobromomethyl, dibromomethyl or trifluoromethyl group.

- 5 The aliphatic hydrocarbon groups represented by R_1 preferably contain up to 8 carbon atoms and are more especially linear or branched alkyl groups, for example methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, heptyl or octyl groups.

- 10 In the general formula n may be represented by 1 or 2.

- 15 The new compounds may be manufactured, for example, by the action of an oxidizing agent on a corresponding 5-mercapto-1,3,4-thiadiazole of the general formula



in which the R_1 and R_2 have the meanings given above.

- 20 Compounds of the general formula in which $n=1$ can be manufactured, for example, with the use as oxidizing agents of organic hydroperoxides, for example tertiary butylhydroper-

oxide, or, for example, meta-chloroperbenzoic acid, or inorganic oxidizing agents, for example hydrogen peroxide or sodium metaperiodate. It is advantageous to use for this purpose two oxidation equivalents of the oxidizing agent for every mol of the mercapto compound at a temperature within the range of from $+40^\circ\text{C}$ to 0°C .

For the manufacture of compounds in which $n=2$ there may be used, apart from the oxidizing agents mentioned above inorganic oxidizing agents, for example potassium permanganate, chromic acid or its salts or nitric acid at a temperature within the range of from 0°C to 120°C . In this case 1 mol of mercapto compound is reacted with 4 oxidation equivalents of the oxidizing agent, that is to say with twice as much as is required for the sulphoxidation described above.

As reaction media there may be used, if desired or necessary, organic solvents, for example, acetic acid, ethers, for example dioxan, ketones, for example acetone, or others, either as such or in admixture with water.

Some compounds according to the present invention are listed in the following Table.

TABLE 1

Compound No.	Name of compound	Physical constant
1	2-Trifluoromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 88°C
2	2-Chloromethyl-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5911$
3	2-Dichloromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 86°C
4	2-Dichloromethyl-5-ethylsulphonyl-1,3,4-thiadiazole	M.p.: 61°C
5	2-Dichloromethyl-5-propylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5703$
6	2-Dichloromethyl-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 60°C
7	2-Dichloromethyl-5-amylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5541$
8	2-Trichloromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 89°C
9	2-Trichloromethyl-5-ethylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5830$
10	2-Trichloromethyl-5-propylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5740$
11	2-Trichloromethyl-5-isopropylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5743$

TABLE 1 (Continued)

Compound No.	Name of compound	Physical constant
12	2-Trichloromethyl-5-butylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5652$
13	2-Trichloromethyl-5-heptylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5391$
14	2-Trichloromethyl-5-octylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5380$
15	2-Chloromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 50°C.
16	2-Chloromethyl-5-isopropylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5482$
17	2-Dichloromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 75°C
18	2-Dichloromethyl-5-ethylsulphonyl-1,3,4-thiadiazole	M.p.: 76°C
19	2-Dichloromethyl-5-propylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5554$
20	2-Dichloromethyl-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 58°C.
21	2-Trichloromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 123°C.
22	2-Trichloromethyl-5-ethylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5593$
23	2-Trichloromethyl-5-propylsulphonyl-1,3,4-thiadiazole	M.p.: 78°C.
24	2-Trichloromethyl-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 98°C.
25	2-Trichloromethyl-5-butylsulphonyl-1,3,4-thiadiazole	M.p.: 77°C.
26	2-Trichloromethyl-5-amylsulphonyl-1,3,4-thiadiazole	M.p.: 50°C
27	2-Trichloromethyl-5-hexylsulphonyl-1,3,4-thiadiazole	M.p.: 47°C
28	2-Trichloromethyl-5-heptylsulphonyl-1,3,4-thiadiazole	M.p.: 54°C
29	2-Trichloromethyl-5-octylsulphonyl-1,3,4-thiadiazole	M.p.: 50°C
30	2-Bromomethyl-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5993$
31	2-Bromomethyl-5-ethylsulphonyl-1,3,4-thiadiazole	M.p.: 99°C.

TABLE 1 (Continued)

Compound No.	Name of compound	Physical constant
32	2-Dibromomethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 113°C
33	2-Fluoromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 45°C.
34	2-Fluoromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 64°C
35	2-Trifluoromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 53°C
36	2-Trifluoromethyl-5-ethylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.4897$
37	2-Trifluoromethyl-5-isobutylsulphonyl-1,3,4-thiadiazole	M.p.: 54°C
38	2-Trifluoromethyl-5-pentylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.4801$
39	2-Trifluoromethyl-5-hexylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.4790$
40	2-Trifluoromethyl-5-ethylsulphonyl-1,3,4-thiadiazole	B.p.: 79°C/0.05 Torr
41	2-Trifluoromethyl-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 77°C
42	2-Trifluoromethyl-5-isobutylsulphonyl-1,3,4-thiadiazole	M.p.: 41°C
43	2-Trifluoromethyl-5-hexylsulphonyl-1,3,4-thiadiazole	M.p.: 47°C
44	2-Trifluoromethyl-5-heptylsulphonyl-1,3,4-thiadiazole	M.p.: 64°C
45	2-Pentafluoroethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 66°C.
46	2-Heptafluoropropyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 71°C
47	2-(1,1-Dichloroethyl)-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 63°C
48	2-(1-Chloropropyl)-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5661$
49	2-(1-Chloropropyl)-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 56°C.
50	2-(1-Bromoethyl)-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5730$
51	2-(1-Bromoisobutyl)-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5529$

TABLE I (Continued)

Compound No.	Name of compound	Physical constant
52	2-(1-Bromopentyl)-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5443$
53	2-(1-Bromoisopentyl)-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20} = 1.5401$
54	2-Chlorodifluoromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 56°C
55	2-Chlorodifluoromethyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 52°C
56	2-Trifluoromethyl-5-propylsulphonyl-1,3,4-thiadiazole	B.p.: 83°C/0.15 Torr
57	2-Trifluoromethyl-5-propylsulphonyl-1,3,4-thiadiazole	B.p.: 136°C/18 Torr
58	2-Trifluoromethyl-5-isopropylsulphonyl-1,3,4-thiadiazole	B.p.: 58—61°C/0.7 Torr

5 The compounds are soluble in chlorinated hydrocarbons, for example chloroform and 1,3-dichloropropene, ethers, for example dioxan, ketones, for example acetone and cyclohexanone, esters, for example ethyl acetate, acids, for example acetic acid, dimethylformamide, dimethylsulphoxide and other solvents.

10 The following Examples illustrate the invention. Examples 1 to 3 describe the manufacture of 1,3,4-thiadiazoles according to the process of the present invention and Examples 4 to 15 describe and show the activity of the active compounds of the present invention.

15 Example 1

11.3 Grams of hydrogen peroxide of 30% strength were dropped into a solution of 24.9 g of 2 - trichloromethyl - 5 - methylmercapto-1,3,4-thiadiazole in 200 ml of glacial acetic acid and the whole was allowed to stand overnight, then evaporated under vacuum, the residue was taken up in methylene chloride, the residual acetic acid was removed with dilute sodium carbonate solution, the organic phase was dried and evaporated and the residue was recrystallized from a small quantity of isopropyl ether.

20 Yield: 23.4 g, corresponding to 88% of the theoretical yield, of 2 - trichloromethyl-5 - methylsulphonyl - 1,3,4 - thiadiazole, melting at 89 to 90°C.

25 Example 2

30 105.5 g of potassium permanganate were slowly added in portions to a solution of 107.6 g of 2 - dichloromethyl - 5 - methylmercapto-1,3,4-thiadiazole in 750 ml of glacial acetic

acid and 300 ml of water. During this addition the temperature was kept at 10°C and the whole was vigorously stirred. The batch was allowed to react for a further 30 minutes at the same temperature. Then 2.5 litres of water were added and the precipitated manganese dioxide (MnO_2) was reduced between 0° and 5°C by dropping in a solution of 95 g of sodium metabisulphite in 400 ml of water. When practically all of this solution had been added, the reduction had been completed and the reaction mixture has lost its colour. The precipitated substance was filtered off with suction, washed with water and recrystallized from about 170 ml of isopropanol.

Yield: 92 g, corresponding to 74% of the theoretical yield, of 2 - dichloromethyl-5 - methylsulphonyl - 1,3,4 - thiadiazole, melting at 75°C.

35 Example 3

While cooling a solution of 36.75 g of 2-dichloromethyl - 5 - ethylmercapto - 1,3,4-thiadiazole in 200 ml of chloroform, 28.5 g of meta-chloroperbenzoic acid were slowly stirred in. The batch was allowed to react for a further 1 hour, then the meta-chloroperbenzoic acid was extracted with dilute sodium carbonate solution, washed with water and dried over magnesium sulphate. The solvent was then evaporated and the residue recrystallized from a small quantity of isopropyl ether.

Yield: 33 g, corresponding to 88% of the theoretical yield, of 2 - dichloromethyl-5 - ethylsulphonyl - 1,3,4 - thiadiazole, melting at 75°C.

Example 4

Limiting concentrations of the soil-fungicidal activity of 1,3,4-thiadiazoles of the present invention were determined by uniformly mixing preparations containing them with infested soil and the results obtained are given in Table 2 below where the compound numbers correspond to those given in Table 1 above. Preconditions for the assessment were a healthy formation of roots without fungus necroses and a germination of at least 90% of the seeds as compared with the result obtained in steamed soil. For each of the con-

centrations 25 grains of peas of the variety "Wunder von Kelvedon" (registered name) were planted without a waiting period. The cultivation period in the tests was 20 to 23 days at a temperature ranging from 22 to 25°C. Four commercial products were also included in the series of tests:

Pythium ultimum: Steamed compost soil was inoculated with the mycelium of *Pythium ultimum*.

Rhizoctonia solani: Steamed compost soil was inoculated with the mycelium of *Rhizoctonia solani*.

TABLE 2

Limiting concentrations of the fungicidal activity so far recorded
(mg of active substance per litre of soil)

Compound No.	<i>Pythium ultimum</i>	<i>Rhizoctonia solani</i>
1	10 mg	25 mg
2	30 mg	50 mg
3	10 mg	30 mg
4	100 mg	20 mg
5	100 mg	20 mg
6	above 200 mg	50 mg
7	above 200 mg	50 mg
8	20 mg	10 mg
9	200 mg	10 mg
10	100 mg	20 mg
11	above 200 mg	50 mg
12	200 mg	50 mg
13	above 200 mg	200 mg
14	above 200 mg	100 mg
15	10 mg	100 mg
16	150 mg	200 mg
17	10 mg	20 mg
18	above 200 mg	100 mg
19	100 mg	50 mg
20	200 mg	50 mg
21	40 mg	10 mg
22	50 mg	50 mg

TABLE 2 (Continued)

Compound No.	Pythium ultimum	Rhizoctonia solani
23	150 mg	30 mg
24	150 mg	30 mg
25	above 200 mg	25 mg
26	above 200 mg	25 mg
27	above 200 mg	25 mg
28	above 200 mg	200 mg
29	above 200 mg	above 200 mg
30	20 mg	150 mg
31	50 mg	above 200 mg
32	20 mg	50 mg
33	50 mg	20 mg
34	50 mg	30 mg
35	10 mg	20 mg
36	10 mg	20 mg
37	30 mg	100 mg
38	100 mg	40 mg
39	100 mg	40 mg
40	10 mg	20 mg
41	10 mg	20 mg
42	20 mg	100 mg
43	above 100 mg	50 mg
44	above 100 mg	50 mg
45	100 mg	above 100 mg
46	100 mg	100 mg
47	80 mg	50 mg
48	above 100 mg	100 mg
49	100 mg	50 mg
50	40 mg	100 mg
51	above 100 mg	50 mg
52	no effect	100 mg

TABLE 2 (Continued)

Compound No.	Pythium ultimum	Rhizoctonia solani
53	no effect	100 mg
54	10 mg	20 mg
55	10 mg	10 mg

Comparison substances

5-Ethoxy-3-trichloro-methyl-1,2,4-thiadiazole	20 mg	effect insufficient
1,4-Dichloro-2,5-dimethoxy-benzene	effect insufficient	30 mg
Pentachloronitrobenzene	" "	75 mg
N-(Trichloromethylthio)-cyclohex-4-ene-1,2-dicarboximide	300 mg	300 mg

5 These test results demonstrate the superiority of the compounds according to the present invention as compared with the aforesaid known fungicides.

Example 5

10 Steamed compost soil was inoculated with mycelium of *Pythium ultimum*. Preparations containing 1,3,4-thiadiazoles of the present invention in the form of powders of 20% strength were uniformly mixed with the infected soil and, without a waiting period, 25 grains of branched peas of the variety "Wunder von Kelvedon" for each of the concentrations

were planted in clay dishes each containing 15 1 litre of soil. The following Table 3 shows the number of emerged sound peas, the fresh weight of the plants, and the result of the inspection of the roots after a cultivation period of 3 weeks at 22 to 25°C, the compound numbers corresponding to those given in Table 1 above. The roots were assessed as follows:

4=white roots, no fungus necroses
 3=white roots, minor fungus necroses
 2=brown roots, major fungus necroses 25
 have already appeared
 1=strong fungus necroses, roots withered

TABLE 3

Compound No.	mg of active substance per litre of soil	Number of sound peas after 3 weeks	Fresh weight (g) of plants	Root assessment (1—4)
1	10 mg	25	20 g	4
	20 mg	22	19 g	4
	30 mg	23	19 g	4
3	10 mg	24	22 g	4
	20 mg	24	24 g	4
	30 mg	25	22 g	4
8	10 mg	19	12 g	1
	20 mg	24	22 g	4
	30 mg	25	22 g	4
15	10 mg	22	20 g	4
	20 mg	23	20 g	4
	30 mg	24	20 g	4
17	10 mg	23	24 g	4
	20 mg	24	22 g	4
	30 mg	24	26 g	4
30	10 mg	21	18 g	1
	20 mg	24	24 g	4
	30 mg	22	18 g	4

Comparison substances

5-Ethoxy-3-trichloro-methyl-1,2,4-thiadiazole	10 mg	12	10 g	1
	20 mg	21	16 g	4
	30 mg	19	14 g	4
1,4-dichloro-2,5-dimethoxy-benzene	200 mg	2	1 g	1
N-(Trichloro-methylthio)-cyclohex-4-ene-1,2-dicarboximide	200 mg	13	6 g	1
Zinc ethylene-bis-dithio-carbamate	200 mg	14	7 g	1
Steamed soil	—	20	16 g	4
Untreated soil	—	0	0 g	—

As the above figures show even the hitherto known 1,2,4-thiadiazole derivative known for its special activity against *Pythium* does not exceed the activity of the compounds accord-

ing to the present invention against this fungus but that on the contrary it is even slightly less active than some of the new compounds.

Example 6

Steamed compost soil was inoculated with mycelium of *Rhizoctonia solani*. Preparations containing 1,3,4-thiadiazoles of the present invention (in the form of powders of 20% strength) were uniformly mixed with the infected soil and then, without a waiting period, 25 grains of branded peas of the variety "Wunder von Kelvedon" for each of the con-

centrations were planted in clay dishes each containing 1 litre of soil. The following Table 4 shows the number of emerged healthy peas, the fresh weight of the plants and an assessment (as defined in Example 5) of the roots after a cultivation period of 3 weeks at 22 to 25°C, the compound numbers corresponding to those given in Table 1 above.

TABLE 4

Compound No.	mg of Active substance per litre of soil	Number of sound peas after 3 weeks	Fresh weight (g) of plants	Root assessment (1—4)
3	10 mg	0	0 g	—
	20 mg	2	2 g	1
	30 mg	22	21 g	4
8	10 mg	21	17 g	4
	20 mg	24	17 g	4
	30 mg	24	17 g	4
9	10 mg	22	18 g	4
	20 mg	22	16 g	4
	30 mg	23	17 g	4
17	10 mg	0	0 g	—
	20 mg	23	14 g	4
	30 mg	22	14 g	4
21	10 mg	17	11 g	4
	20 mg	24	17 g	4
	30 mg	24	17 g	4
23	10 mg	13	9 g	1
	20 mg	21	17 g	3
	30 mg	24	20 g	4
Comparison substances				
1,4-Dichloro-2,5-dimethoxybenzene	10 mg	0	0 g	—
	20 mg	0	0 g	—
	30 mg	21	18 g	4
	40 mg	22	18 g	4
Pentachloro-nitrobenzene	50 mg	4	4 g	1
	100 mg	25	15 g	4
Steamed soil	—	20	17 g	4
Untreated soil	—	0	0 g	—

The test results document the superior activity of the compounds of the present invention against *Rhizoctonia* as compared with that of the aforesaid hitherto known commercial preparations.

Example 7

A comparison of the fungistatic and fungicidal activity against *Pythium ultimum* was carried out, using preparations containing different concentrations of an active 1,2,4-thiadiazole of the present invention on Tonsil. Steamed compost soil was inoculated with mycelium of *Pythium ultimum*. The preparations (in the form of powders of 20% strength) were uniformly mixed with the infested soil and, without a waiting period, 25

grains of branded peas of the variety "Wunder von Kelvedon" for each of the concentrations were planted in clay dishes each containing 1 litre of soil. The following Table 5 shows the number of emerged healthy peas, the fresh weight of the plants and an assessment (as defined in example 5) of the roots after a cultivation period of 3 weeks at 22 to 25°C, the compound number corresponding to that given in Table 1 above.

TABLE 5

Compound No. 17	mg of active substance per litre of soil	Number of sound peas after 3 weeks	Fresh weight of peas (g)	Assessment of roots (1—4)
Formulation of 20% strength	6 mg	22	17 g	2
	10 mg	24	16 g	4
Formulation of 10% strength	6 mg	24	15 g	1
	10 mg	22	24 g	4
Formulation of 5% strength	6 mg	12	9 g	1
	10 mg	24	20 g	4
steamed soil	—	24	20 g	4
untreated soil	—	0	0 g	—

As this experiment shows, remarkable fungistatic effects were achieved in some cases with a concentration of only 6 mg of active substance per litre of soil. When this concentration was increased to only 10 mg of active substance per litre of soil, an optimal effect of the preparations tested was found.

Example 8

Steamed compost soil was inoculated with a suspension of spores of *Fusarium oxysporum*

f. callistephi. Preparations containing 1,3,4-thiadiazoles of the present invention (in the form of powders of 20% strength) were uniformly mixed with the infested soil and, after a waiting period of 8 days, 4 young plants of *Callistephus chinensis*, master aster "Sonnenstrahl", for each of the concentrations were planted as host plants. The following Table 6 shows the number of infested plants counted after 3 weeks, the compound numbers corresponding to those given in Table 1 above.

TABLE 6

Compound No.	mg of active substance per litre of soil	Number of infested plants after 3 weeks
3	50 mg	0
	100 mg	0
8	50 mg	0
	100 mg	0
9	50 mg	0
	100 mg	0
17	50 mg	0
	100 mg	0
19	50 mg	0
	100 mg	0
21	50 mg	0
	100 mg	0
22	50 mg	0
	100 mg	0
25	50 mg	0
	100 mg	0
Comparison substances		
N-(Trichloromethyl- thio)-cyclohex-4- ene-1,2-dicarboximide	50 mg	4
	100 mg	4
	200 mg	4
5-Ethoxy-3-tri- chloromethyl-1,2,4- thiadiazole	50 mg	4
	100 mg	4
	200 mg	4
1,4-Dichloro-2,5- dimethoxy-benzene	50 mg	4
	100 mg	4
	200 mg	4
Steamed soil		0
Untreated soil		4

This experiment likewise demonstrates the superiority of the compounds of this invention over commercial fungicides.

5

Example 9

25 Grains of cotton seeds that had been dressed with preparations of 10% strength containing 1,3,4-thiadiazoles of the present

invention were planted for each of the concentrations in normal compost soil. After a cultivation period of 15 days at 22 to 25°C the number of emerged sound cotton seedlings and their fresh weight were determined. The results are shown in Table 7 below, the compound numbers corresponding to those given in Table 1 above.

10

15

TABLE 7

Compound No.	Active substance per kg of seeds	Sound plants as a %	Fresh weight (g) of plants
3	100 mg	100 %	29 g
8	100 mg	96 %	29 g
17	100 mg	100 %	23 g
21	100 mg	100 %	23 g
Steamed soil, seeds undressed		100 %	27 g
Untreated soil, seeds undressed		50 %	14.5 g

This experiment reveals the excellent activity of the compounds of the present invention when used for dressing cotton seeds.

5

Example 10

The fungicidal activity of the compounds of the present invention against phytopathogenic fungi was tested on synthetic nutrients in Petri dishes (agar test). For the examination the nutrient consisting of 2% of malt extract and 1.5% of agar-agar powder was sterilized; before it solidified, the active substances were

added and thoroughly mixed with it so that the nutrient contained 10 parts of active substance per million parts (ppm). After the nutrient had solidified, it was inoculated with the aid of a loop of platinum wire containing 100 spores each of the fungi to be tested. After a cultivation period of 5 days at 22°C evaluation was performed by measuring the diameter of the colonies in mm. The results are shown in Table 8 below, the compound numbers corresponding to those given in Table 1 above.

15

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TABLE 8

Average relative growth in mm

Compound No.	<i>Aspergillus niger</i>	<i>Botrytis cinerea</i>	<i>Colletotrichum gloeosporioides</i>	<i>Helminthosporium sativum</i>	<i>Stemphylium ilicis</i>
1	0	0	0	0	0
3	50	36	0	0	0
7	0	22	0	0	0
8	0	0	0	0	0
9	0	0	0	0	0
10	0	0	0	0	0
12	0	0	0	0	0
13	0	13	0	0	0
17	0	0	0	0	0
18	0	13	41	0	0
19	0	0	0	0	0

TABLE 8 (Continued)

Compound No.	Average relative growth in mm				
	<i>Aspergillus niger</i>	<i>Botrytis cinerea</i>	<i>Colletotrichum gloeosporioides</i>	<i>Helminthosporium sativum</i>	<i>Stemphylium ilicis</i>
21	0	0	0	0	0
22	0	0	0	0	0
23	0	0	0	0	0
24	0	0	0	0	0
25	0	0	0	0	0
26	0	0	0	0	0
27	0	0	0	0	0
28	0	0	0	0	0
29	19	18	0	0	0
32	0	0	0	0	0
Comparison substance					
Zinc ethylene-bis-dithiocarbamate	78	36	81	50	55
Control	100	100	100	100	100

These results clearly show the better fungicidal activity of the compounds of the present invention as compared with the known control agent zinc ethylene-bis-dithiocarbamate.

Example 11

Preparations containing 1,3,4-thiadiazoles of the present invention, in the form of powders of 20% strength, were uniformly mixed with compost soil strongly infested by root gall nematodes. Without a waiting period, 20

cucumber pips for each of the concentrations were then planted. After a cultivation period of 30 days at a temperature between 23 and 25°C, the nematocidal effect was assessed by counting the root galls formed in a water-bath. Table 9 below shows the reduction in infestation as a percentage, the compound numbers corresponding to those given in Table 1 above. In the control experiment an average of 90 root galls per seedling had formed.

15

20

TABLE 9

Compound No.	Active substance per litre of soil	Nematocidal effect as a % (Meloidogyne incognita)
3	40 mg	100 %
	60 mg	100 %
4	40 mg	96 %
	60 mg	99 %
5	40 mg	90 %
	60 mg	98 %
17	40 mg	90 %
	60 mg	94 %
18	40 mg	61 %
	60 mg	90 %
19	40 mg	72 %
	60 mg	82 %

The results of this experiment clearly show the nematocidal effect of the compounds of the present invention.

- 5 Example 12
Combating *Pyrenochaeta lycopersici* (corky root) on tomatoes
2 - Dichloromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole, in the form of a 10% granulate preparation, was scattered over a

naturally infested field and worked in to a depth of 20 cm with a rotary hoe. At the time of this treatment the sandy clay soil had a relative soil humidity of 10%. After having allowed the substance to act for 3 weeks, 8-week-old tomato plants of the variety "Ronald-M" were planted at a distance of 50×70 cm. The yields shown in Table 10 below are average values from 40 plants per plot and indicate harvested ripe tomatoes.

TABLE 10

g of active substance/square metre	Yield per plant	Tomatoes per plant	Weight of each tomato
20 g	2209 g (213 %)	28 (165 %)	78 g (130 %)
10 g	1774 g (171 %)	27 (159 %)	66 g (110 %)
0 g	1036 g (100 %)	17 (100 %)	60 g (100 %)

- 25 Example 13
Combating *Thielaviopsis basicola* on tobacco
A preparation containing 2 - trifluoromethyl - 5 - methylsulphonyl - 1,3,4 - thiadiazole in the form of a powder of 10% strength was uniformly mixed with a soil strongly infested with *Thielaviopsis basicola*. After a reaction time of one week, tobacco

seedlings of the kind *Nicotiana tabacum* var. "White Burley" were planted in the soil and cultivated in a greenhouse for 5 weeks at 22 to 32°C. The amount of infestation and the fresh weight of the plants are shown in Table 11 below, the infestation being calculated in the manner indicated after the Table.

TABLE 11

Active substance per litre of soil	Infestation 0 — 5	Fresh weight of plants (leaves and stalks)	Weight of roots (air dried)
20 mg	0.5	115 g	11 g
30 mg	0	118 g	11 g
40 mg	0	104 g	9 g
Steamed soil	0	111 g	12 g
Infested soil	5	21 g	0.5 g

0 = no infestation
 1 = very little infestation
 2 = minor infestation
 3 = medium infestation
 4 = strong infestation
 5 = very strong infestation

Example 14

The fungicidal effects of

- 5 2 - trifluoromethyl - 5 - methylsulphonyl-
1,3,4-thiadiazole,
2 - trifluoromethyl - 5 - ethylsulphonyl-
1,3,4-thiadiazole,
2 - trifluoromethyl - 5 - methylsulphanyl-
1,3,4-thiadiazole and
10 2 - trifluoromethyl - 5 - ethylsulphanyl-
1,3,4-thiadiazole

in the vapour phase were determined:

- Open Petri dishes containing nutrient soil
15 inoculated with mycelium of *Pythium ultimum*
or *Rhizoctonia solani* were placed in glass
vessels 12 cm high, the bottom of each vessel
having first been covered with a preparation
containing one of the four 1,3,4-thiadiazoles
20 listed at the beginning of this Example in the
form of a powder of 10% strength. After a
reaction time of 3 days (for *Pythium*) and
5 days (for *Rhizoctonia*) at a temperature of
22°C in each of the covered glass vessels the
mycelium growth was assessed. Whereas in
25 the untreated glass vessels the Petri dishes
were completely overgrown by *Pythium* and
Rhizoctonia respectively, the treated speci-
mens displayed no mycelial growth even at
concentration of only 1 mg of active substance
30 per litre.

Example 15

Manufacture of a dry dressing

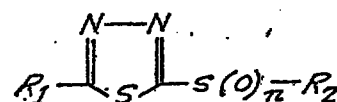
The following ingredients were mixed to-
gether, the percentages being by weight:

- 35 10% of 2 - trifluoromethyl - 5 - methyl-
sulphonyl-1,3,4-thiadiazole
87.8% talc
0.2% of new fuchsin
2% of liquid paraffin

- 40 The mixture was ground in an air jet mill
until a finely dispersed powder had formed.
This preparation was suitable for use as a
seed dressing as described above in Example
9.

WHAT WE CLAIM IS:—

1. A compound of the general formula



in which R_1 represents a lower halogenoalkyl
group, as hereinbefore defined, R_2 represents
an aliphatic hydrocarbon group and n repre-
sents 1 or 2.

2. A compound as claimed in claim 1,
wherein R_1 represents a halogenomethyl
group.

3. A compound as claimed in claim 2,
wherein R_1 represents a mono-, di- or tri-
halogenomethyl group.

4. A compound as claimed in claim 3,
wherein R_1 represents a monochloromethyl,
dichloromethyl, trichloromethyl, monobromo-
methyl, dibromomethyl or trifluoromethyl
group.

5. A compound as claimed in any one of
claims 1 to 4, wherein R_2 contains up to 8
carbon atoms.

6. A compound as claimed in any one of
claims 1 to 4, wherein R_2 represents an alkyl
group.

7. A compound as claimed in claim 6,
wherein R_2 represents an alkyl group con-
taining 1 to 8 carbon atoms.

8. 2 - Trifluoromethyl - 5 - methylsul-
phonyl-1,3,4-thiadiazole.

9. 2 - Chloromethyl - 5 - methylsulphanyl-
1,3,4-thiadiazole.

10. 2 - Dichloromethyl - 5 - methylsul-
phanyl-1,3,4-thiadiazole.

11. 2 - Dichloromethyl - 5 - ethylsulphanyl-
1,3,4-thiadiazole.

12. 2 - Dichloromethyl - 5 - propylsul-
phanyl-1,3,4-thiadiazole.



TABLE 11

Active substance per litre of soil	Infestation 0 — 5	Fresh weight of plants (leaves and stalks)	Weight of roots (air dried)
20 mg	0.5	115 g	11 g
30 mg	0	118 g	11 g
40 mg	0	104 g	9 g
Steamed soil	0	111 g	12 g
Infested soil	5	21 g	0.5 g

0 = no infestation
1 = very little infestation
2 = minor infestation

3 = medium infestation
4 = strong infestation
5 = very strong infestation

Example 14

The fungicidal effects of

- 2 - trifluoromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole,
- 2 - trifluoromethyl - 5 - ethylsulphonyl-1,3,4-thiadiazole,
- 2 - trifluoromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole and
- 2 - trifluoromethyl - 5 - ethylsulphonyl-1,3,4-thiadiazole

in the vapour phase were determined:

Open Petri dishes containing nutrient soil inoculated with mycelium of *Pythium ultimum* or *Rhizoctonia solani* were placed in glass vessels 12 cm high, the bottom of each vessel having first been covered with a preparation containing one of the four 1,3,4-thiadiazoles listed at the beginning of this Example in the form of a powder of 10% strength. After a reaction time of 3 days (for *Pythium*) and 5 days (for *Rhizoctonia*) at a temperature of 22°C in each of the covered glass vessels the mycelium growth was assessed. Whereas in the untreated glass vessels the Petri dishes were completely overgrown by *Pythium* and *Rhizoctonia* respectively, the treated specimens displayed no mycelial growth even at concentration of only 1 mg of active substance per litre.

Example 15

Manufacture of a dry dressing

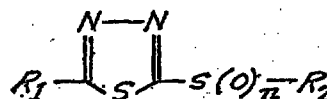
The following ingredients were mixed together, the percentages being by weight:

- 10% of 2 - trifluoromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole
- 87.8% talc
- 0.2% of new fuchsin
- 2% of liquid paraffin

The mixture was ground in an air jet mill until a finely dispersed powder had formed. This preparation was suitable for use as a seed dressing as described above in Example 9.

WHAT WE CLAIM IS:—

1. A compound of the general formula



in which R_1 represents a lower halogenoalkyl group, as hereinbefore defined, R_2 represents an aliphatic hydrocarbon group and n represents 1 or 2.

2. A compound as claimed in claim 1, wherein R_1 represents a halogenomethyl group.

3. A compound as claimed in claim 2, wherein R_1 represents a mono-, di- or trihalogenomethyl group.

4. A compound as claimed in claim 3, wherein R_1 represents a monochloromethyl, dichloromethyl, trichloromethyl, monobromomethyl, dibromomethyl or trifluoromethyl group.

5. A compound as claimed in any one of claims 1 to 4, wherein R_2 contains up to 8 carbon atoms.

6. A compound as claimed in any one of claims 1 to 4, wherein R_2 represents an alkyl group.

7. A compound as claimed in claim 6, wherein R_2 represents an alkyl group containing 1 to 8 carbon atoms.

8. 2 - Trifluoromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole.

9. 2 - Chloromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole.

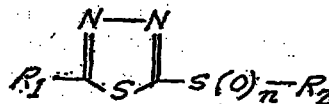
10. 2 - Dichloromethyl - 5 - methylsulphonyl-1,3,4-thiadiazole.

11. 2 - Dichloromethyl - 5 - ethylsulphonyl-1,3,4-thiadiazole.

12. 2 - Dichloromethyl - 5 - propylsulphonyl-1,3,4-thiadiazole.



13. 2 - Dichloromethyl - 5 - isopropylsulphanyl-1,3,4-thiadiazole.
14. 2 - Dichloromethyl - 5 - amylsulphanyl-1,3,4-thiadiazole.
- 5 15. 2 - Trichloromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
16. 2 - Trichloromethyl - 5 - ethylsulphanyl-1,3,4-thiadiazole.
17. 2 - Trichloromethyl - 5 - propylsulphanyl-1,3,4-thiadiazole.
- 10 18. 2 - Trichloromethyl - 5 - isopropylsulphanyl-1,3,4-thiadiazole.
19. 2 - Trichloromethyl - 5 - butylsulphanyl-1,3,4-thiadiazole.
- 15 20. 2 - Trichloromethyl - 5 - heptylsulphanyl-1,3,4-thiadiazole.
21. 2 - Trichloromethyl - 5 - octylsulphanyl-1,3,4-thiadiazole.
22. 2 - Chloromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 20 23. 2 - Chloromethyl - 5 - isopropylsulphanyl-1,3,4-thiadiazole.
24. 2 - Dichloromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 25 25. 2 - Dichloromethyl - 5 - ethylsulphanyl-1,3,4-thiadiazole.
26. 2 - Dichloromethyl - 5 - propylsulphanyl-1,3,4-thiadiazole.
27. 2 - Dichloromethyl - 5 - isopropylsulphanyl-1,3,4-thiadiazole.
- 30 28. 2 - Trichloromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
29. 2 - Trichloromethyl - 5 - ethylsulphanyl-1,3,4-thiadiazole.
- 35 30. 2 - Trichloromethyl - 5 - propylsulphanyl-1,3,4-thiadiazole.
31. 2 - Trichloromethyl - 5 - isopropylsulphanyl-1,3,4-thiadiazole.
32. 2 - Trichloromethyl - 5 - butylsulphanyl-1,3,4-thiadiazole.
- 40 33. 2 - Trichloromethyl - 5 - amylsulphanyl-1,3,4-thiadiazole.
34. 2 - Trichloromethyl - 5 - hexylsulphanyl-1,3,4-thiadiazole.
- 45 35. 2 - Trichloromethyl - 5 - heptylsulphanyl-1,3,4-thiadiazole.
36. 2 - Trichloromethyl - 5 - octylsulphanyl-1,3,4-thiadiazole.
37. 2 - Bromomethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 50 38. 2 - Bromomethyl - 5 - ethylsulphanyl-1,3,4-thiadiazole.
39. 2 - Dibromomethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 55 40. 2 - Fluoromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
41. 2 - Fluoromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
42. 2 - Trifluoromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 60 43. 2 - Trifluoromethyl - 5 - ethylsulphanyl-1,3,4-thiadiazole.
44. 2 - Trifluoromethyl - 5 - isobutylsulphanyl-1,3,4-thiadiazole.
45. 2 - Trifluoromethyl - 5 - pentylsulphanyl-1,3,4-thiadiazole.
46. 2 - Trifluoromethyl - 5 - hexylsulphanyl-1,3,4-thiadiazole.
47. 2 - Trifluoromethyl - 5 - ethylsulphanyl-1,3,4-thiadiazole.
- 70 48. 2 - Trifluoromethyl - 5 - isopropylsulphanyl-1,3,4-thiadiazole.
49. 2 - Trifluoromethyl - 5 - isobutylsulphanyl-1,3,4-thiadiazole.
50. 2 - Trifluoromethyl - 5 - hexylsulphanyl-1,3,4-thiadiazole.
- 75 51. 2 - Trifluoromethyl - 5 - heptylsulphanyl-1,3,4-thiadiazole.
52. 2 - Pentafluoroethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 80 53. 2 - Heptafluoropropyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
54. 2 - (1,1 - Dichloroethyl) - 5 - methylsulphanyl-1,3,4-thiadiazole.
55. 2 - (1 - Chloropropyl) - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 85 56. 2 - (1 - Chloropropyl) - 5 - methylsulphanyl-1,3,4-thiadiazole.
57. 2 - (1 - Bromoethyl) - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 90 58. 2 - (1 - Bromoisobutyl) - 5 - methylsulphanyl-1,3,4-thiadiazole.
59. 2 - (1 - Bromopentyl) - 5 - methylsulphanyl-1,3,4-thiadiazole.
60. 2 - (1 - Bromoisopentyl) - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 95 61. 2 - Chlorodifluoromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
62. 2 - Chlorodifluoromethyl - 5 - methylsulphanyl-1,3,4-thiadiazole.
- 100 63. 2 - Trifluoromethyl - 5 - propylsulphanyl-1,3,4-thiadiazole.
64. 2 - Trifluoromethyl - 5 - propylsulphanyl-1,3,4-thiadiazole.
65. 2 - Trifluoromethyl - 5 - isopropylsulphanyl-1,3,4-thiadiazole.
- 105 66. A process for the manufacture of a compound of the general formula



in which R₁ represents a lower halogenoalkyl group, as hereinbefore defined, R₂ represents an aliphatic hydrocarbon group and n represents 1 or 2, wherein a mercapto compound of the general formula



in which R₁ and R₂ have the meanings given above, is reacted with an oxidizing agent.

67. A process as claimed in claim 66, wherein R₁ represents a halogenomethyl group.



68. A process as claimed in claim 66 or 67, wherein R_2 represents an aliphatic hydrocarbon group containing up to 8 carbon atoms.
- 5 69. A process as claimed in any one of claims 66 to 68, wherein n represents 1 and the oxidizing agent is an organic hydroperoxide, meta-chloroperbenzoic acid or an inorganic oxidizing agent.
- 10 70. A process as claimed in claim 69, wherein the organic hydroperoxide is tertiary butyl hydroperoxide.
- 15 71. A process as claimed in claim 69, wherein the inorganic oxidizing agent is hydrogen peroxide or sodium meta-periodate.
- 20 72. A process as claimed in any one of claims 69 to 71, wherein two oxidation equivalents of the oxidizing agent, per mol of the mercapto compound, are used and the reaction is carried out at a temperature within the range of from $+40^{\circ}\text{C}$ to 0°C .
- 25 73. A process as claimed in any one of claims 66 to 68, wherein n represents 2 and the oxidizing agent is an organic hydroperoxide, meta-chloroperbenzoic acid or an inorganic oxidizing agent.
- 30 74. A process as claimed in claim 73, wherein the organic hydroperoxide is tertiary butyl hydroperoxide.
- 35 75. A process as claimed in claim 73, wherein the inorganic oxidizing agent is hydrogen peroxide, sodium meta-periodate, potassium permanganate, chromic acid, a salt of chromic acid or nitric acid.
- 40 76. A process as claimed in any one of claims 73 to 75, wherein four oxidation equivalents of the oxidizing agent, per mol of the mercapto compound, are used and the reaction is carried out at a temperature within the range of from 0°C to 120°C .
- 45 77. A process as claimed in claim 66, conducted substantially as described in any one of Examples 1 to 3 herein.
- 50 78. A fungicidal preparation which comprises a compound as claimed in any one of claims 1 to 7, in admixture or conjunction with a suitable carrier.
- 55 79. A fungicidal preparation which comprises the compound claimed in any one of claims 8 to 39, in admixture or conjunction with a suitable carrier.
- 60 80. A fungicidal preparation which comprises the compound claimed in any one of claims 40 to 65, in admixture or conjunction with a suitable carrier.
81. Any one of the fungicidal preparations as claimed in claim 78 and substantially as described in Examples 5 to 9 and 11 herein.
82. Any one of the fungicidal preparations as claimed in claim 78 and substantially as described in Examples 12 to 15 herein.
83. A method of controlling fungi and/or nematocides and/or bacteria, wherein a crop area is treated with a compound as claimed in any one of claims 1 to 7.
- 65 84. A method of controlling fungi and/or nematocides and/or bacteria, wherein a crop area is treated with the compound claimed in any one of claims 8 to 39.
- 70 85. A method of controlling fungi and/or nematocides and/or bacteria, wherein a crop area is treated with the compound claimed in any one of claims 40 to 65.
- 75 86. Any one of the methods as claimed in claim 83, conducted substantially as described in Examples 5, 7, 8 and 11 herein.
- 80 87. Any one of the methods as claimed in claim 83, conducted substantially as described in Examples 12 and 13 herein.
- 85 88. Any one of the methods as claimed in claim 83, conducted substantially as described in Example 6 herein, excluding the methods using 10 mg per litre of soil of the 1,3,4-thiadiazoles numbered as compounds 3 and 17.
- 90 89. A method of controlling fungi and/or nematocides and/or bacteria, wherein seeds are treated with a compound as claimed in any one of claims 1 to 7.
- 95 90. A method of controlling fungi and/or nematocides and/or bacteria, wherein seeds are treated with the compound claimed in any one of claims 8 to 39.
- 100 91. A method of controlling fungi and/or nematocides and/or bacteria, wherein seeds are treated with the compound claimed in any one of claims 40 to 65.
- 105 92. Any one of the methods as claimed in claim 89, conducted substantially as described in Example 9 herein.
- 110 93. A method as claimed in claim 89, conducted substantially as described in Example 15 herein.
- 115 94. A method of controlling fungi and/or nematocides and/or bacteria, wherein a living plant is treated with a compound as claimed in any one of claims 1 to 7.
95. A method of controlling fungi and/or nematocides and/or bacteria, wherein a living plant is treated with the compound claimed in any one of claims 8 to 39.
96. A method of controlling fungi and/or nematocides and/or bacteria, wherein a living plant is treated with the compound claimed in any one of claims 40 to 65.

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