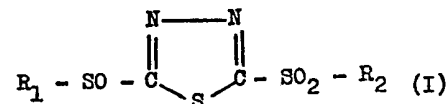


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(54) **Fungicidally active 2-sulphinyl-5-sulphonyl-1,3,4-thiadiazole derivatives and their manufacture and use**

(57) Novel 2-sulphinyl-5-sulphonyl-1,3,4-thiadiazole derivatives of the general formula I



(wherein R<sub>1</sub> and R<sub>2</sub> each represents C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkynyl or C<sub>3</sub>-C<sub>6</sub>-cycloalkyl) have a fungicidal action against phytopathogenic fungi.

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The chemical formulae appearing in the printed specification were submitted after the date of filing, the formulae originally submitted being incapable of being satisfactorily reproduced.

This print embodies corrections made under Section 117(1) of the Patents Act 1977.

## SPECIFICATION

**Fungicidally active 2-sulphinyl-5-sulphonyl-1,3,4-thiadiazole derivatives and their manufacture and use**

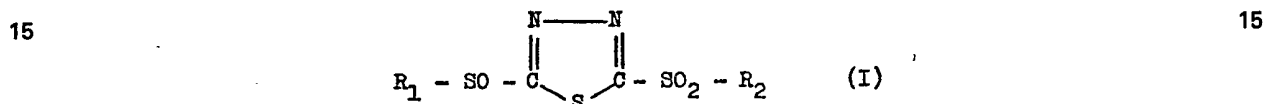
5 The present invention is concerned with new 2-sulphinyl-5-sulphonyl-1,3,4-thiadiazole derivatives, with a process for the manufacture of these compound and with their use as fungicidal agents in agriculture. 5

Fungicidally active 2,5-sulphonyl-1,3,4-thiadiazole derivatives are already known (German Patent Specification No. 1,695,847). These do not always, however, exhibit a satisfactory action especially against cereal fungi.

10 The problem upon which the present invention is based has been to develop a fungicidal agent with a special action against cereal fungi. 10

This problem is now solved by the new compounds of the present invention, as defined below.

The present invention provides compounds of the general formula I



20 in which R<sub>1</sub> and R<sub>2</sub> each represents a C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkynyl or C<sub>3</sub>-C<sub>6</sub>-cycloalkyl group. 20  
The groups represented by the symbols R<sub>1</sub> and R<sub>2</sub> may be the same or different.

The compounds of the present invention surprisingly have a better action against cereal fungi than known compounds of similar constitution and can therefore be used with special advantage for the protection of cereal crops, for example barley, oats, rye and wheat, against fungal attack.

25 These compounds furthermore exhibit an excellent action against leaf and soil fungi of the most varied categories and also have an adequate chemotherapeutic index. 25

A further significant advantage is that in comparison with mercury compounds, which although fungicidally very effective are however toxicologically objectionable, they have especially little pollution effect.

30 Some of the compounds of the present invention are furthermore superior to agents of different constitution also known in practice, for example manganese ethylene-bis-dithiocarbamate, N-trichloromethylthio-tetrahydro-phthalimide, 3-trichloromethyl-5-ethoxy-1,2,4-thiadiazole, pentachloronitrobenzene, methyl-1-(butylcarbamoyl)-2-benzimidazole carbamate and 3-(3,5-dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione. 30

35 Since, in addition, the amounts of the compounds of the present invention found to be suitable for use in practice are not phytotoxic if the soil stability is good, they can also be used with great success for treating soil and earth. 35

Fungi that can be well controlled by the compounds of the present invention include the following:

40 *Botrytis cinerea*, *Leptosphaeria nodorum* (= *Septoria nodorum*), *Micronectriella nivalis* (= *Fusarium nivale*), *Phytophthora infestans*, *Piricularia oryzae*, *Plasmopara viticola*, *Pyrenophora graminea* (= *Helminthosporium gramineum*), *Tilletia caries*, *Uromyces appendiculatus* (= *Uromyces phaseoli*), *Ustilago avenae*, *Venturia inaequalis* (= *Fusicladium dentriticum*) and others. 40

The present invention accordingly also provides a fungicidal preparation which comprises a compound of the general formula I, in admixture or conjunction with a suitable carrier. The preparation may of course

45 contain one or more compounds of the general formula I. 45

The present invention further provides a method of protecting a living plant against phytopathogenic fungi, wherein the living plant and/or the area in the vicinity of the living plant is/are treated with a compound of the general formula I.

The present invention further provides a method of protecting a crop area against phytopathogenic fungi,

50 wherein the crop area is treated with a compound of the general formula I. 50

The present invention further provides a method of dressing seeds, wherein the seeds are treated with a compound of the general formula I.

The present invention further provides a pack which comprises a compound of the general formula I together with instructions for its use for controlling phytopathogenic fungi.

55 The compounds of the present invention that are distinguished by a very good fungicidal action are those of the general formula I in which R<sub>1</sub> and R<sub>2</sub> each represents a methyl, ethyl, propyl, isopropyl, cyclopropyl, prop-2-enyl, prop-2-ynyl, *n*-butyl, isobutyl, sec.-butyl, *n*-pentyl, sec.-pentyl, isopentyl, *n*-hexyl, sec.-hexyl or isohexyl group. 55

Of these, the following compounds in particular exhibit an outstanding action:

60 2-ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole, 2-ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole, 2-ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole, 2-ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole and 2-ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole. 60

65 The compounds of the present invention may be used singly or in the form of mixtures with one another or 65

with other active substances. If desired, other fungicides, nematocides, insecticides and/or other pesticides may be added, depending on the desired purpose.

Advantageously, the active substances are used in the form of fungicidal preparations, for example powders, strewable preparations, granules, solutions, emulsions or suspensions, with the addition of liquid and/or solid vehicles or diluents and, if desired, of surface-active agents.

Suitable liquid carriers are water, mineral oils, or other organic solvents, for example xylene, chlorobenzene, cyclohexanol, dioxan, acetonitrile, ethyl acetate, dimethylformamide, isophorone and dimethyl sulphoxide.

Suitable solid carriers are lime, kaolin, chalk, talc, attaclay and other clays, as well as natural or synthetic silicic acid.

As surface-active substances there may be mentioned, for example, salts of ligninsulphonic acids, salts of alkylated benzenesulphonic acids, sulphonated acid amides and salts thereof, polyethoxylated amines and alcohols.

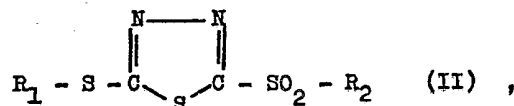
If the active substances are to be used for dressing seeds, colouring matter may also be added in order to give the dressed seeds a clearly visible colour.

The proportion of active substance or substances in the fungicidal preparations may vary within wide limits, the exact concentration of the active substance used for the preparations depending primarily on the quantity in which the preparations are to be used. For example, the preparations may contain approximately 1 to 95% by weight, preferably 20 to 50% by weight, of active substance(s) and approximately 99 to 5% by weight of liquid or solid carrier as well as, if desired, up to 20% by weight of surface-active agent(s).

The application of the active substances may be carried out in the usual manner, for example, by spraying, sprinkling, atomizing, dusting, applying in the form of a gas, fumigating, scattering, drenching or dressing.

The compounds of the present invention may be manufactured, for example, by the process of the present invention, as defined below.

The present invention further provides a process for the manufacture of a compound of the general formula I, wherein a compound of the general formula II

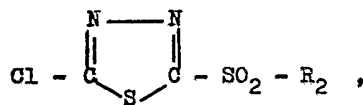


in which  $R_1$  and  $R_2$  have the meanings, given above, is treated in an inert solvent with an oxidizing agent, preferably an organic hydroperoxide, peracid or inorganic oxidizing agent, in an equimolar amount.

The compound of the general formula II may be prepared by the reaction of a compound of the general formula



in which  $R_1$  has the meaning given above, either in the free form in the presence of an organic base or in the form of an alkali salt thereof with a compound of the general formula



in which  $R_2$  has the meaning given above.

These 2-chloro-5-sulphonyl-1,3,4-thiadiazole derivatives are produced according to methods known *per se*. In the reaction of these derivatives with the thiols of the general formula  $R_1\text{-SH}$ , the organic bases used may be pyridine, 4-dimethylaminopyridine or 4-pyrrolidino-pyridine or tertiary amines, for example triethylamine or *N,N*-dimethylaniline. There come into consideration as the alkali salts of the thiols especially those of sodium and potassium.

For the sulfoxidation there may be used as organic oxidizing agents hydroperoxides, for example tert.-butylhydroperoxide, or peracids, for example *m*-chloroperbenzoic acid, or *N*-halocarboxylic acid amides, for example *N*-bromosuccinimide.

It is equally possible to use inorganic oxidizing agents, for example hydrogen peroxide or sodium metaperiodate. For this, 2 oxidation equivalents are used per mole of the thio compound.

The reactions are generally carried out between 0°C and the boiling points of the solvents used. For the sulfoxidation the reaction temperature should not exceed 60°. For the synthesis of the compounds of the present invention the reactants are preferably used in approximately equimolar amounts.

Suitable reaction media are solvents that are inert towards the reactants. The choice of these depends, in accordance with generally known considerations, on the objective of the reactions to be carried out.

The following may be mentioned as suitable solvents: carboxylic acids, for example acetic acid, carboxylic acid amides, for example dimethylformamide, carboxylic acid nitriles, for example acetonitrile, alcohols, for

example methanol, ethers, for example dioxan, and many others.

The isolation of the resulting compounds of the present invention is finally effected by distilling off the solvents used at normal or a reduced pressure, or by precipitation with water in the case of hydrophilic solvents and finally by crystallization.

- 5 The compounds of the present invention are colourless and odourless, stable oils or crystalline substances, which are insoluble in water, sparingly soluble in lower hydrocarbons, but readily soluble in the customary organic solvents, for example carboxylic acids, carboxylic acid amides, carboxylic acid esters, alcohols and ethers. 5

- 10 The compounds of the general formula II used as starting materials or intermediates in the process of the present invention are likewise stable oils or crystalline substances. They are readily soluble in carboxylic acids, carboxylic acid amides, carboxylic acid esters, alcohols, ketones and ethers, and insoluble in water. 10

- The following Examples illustrate the invention. Examples 1 and 2 illustrate the manufacture of the compounds of the present invention, Example 3 illustrates the manufacture of the starting materials of the general formula II, and Examples 4 to 18 illustrate the superior fungicidal action and the possible uses of the compounds of the present invention, the active compounds in Examples 4 to 18 being employed in the form of preparations. 15

#### EXAMPLE 1

##### *2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole*

- 20 A solution of 53.29 g of 2-ethylthio-5-butylsulphonyl-1,3,4-thiadiazole in 500 ml of acetic acid was mixed with 23 g of 30% hydrogen peroxide. The reaction was carried out by allowing the reaction mixture to stand overnight at room temperature. 1 litre of water was then added to the reaction solution, the oil that separated was extracted with dichloromethane, the acetic acid was removed from the extract by shaking with a soda solution, the dichloromethane phase was dried with magnesium sulphate and the solvent was distilled off completely, ultimately *in vacuo*. The remaining residue was recrystallized from isopropyl ether/isopropanol. 25  
Yield: 48.9 g = 87% of the theoretical yield.  
M.p.: 43°C.

#### EXAMPLE 2

- 30 *2-Isopropylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole* 30  
13.3 g of 2-isopropylthio-5-isopropylsulphonyl-1,3,4-thiadiazole were dissolved in 50 ml of dichloromethane and, while stirring and cooling at 10 to 15°C, a solution of 8.63 g of *m*-chloroperbenzoic acid in 200 ml of dichloromethane was added dropwise. The reaction mixture was stirred for a further 30 minutes, then shaken with an aqueous soda solution to remove the *m*-chloroperbenzoic acid, and the organic phase 35  
was separated off and dried over magnesium sulphate. After distilling off the solvent, a residue was obtained which was recrystallized from acetonitrile.  
Yield: 12.0 g = 85% of the theoretical yield.  
M.p.: 165°C (with decomposition).

- 40 The compounds of the present invention listed in the following Table can be produced in an analogous manner. 40

	Name of the compound	Physical constant	
5	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 75°C	5
	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	M.p.: 61°C	
10	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	M.p.: 38°C	10
	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 118°C	
15	2-Ethylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5361	15
	2-Methylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	M.p.: 87°C	
20	2-Isopropylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	M.p.: 78°C	20
	2-Butylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 66°C	
25	2-Isobutylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 93°C	25
	2-Hexylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5375	
30	2-Isopropylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	M.p.: 64°C	30
	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	M.p.: 99°C	
35	2-Ethylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	$n_D^{20}$ : 1.5299	35
	2-(1-Ethylbutylsulphinyl)-5-ethylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5284	
40	2-(1-Methylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5288	40
	2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5249	
45	2-Butylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	$n_D^{20}$ : 1.5222	45
	2-(1-Methylbutylsulphinyl)-5-pentylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5195	
50	2-(1-Methylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole	$n_D^{20}$ : 1.5222	50
	2-(1-Methylbutylsulphinyl)-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5280	
55	2-(1-Ethylbutylsulphinyl)-5-butylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5173	55
60			60
65			65

	Name of the compound	Physical constant	
5	2-(1-Ethylbutylsulphinyl)-5-pentylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5128	5
	2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5168	
10	2-(1-Ethylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole	$n_D^{20}$ : 1.5150	10
	2-(1-Ethylbutylsulphinyl)-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5220	
15	2-Methylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 145°C	15
	2-Methylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	M.p.: 62°C	
20	2-Isopropylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 63°C	20
	2-Ethylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	M.p.: 93°C	
25	2-Ethylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	M.p.: 63°C	25
	2-Ethylsulphonyl-5-butylsulphinyl-1,3,4-thiadiazole	M.p.: 52°C	
30	2-Ethylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5488	30
	2-Ethylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5420	
35	2-Ethylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole	M.p.: 71°C	35
	2-Ethylsulphonyl-5-sec.-butylsulphinyl-1,3,4-thiadiazole	M.p.: 76°C	
40	2-Butylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	M.p.: 63°C	40
	2-sec.-Butylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5508	
45	2-Sec.-Butylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	M.p.: 92°C	45
	2-Ethylsulphonyl-5-tert.-butylsulphinyl-1,3,4-thiadiazole	M.p.: 112°C (with decomposition)	
50	2-Butylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	M.p.: 43°C	50
	2-Butylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	M.p.: 62°C	
55	2-Butylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	M.p.: 68°C	55
60			60
65			65

	Name of the compound	Physical constant	
5	2-Butylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole	M.p.: 73°C	5
	2-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 56°C	
10	2-tert.-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 108°C (with decomposition)	10
	2-Isobutylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 106°C	
15	2-tert.-Butylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	M.p.: 62°C	15
	2-Butylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	M.p.: 52°C	
20	2-Butylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole	M.p.: 52°C	20
	2-Hexylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 65°C	
25	2-Hexylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 65°C	25
	2-Methylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	M.p.: 75°C	
30	2-sec.-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 84°C	30
	2-Isopentylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 73°C	
35	2-Isopentylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 73°C	35

## EXAMPLE 3

*2-Ethylthio-5-butylsulphonyl-1,3,4-thiadiazole*

114.5 g of 2-butylsulphonyl-5-chloro-1,3,4-thiadiazole were dissolved together with 36 ml of ethyl mercaptan in 400 ml of dioxan. 70 ml of triethylamine were then added dropwise, while stirring, and the solution was heated at the boiling temperature under reflux for 1 hour. After cooling, the reaction mixture was introduced into ice-water, the oil that separated was extracted with dichloromethane, the dichloromethane phase was dried with magnesium sulphate and the solvent was completely distilled off, at the end in a high vacuum. The resulting yield was 125.3 g = 99% of the theoretical yield, of a colourless oil;

$n_D^{20} = 1.5552$ .

The starting materials or intermediates listed in the following Table can be produced in an analogous manner.

	Name of the compound	Physical constant	
50	2-Ethylthio-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 78°C	50
	2-Ethylthio-5-propylsulphonyl-1,3,4-thiadiazole	M.p.: 36°C	
55	2-Ethylthio-5-sec.-butylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5401	55
	2-Ethylthio-5-isopropylsulphonyl-1,3,4-thiadiazole	M.p.: 42°C	
60	2-Isopropylsulphonyl-5-propylthio-1,3,4-thiadiazole	M.p.: 31°C	60

	Name of the compound	Physical constant	
5	2-Isopropylsulphonyl-5-isopropylthio-1,3,4-thiadiazole	M.p.: 48°C	5
	2-Isobutylthio-5-isopropylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5490	
10	2-Butylthio-5-isopropylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5490	10
	2-Hexylthio-5-isopropylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5420	
15	2-Ethylsulphonyl-5-isopropylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5653	15
	2-Methylsulphonyl-5-methylthio-1,3,4-thiadiazole	M.p.: 67°C	
20	2-Methylsulphonyl-5-propylthio-1,3,4-thiadiazole	M.p.: 47°C	20
	2-Isopropylthio-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 36°C	
25	2-Ethylsulphonyl-5-methylthio-1,3,4-thiadiazole	M.p.: 50°C	25
	2-Ethylsulphonyl-5-propylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5692	
30	2-Ethylsulphonyl-5-butylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5600	30
	2-Ethylsulphonyl-5-pentylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5552	
35	2-Ethylsulphonyl-5-hexylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5481	35
	2-Ethylsulphonyl-5-isobutylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5616	
40	2-Ethylsulphonyl-5-sec.-butylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5630	40
	2-sec.-Butylsulphonyl-5-propylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5542	
45	2-sec.-Butylsulphonyl-5-isopropylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5457	45
	2-Ethylsulphonyl-5-tert.-butylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5575	
50	2-Butylthio-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5687	50
	2-tert.-Butylthio-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5633	
55	2-Isobutylthio-5-methylsulphonyl-1,3,4-thiadiazole	M.p.: 54°C	55
60			60
65			65



	Name of the compound	Physical constant	
5	2-Methylsulphonyl-5-pentylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5614	5
	2-Hexylthio-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5542	
10	2-Butylsulphonyl-5-methylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5772	10
	2-Butylsulphonyl-5-propylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5551	
15	2-Butylsulphonyl-5-isopropylthio-1,3,4-thiadiazole	$n_D^{20}$ : 1.5533	15
	2-Butylsulphonyl-5-butylthio-1,3,4-thiadiazole	M.p.: 40°C	
20	2-Isopentylthio-5-methylsulphonyl-1,3,4-thiadiazole	$n_D^{20}$ : 1.5620	20

## EXAMPLE 4

25 *Limiting concentration test in the control of Pythium ultimum* 25

In a series of tests 20% strength pulverulent active substance preparations were mixed uniformly with soil severely infected with *Pythium ultimum*. 0.5 Litre earth-holding clay dishes were filled with the treated soil and, without a waiting period, 20 marrowfat pea seeds (*Pisum sativum* L. convar. *medullare* Alef.) of the variety "Wunder von Kelvedon" (Wonder of Kelvedon) were sown in each dish. After a cultivation period of 30 weeks at 20 to 24°C in a greenhouse, the number of sound peas was determined, and an evaluation (1-4 as defined below) of the roots was carried out. 30

The active substances used and their application quantities, and also the results, are listed in the following Table.

35 *Root evaluation:* 35

- 4 = white roots without fungal necrosis;  
 3 = white roots, slight fungal necrosis;  
 2 = brown roots, already more pronounced fungal necrosis;  
 1 = severe fungal necrosis, roots mouldy.

40 *Limiting concentration test in the control of Pythium ultimum* 40

45	Compounds according to the invention	Active substance concentration in mg/l of earth	Number of sound peas	Root evaluation (1-4)	45
50	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	20 mg	17	4	50
		40 mg	18	4	
		80 mg	19	4	
55	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	20 mg	18	4	55
		40 mg	19	4	
		80 mg	19	4	
60	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	20 mg	6	1	60
		40 mg	20	4	
		80 mg	19	4	
65	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	20 mg	17	3	65
		40 mg	18	4	
		80 mg	18	4	
65	2-Ethylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	20 mg	8	2	65
		40 mg	15	4	
		80 mg	15	4	

	Compounds according to the invention	Active substance concentration in mg/l of earth	Number of sound peas	Root evaluation (1-4)	
5	2-Methylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	6 8 17	1 1 4	5
10	2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	12 18 17	2 4 4	10
15	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	17 18 17	4 4 4	15
20	2-Isopropylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	13 15 15	1 3 4	20
25	2-Butylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	8 14 17	1 2 4	25
30	2-Isobutylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	8 8 17	1 1 4	30
35	<i>Agents for comparison</i>				30
40	Manganese ethylene-1,2-bis-dithio-carbamate	20 mg 40 mg 80 mg	4 5 10	1 1 2	35
45	N-Trichloromethylthio-tetrahydrophthalimide	20 mg 40 mg 80 mg	2 2 9	1 1 2	40
50	<i>Control I (3 repetitions)</i>				45
55	Infected soil without treatment	- - -	0 1 0	1 1 1	
60	<i>Control II (3 repetitions)</i>				45
65	Steamed soil	- - -	18 20 19	4 4 4	

## EXAMPLE 5

*Limiting concentration test in the control of Fusarium avenaceum*

In a series of tests 20% strength pulverulent active substance preparations were uniformly mixed with soil severely infected with *Fusarium avenaceum*. 0.5 Litre earth-holding clay dishes were filled with the treated soil and, without a waiting period, 20 marrowfat pea seeds (*Pisum sativum L. convar. medullare Alef.*) of the variety "Wunder von Kelvedon" (Wonder of Kelvedon) were sown in each dish. After a cultivation period of 18 days at 20 to 24°C in a greenhouse, the number of sound peas was determined, and an evaluation (1-4 as defined below) of the roots was carried out.

The active substances used and their application quantities, and also the results, are listed in the following Table.

*Root evaluation:*

4 = white roots without fungal necrosis;

3 = white roots, slight fungal necrosis;

2 = brown roots, already more pronounced fungal necrosis;

1 = severe fungal necrosis, roots mouldy.

*Limiting concentration test in the control of Fusarium avenaceum*

20	Compounds according to the invention	Active substance concentration in mg/l of earth	Number of sound peas	Root evaluation (1-4)	20
25	2-Ethylsulphonyl-5-isopropylsulphonyl-1,3,4-thiadiazole	25 mg	14	4	25
		50 mg	18	4	
		100 mg	18	4	
30	2-Isopropylsulphonyl-5-methylsulphonyl-1,3,4-thiadiazole	25 mg	14	2	30
		50 mg	19	4	
		100 mg	19	4	
35	2-Ethylsulphonyl-5-ethylsulphonyl-1,3,4-thiadiazole	25 mg	12	3	35
		50 mg	19	4	
		100 mg	16	4	
40	2-Ethylsulphonyl-5-propylsulphonyl-1,3,4-thiadiazole	25 mg	17	3	40
		50 mg	19	4	
		100 mg	20	4	
45	2-Ethylsulphonyl-5-butylsulphonyl-1,3,4-thiadiazole	25 mg	11	2	45
		50 mg	18	4	
		100 mg	16	4	
50	2-Hexylsulphonyl-5-isopropylsulphonyl-1,3,4-thiadiazole	25 mg	6	2	50
		50 mg	14	4	
		100 mg	16	4	
55	2-Isopropylsulphonyl-5-propylsulphonyl-1,3,4-thiadiazole	25 mg	11	2	55
		50 mg	11	3	
		100 mg	17	4	
60	2-Methylsulphonyl-5-propylsulphonyl-1,3,4-thiadiazole	25 mg	3	1	60
		50 mg	14	3	
		100 mg	18	4	
60	2-Ethylsulphonyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	25 mg	5	1	60
		50 mg	13	2	
		100 mg	16	4	

	Compounds according to the invention	Active substance concentration in mg/l of earth	Number of sound peas	Root evaluation (1-4)	
5	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	25 mg 50 mg 100 mg	4 7 16	2 3 4	5
	<i>Agents for comparison</i>				
10	3-Trichloromethyl-5-ethoxy-1,2,4-thiadiazole	25 mg 50 mg 100 mg	0 0 0	1 1 1	10
15	Manganese ethylene-1,2-bis-dithio-carbamate	25 mg 50 mg 100 mg	0 0 11	1 1 1	15
	<i>Control I (3 repetitions)</i>				
20	Infected soil without treatment	- - -	0 0 0	1 1 1	20
	<i>Control II (3 repetitions)</i>				
25	Steamed soil	- - -	18 19 18	4 4 4	25
30	<b>EXAMPLE 6</b>				30
	<i>Inhibition of fungal growth on nutrient solution</i>				
35	In a series of tests 20 ml amounts of a nutrient solution of grape juice and water (1 : 1) were introduced into 100 ml glass flasks and pulverulent active substance preparations were added thereto. The mixtures were then inoculated with conidia (spores) or sclerotia of the test fungi. After an incubation period of 6 days at 21 to 23°C, the development of fungus on the surface of the nutrient solution was assessed (1-5) as defined below).				35
	Test fungi: <i>Penicillium digitatum</i> , <i>Botrytis cinerea</i> , <i>Alternaria solani</i> , <i>Fusarium avenaceum</i> and <i>Corticium rolfsii</i> .				
40	<i>Evaluation:</i>				40
	0 = no fungal growth;				
	1 = isolated colonies of fungus on the surface;				
	2 = 5-10% of the surface covered by fungal fur;				
45	3 = 10-30% of the surface covered by fungal fur;				45
	4 = 30-60% of the surface covered by fungal fur;				
	5 = 60-100% of the surface covered by fungal fur.				
50	The active substances used, the active substances concentrations in the nutrient solution and the results are listed in the following Table.				50

## Inhibition of fungal growth on nutrient solution

Compounds of the invention	Active substance concentration in the nutrient solution	<i>Penicillium digitatum</i>	<i>Botrytis cinerea</i>	<i>Alternaria solani</i>	<i>Fusarium avenaceum</i>	<i>Corticium rolfsii</i>
2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	0.002 % 0.004 %	0 0	1 0	0 0	0 0	1 0
2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	0.002 % 0.004 %	1 0	1 0	0 0	0 0	0 0
2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	0.002 % 0.004 %	1 0	1 0	0 0	0 0	1 0
2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	0.002 % 0.004 %	1 0	2 1	0 0	0 0	1 0
2-Ethylsulphinyl-5-sec-butylsulphonyl-1,3,4-thiadiazole	0.002 % 0.004 %	1 0	1 0	0 0	0 0	1 0
2-Isopropylsulphonyl-5-propylsulphonyl-1,3,4-thiadiazole	0.002 % 0.004 %	1 0	1 0	0 0	0 0	1 1
2-Methylsulphonyl-5-propylsulphonyl-1,3,4-thiadiazole	0.002 % 0.004 %	1 0	1 0	0 0	0 0	1 1

Compounds of the invention	Active substance concentration in the nutrient solution	<i>Penicillium digitatum</i>	<i>Botrytis cinerea</i>	<i>Alternaria solani</i>	<i>Fusarium avenaceum</i>	<i>Corticium rolfsii</i>
<i>Comparison preparations</i>						
Methyl-1-(butylcarbamoyl)-2-benzimidazole carbamate	0.002 % 0.004 %	5 5	0 0	5 5	0 0	5 5
3-(3,5-Dichlorophenyl)-5-methyl-5-vinyl-1,3-oxazolidine-2,4-dione	0.002 % 0.004 %	3 3	0 0	4 4	5 5	5 5
<i>Control</i>	-	5	5	5	5	5

## EXAMPLE 7

*Limiting concentration test in the control of Rhizoctonia solani*

In a series of tests 20% strength pulverulent active substance preparations were uniformly mixed with soil severely infected with *Rhizoctonia solani*. 1.0 Litre earth-holding clay dishes were filled with the treated soil and, without a waiting period, 25 marrowfat pea seeds (*Pisum sativum* L. convar. *medullare* Alef.) of the variety "Wunder von Kelvedon" (Wonder of Kelvedon) were sown in each dish. After a cultivation period of 18 days at 20 to 24°C in a greenhouse, the number of sound peas was determined, and an evaluation (1-4 as defined below) of the roots was carried out.

The active substances used and their application quantities, and also the results, are listed in the following Table.

*Root evaluation:*

4 = white roots without fungal necrosis;

3 = white roots, slight fungal necrosis;

2 = brown roots, already more pronounced fungal necrosis;

1 = severe fungal necrosis, roots mouldy.

*Limiting concentration test in the control of Rhizoctonia solani*

Compounds of the invention	Active substance concentration in mg/l of earth	% of sound peas from the seed	Root evaluation (1-4)
2-(1-Ethylbutylsulphinyl)-5-butylsulphonyl-1,3,4-thiadiazole	50 mg 100 mg	96 % 100 %	3 4
2-(1-Methylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	50 mg 100 mg	84 % 100 %	3 4
2-(1-Ethylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole	50 mg 100 mg	80 % 100 %	3 4
2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	50 mg 100 mg	68 % 92 %	2 3
<i>Comparison preparations</i>			
Pentachloronitrobenzene	50 mg 100 mg	24 % 60 %	1 3
3-Trichloromethyl-5-ethoxy-1,2,4-thiadiazole	50 mg 100 mg	20 % 64 %	1 1
<i>Control I</i>			
Infected soil without treatment	-	8 %	1
<i>Control II</i>			
Steamed soil	-	100 %	4

## EXAMPLE 8

*Control of Pythium splendens in the scion propagation of Pelargonium peltatum by a watering treatment*

In a series of tests clay pots 6 cm in diameter were filled with the infected substrate (peat-sand mixture 1:1) and 30 ml of the active substance preparation under test having the given concentration were introduced into each pot. Scions of the variety "Luisenhof" were then put in the pots, 12 unrooted shoots per concentration. After a rooting time of 4 weeks in the propagation bed at a soil temperature of 23°C, evaluation was carried out.

The active substances used, the active substance concentrations and the results are listed in the following Table.

*Control of Pythium splendens in the scion propagation of Pelargonium peltatum by a watering treatment*

Compounds of the invention	Active substance concentrations	Plant loss from <i>Pythium splendens</i>	Average plant fresh weight
2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	0.0025 %	8 %	8.4 g
	0.005 %	8 %	9.1 g
	0.01 %	0 %	8.7 g
	0.02 %	0 %	8.9 g
2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	0.0025 %	0 %	10.5 g
	0.005 %	0 %	8.8 g
	0.01 %	0 %	9.4 g
	0.02 %	0 %	9.1 g
2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	0.0025 %	0 %	9.5 g
	0.005 %	0 %	8.8 g
	0.01 %	0 %	8.0 g
	0.02 %	0 %	7.3 g
<i>Control I</i>			
Infected substrate without treatment		92 %	7.5 g
<i>Control II</i>			
Steamed substrate		0 %	8.3 g



## EXAMPLE 9

*Effect of a prophylactic leaf treatment against Plasmopara viticola on vines in a greenhouse*

In a series of tests young vines having approximately 5 to 8 leaves were sprayed until dripping wet with the active substance concentration given in the Table below, and after the spray coating had dried the undersides of the leaves were sprayed with an aqueous suspension of the sporangia of the fungus indicated in the heading above (approximately 20,000 per ml); the vines were then immediately incubated in a greenhouse at 22 to 24°C in an atmosphere as saturated with water vapour as possible. From the second day onwards the air humidity was reduced to the normal level for 3 to 4 days (30 to 70% saturation) and then water vapour saturation was maintained for a further day. The percentage proportion of the surface of each leaf attacked by fungus was then noted and the average per treatment was calculated as follows to determine the fungicidal effect:

$$100 - \frac{100 \cdot \text{attack in treated vines}}{\text{attack in untreated vines}} = \% \text{ effect}$$

The results are listed in the following Table. The compounds of the present invention being tested were formulated as 20% strength sprayable powders.

20	Compounds according to the invention	% Effect after treatment with 0.025% of active substance	20
25	2-Isopropylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	99	25
30	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	91	30
35	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	91	35
40	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	100	40
45	2-Butylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	99	45
50	2-Isobutylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	100	50
55	2-Hexylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	98	55
60	2-Isopropylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	90	60
65	2-Ethylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	99	65
	2-(1-Ethylbutylsulphinyl)-5-ethylsulphonyl-1,3,4-thiadiazole	100	
	2-(1-Methylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	94	
	2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	100	
	2-Butylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	100	
	2-(1-Methylbutylsulphinyl)-5-pentylsulphonyl-1,3,4-thiadiazole	100	

	Compounds according to the invention	% Effect after treatment with 0.025% of active substance	
5	2-(1-Methylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole	99	5
10	2-(1-Methylbutylsulphinyl)-5-methylsulphonyl-1,3,4-thiadiazole	100	10
	2-(1-Ethylbutylsulphinyl)-5-butylsulphonyl-1,3,4-thiadiazole	100	
15	2-(1-Ethylbutylsulphinyl)-5-pentylsulphonyl-1,3,4-thiadiazole	100	15
	2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	100	
20	2-(1-Ethylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole	100	20
	2-(1-Ethylbutylsulphinyl)-5-methylsulphonyl-1,3,4-thiadiazole	90	
25	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	89	25
	2-Methylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	97	
30	2-Methylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	98	30
	2-Isopropylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	98	
35	2-Ethylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	80	35
	2-Ethylsulphonyl-5-butylsulphinyl-1,3,4-thiadiazole	80	
40	2-Ethylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	100	40
	2-Ethylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole	99	
45	2-Isopropylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	99	45
	2-Butylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	100	
50	2-Butylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	99	50
	2-Butylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	100	
55	2-Butylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole	100	55
	2-Butylsulphonyl-5-butylsulphonyl-1,3,4-thiadiazole	100	
60	2-Butylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole	100	60

	Compounds according to the invention	% Effect after treatment with 0.025% of active substance	
5	2-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	80	5
10	2-tert.-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	80	10
	2-Isobutylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	80	
15	2-Butylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	80	15
	2-Butylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole	80	
20	2-Hexylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	80	20
	2-Methylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	80	
25	2-sec.-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	80	25
	2-Isopentylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	80	
30			30

## EXAMPLE 10

*Effect of a prophylactic leaf treatment against Botrytis cinerea on tomato plants*

35	In a series of tests young tomato plants were sprayed until dripping wet with the active substance concentration given in the Table below. After the spray coating had dried, the treated plants and also untreated plants were inoculated by spraying them with a suspension of spores (approximately 1 million per ml of fruit juice solution) of the fungal pathogen of grey mould, <i>Botrytis cinerea</i> , and incubated while damp in a greenhouse at approximately 20°C. After the collapse of the untreated plants (= 100% attack) the degree of attack in the treated plants was ascertained and the fungicidal effect given in the following Table was calculated as follows:	35
40		40

45	$100 - \frac{100 \cdot \text{attack in treated plants}}{\text{attack in untreated plants}} = \% \text{ effect}$	45
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The compounds of the present invention being tested were formulated as 20% strength sprayable powders.

	Compounds according to the invention	% Effect after treatment with 0.025% of active substance	
50			50
55	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	100	55
	2-Isobutylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	80	
60			60

## EXAMPLE 11

*Effect of a prophylactic leaf treatment against Piricularia oryzae on rice seedlings in a greenhouse*

65	In a series of tests young rice plants were sprayed until dripping wet with the active substance concentration given in the Table below. After the spray coating had dried the treated plants and also untreated control plants were inoculated by spraying them with a suspension of spores (approximately	65
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200,000 per ml) of the fungal pathogen of leaf spot, *Piricularia oryzae*, and incubated while damp in a greenhouse at 25 to 27°C.

After 5 days the percentage of the leaf surface that had been attacked was ascertained. From these attack figures, the fungicidal effect given in the following Table was calculated as follows:

5

$$100 - \frac{100 \cdot \text{attack in treated plants}}{\text{attack in untreated plants}} = \% \text{ effect}$$

5

10 The compounds being tested were formulated as 20% strength sprayable powders.

10

	Compounds according to the invention	% Effect with 0.1% of active substance	
15	2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	93	15
20	2-Isopropylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	90	20
	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	90	
25	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	100	25
	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	83	
30	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	100	30
	2-Ethylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	92	
35	2-Isopropylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	96	35
	2-Butylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	100	
40	2-Isobutylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	98	40
	2-Isopropylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	90	
45	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	60	45
	2-Methylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	80	
50	2-Ethylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	92	50
	2-Ethylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	100	
55	2-Ethylsulphonyl-5-butylsulphinyl-1,3,4-thiadiazole	100	55
	2-Ethylsulphonyl-5-butylsulphinyl-1,3,4-thiadiazole	100	
60	2-Propylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	89	60
65			65

	Compounds according to the invention	% Effect with 0.1% of active substance	
5	2-tert.-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	90	5
10	2-Isobutylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	90	10
10	EXAMPLE 12		
	<i>Seed treatment against Helminthosporium gramineum in barley</i>		
15	In a series of tests barley seed grains naturally attacked by <i>Helminthosporium gramineum</i> were, either untreated or after treatment with the active substances indicated in the Table below, sown in plastic pots filled with earth and left to germinate at temperatures below +16°C. After emergence the seedlings were exposed to artificial light for 12 hours each day. After approximately 5 weeks all of the plants that had emerged as well as those attacked by fungi were counted per test unit. From these figures the fungicidal effect given in the following Table was calculated as follows:		15
20	$100 - \frac{100 \cdot \text{attack in treated samples}}{\text{attack in untreated samples}} = \% \text{ effect}$		20

The compounds being tested were in the form of 20% strength formulations.

	Compounds according to the invention	% Effect with g of active substance: 100 kg of seed grains		
		50g	20g	
5	2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	99	98	5
10	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	100	100	10
15	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	100	100	15
20	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	100	99	20
25	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	100	99	25
30	2-Methylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	85	49	30
35	2-Ethylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	98	87	35
40	2-(1-Ethylbutylsulphinyl)-5-ethylsulphonyl-1,3,4-thiadiazole	100	92	40
45	2-(1-Methylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	92	89	45
	2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	97	77	
	2-Butylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	90	64	
	2-(1-Methylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole	93	92	
	2-(1-Methylbutylsulphinyl)-5-methylsulphonyl-1,3,4-thiadiazole	99	100	
	2-(1-Ethylbutylsulphiny)-5-methylsulphonyl-1,3,4-thiadiazole	97	79	

	Compounds according to the invention	% Effect with g of active substance 100 kg of seed grains		
		50g	20g	
5				5
	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	100	-	
10	2-Methylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	100	-	10
	2-Methylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	100	-	
15	2-Isopropylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	100	-	15
	2-Ethylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	100	-	
20	2-Ethylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	100	-	20
	2-Ethylsulphonyl-5-butylsulphinyl-1,3,4-thiadiazole	100	-	
25	2-Ethylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	94	-	25
	2-Ethylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole	82	-	
30	2-Ethylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole	100	-	30
	2-Ethylsulphonyl-5-sec.-butylsulphinyl-1,3,4-thiadiazole	100	-	
35	2-Butylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	100	-	35
	2-Propylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	100	-	
40	2-Isopropylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	92	-	40
	2-Ethylsulphonyl-5-tert.-butylsulphinyl-1,3,4-thiadiazole	100	-	
45				45
50				50

	Compounds according to the invention	% Effect with g of active substance/100 kg of seed grains		
		50g	20g	
5				5
	2-Butylsulphonyl-5-propylsulphanyl-1,3,4-thiadiazole	100	-	
10	2-Butylsulphonyl-5-isopropylsulphanyl-1,3,4-thiadiazole	85	-	10
	2-Butylsulphonyl-5-butylsulphanyl-1,3,4-thiadiazole	69	-	
15	2-Butylsulphonyl-5-isobutylsulphanyl-1,3,4-thiadiazole	85	-	15
	2-Butylsulphonyl-5-methylsulphanyl-1,3,4-thiadiazole	69	-	
20	2-tert.-Butylsulphonyl-5-methylsulphanyl-1,3,4-thiadiazole	100	-	20
	2-Isobutylsulphonyl-5-methylsulphanyl-1,3,4-thiadiazole	69	-	
25	2-Butylsulphonyl-5-pentylsulphanyl-1,3,4-thiadiazole	100	-	25
	2-Hexylsulphonyl-5-methylsulphanyl-1,3,4-thiadiazole	100	-	
30	2-Methylsulphonyl-5-pentylsulphanyl-1,3,4-thiadiazole	100	-	30
	2-sec.-Butylsulphonyl-5-methylsulphanyl-1,3,4-thiadiazole	100	-	
35	2-Isopentylsulphonyl-5-methylsulphanyl-1,3,4-thiadiazole	100	-	35
	<i>Agent for comparison</i>	5.2g	2.6g	
45	Methoxyethyl mercury silicate	95	79	45

## EXAMPLE 13

*Seed treatment against Tilletia caries in wheat*

In a series of tests wheat seed grains were contaminated with 3g of spores of the fungal pathogen of bunt, *Tilletia caries*, per kg of seed grains. These grains either untreated or treated as indicated in the Table below were pressed with their bearded end into a substrate of moist loam contained in petri dishes, and incubated for three days at temperatures below +12°C. The grains were then removed and the petri dishes with the bunt spores remaining behind were further incubated at approximately 12°C. After 10 days the spores were examined for germination. The fungicidal effect given in the following Table was calculated as follows:

$$100 - \frac{100 \cdot \text{percentage germination in treated grains}}{\text{percentage germination in untreated grains}} = \% \text{ effect}$$

The compounds being tested were in the form of 20% strength formulations.



	Compounds according to the invention	% Effect with 20 g of active substance per 100 kg of seed grains	
5	2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	100	5
	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	97	
10	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	100	10
	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	100	15
15	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	100	
20	2-Methylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	96	20
	2-Butylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	100	25
25	2-Isobutylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	70	
	2-Hexylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	90	30
30	2-Isopropylsulphonyl-5-methylsulphonyl-1,3,4-thiadiazole	70	
35	2-Ethylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	97	35
	2-(1-Ethylbutylsulphinyl)-5-ethylsulphonyl-1,3,4-thiadiazole	100	40
40	2-(1-Methylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	96	
	2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole	96	45
45	2-Butylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole	99	
50	2-(1-Methylbutylsulphinyl)-5-pentylsulphonyl-1,3,4-thiadiazole	99	50

	Compounds according to the invention	% Effect with 20 g of active substance per 100 kg of seed grains	
5	2-(1-Methylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole	100	5
10	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	100	10
	2-Methylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	100	
15	2-Methylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	100	15
	2-Isopropylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	97	
20	2-Ethylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	99	20
	2-Ethylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	99	
25	2-Ethylsulphonyl-5-butylsulphinyl-1,3,4-thiadiazole	99	25
	2-Ethylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole	98	
	2-Ethylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole	97	
30	2-Ethylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole	100	30
	2-Ethylsulphonyl-5-sec.-butylsulphinyl-1,3,4-thiadiazole	99	
35	2-Butylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole	100	35
	2-Propylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	98	
40	2-Ethylsulphonyl-5-tert.-butylsulphinyl-1,3,4-thiadiazole	100	40
	2-Butylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	100	
45	2-Propylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole	98	45
	2-Ethylsulphonyl-5-tert.-butylsulphinyl-1,3,4-thiadiazole	100	
50	2-Butylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole	100	50

	Compounds according to the invention	% Effect with 20 g of active substance per 100 kg of seed grains	
5	2-Butylsulphonyl-5-isopropylsulphanyl-1,3,4-thiadiazole	100	5
10	2-Butylsulphanyl-5-butylsulphonyl-1,3,4-thiadiazole	100	10
	2-Butylsulphonyl-5-isobutylsulphanyl-1,3,4-thiadiazole	100	
15	2-Butylsulphonyl-5-pentylsulphanyl-1,3,4-thiadiazole	100	15
	2-Butylsulphonyl-5-hexylsulphanyl-1,3,4-thiadiazole	100	
20	Compounds according to the invention	% Effect with 50 g of active substance per 100 kg of seed grains	20
25	2-Butylsulphanyl-5-methylsulphonyl-1,3,4-thiadiazole	100	25
	2-tert.-Butylsulphanyl-5-methylsulphonyl-1,3,4-thiadiazole	100	
30	2-Isobutylsulphanyl-5-methylsulphonyl-1,3,4-thiadiazole	100	30
35	2-Hexylsulphanyl-5-methylsulphonyl-1,3,4-thiadiazole	100	35
	2-Methylsulphonyl-5-pentylsulphanyl-1,3,4-thiadiazole	100	
40	2-sec.-Butylsulphanyl-5-methylsulphonyl-1,3,4-thiadiazole	100	40
	2-Isopentylsulphanyl-5-methylsulphonyl-1,3,4-thiadiazole	100	
45	<i>Agent for comparison</i>		45
	Methoxyethyl mercury silicate (2.6g 100 kg of seed grains)	99	
50	EXAMPLE 14		50
	<i>Effect of seed treatment against Septoria nodorum in wheat</i>		
	In a series of tests wheat seed grains naturally attacked by <i>Septoria nodorum</i> (the fungal pathogen of beard brownness), either untreated or after treatment with the active substances indicated in the Table below, were sown out on a moist substrate for germination and incubated in a climatic chamber at		
55	approximately 6°C. After 4 weeks, the proportion of diseased seedlings was determined and from this the fungicidal effect given in the following Table was calculated in accordance with the following formula:		55
60	$100 - \frac{100 \cdot \text{attack in treated grains}}{\text{attack in untreated grains}} = \% \text{ effect}$		60

The compounds being tested were in the form of 20% strength formulations.

	Compounds according to the invention	% Effect with of active substance per 100 kg of seed grains			
		50	20	10 g	
5	2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	94			5
10	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	99	92	72	10
	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	99	94	91	
15	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	99	95	86	15
	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	99	91	72	
20	2-Methylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	97	81	76	20
25	<i>Agent for comparison</i> active substance/100 kg of seed grains	5.2	2.6	1.3 g	25
	Methoxyethyl mercury silicate	99	96	84	
30					30

## EXAMPLE 15

*Seed treatment against Fusarium nivale in rye*

In a series of tests rye seed grains naturally attacked by *Fusarium nivale* (the fungal pathogen of snow mould), either untreated or after treatment with the active substances indicated in the Table below, were sown in plant pots filled with earth and left to germinate at approximately 6°C. After emergence, the seedlings were exposed to 12 hours of artificial light per day. After approximately 4 weeks the percentage attack by fungi was ascertained. The fungicidal effect given in the following Table was calculated as follows:

$$100 - \frac{100 \cdot \text{attack in treated grains}}{\text{attack in untreated grains}} = \% \text{ effect}$$

The compounds being tested were in the form of 20% strength formulations.

	Compounds according to the invention	% Effect with 100 g of active substance/100 kg of seed grains	
45			45
50	2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole	88	50
	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	100	
55	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	100	55
	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	100	
60	2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole	86	60
	2-Methylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	78	
65			65

	<i>Agent for Comparison</i>	active substance			
		10.4	5.2	2.6 g	
		per 100 kg of seed grains			
5	Methoxyethyl mercury silicate	96	86	42	5

## EXAMPLE 16

*Limiting concentration test in the control of Pythium ultimum*

- In a series of tests 20% strength pulverulent active substance preparations were uniformly mixed with soil severely infected with *Pythium ultimum*. 0.5 Litre earth-holding clay dishes were filled with the treated soil and, without a waiting period, 20 marrowfat pea seeds (*Pisum sativum L. convar. medullare Alef.*) of the variety "Wunder von Kelvedon" (Wonder of Kelvedon) were sown in each dish. After a cultivation period of 3 weeks at 20 to 24°C in a greenhouse, the number of sound peas was determined, and an evaluation (1-4 as defined below) of the roots was carried out.
- The active substances used and their application quantities, and also the results, are listed in the following Table.

*Root evaluation:*

- 4 = white roots without fungal necrosis;  
 3 = white roots, slight fungal necrosis;  
 2 = brown roots, already more pronounced fungal necrosis;  
 1 = severe fungal necrosis, roots mouldy.

*Limiting concentration test in the control of Pythium ultimum*

	Compounds according to the invention	Active substance concentration in mg/l of earth	Number of sound peas	Root evaluation (1-4)	
30	2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	17 18 19	4 4 4	30
35	2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	18 19 19	4 4 4	35
40	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	20 mg 40 mg 80 mg	17 18 17	4 4 4	40
<i>Agents for Comparison</i>					
45	2,5-Bis-(methane-1-sulphonyl)-1,3,4-thiadiazole	20 mg 40 mg 80 mg	9 8 10	1 1 2	45
50	2-(Ethane-1-sulphonyl)-5-(methane-1-sulphonyl)-1,3,4-thiadiazole	20 mg 40 mg 80 mg	7 7 9	1 1 1	50
<i>Control I (3 repetitions)</i>					
55	Infected soil without treatment	- - -	0 1 0	1 1 1	55
<i>Control II (3 repetitions)</i>					
60	Steamed soil	- - -	18 20 19	4 4 4	60

## EXAMPLE 17

*Limiting concentration test in the control of Fusarium avenaceum*

In a series of tests 20% strength pulverulent active substance preparations were uniformly mixed with soil severely infected with *Fusarium avenaceum*. 0.5 Litre earth-holding clay dishes were filled with the treated soil and, without a waiting period, 20 marrowfat pea seeds (*Pisum sativum L. convar. medullare Alef.*) of the variety "Wunder von Kelvedon" (Wonder of Kelvedon) were sown in each dish. After a cultivation period of 18 days at 20 to 24°C in a greenhouse, the number of sound peas was determined, and an evaluation (1-4 as defined below) of the roots was carried out.

The active substances used and their application quantities, and also the results, are listed in the following Table.

*Root evaluation:*

- 4 = white roots without fungal necrosis;
- 3 = white roots, slight fungal necrosis;
- 2 = brown roots, already more pronounced fungal necrosis;
- 1 = severe fungal necrosis; roots mouldy.

*Limiting concentration test in the control of Fusarium avenaceum*

20	Compounds according to the invention	Active substance concentration in mg/l of earth	Number of sound peas	Root evaluation (1-4)	20
25	2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole	25 mg	17	3	25
		50 mg	19	4	
		100 mg	20	4	
30	2-Ethylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole	25 mg	14	4	30
		50 mg	18	4	
		100 mg	18	4	
<i>Agents for comparison</i>					
35	2,5-Bis-(methane-1-sulphonyl)-1,3,4-thiadiazole	25 mg	0	1	35
		50 mg	0	1	
		100 mg	0	1	
40	2-(Ethane-1-sulphonyl)-5-(methane-1-sulphonyl)-1,3,4-thiadiazole	25 mg	0	1	40
		50 mg	2	1	
		100 mg	10	3	
<i>Control I (3 repetitions)</i>					
45	Infected soil without treatment	-	0	1	45
		-	0	1	
		-	0	1	
<i>Control II (3 repetitions)</i>					
50	Steamed soil	-	18	4	50
		-	19	4	
		-	18	4	

## EXAMPLE 18

*Seed treatment against Ustilago avenae in oats in a greenhouse*

In a series of tests oat seed grains were immersed in a suspension of spores of the oat loose smut *Ustilago avenae*, and repeatedly subjected to pressure change in a vacuum exsiccator for the purpose of artificial  
 5 contamination. After the seed grains had dried in the air, they were treated with active substances as indicated in the Table below. Then, approximately 300 seeds per test unit were sown in plant pots filled with earth, which were placed in a greenhouse at temperatures varying between 20 and 25°C. After 2½ months healthy and blighted panicles were counted and the fungicidal effect given in the following Table was calculated as follows:

10 10,

$$100 - \frac{100 \cdot \text{proportion of attacked panicles in treated grains}}{\text{proportion of attacked panicles in untreated grains}} = \% \text{ effect}$$

15 15

	% Effect after treatment with 100 g of active sub- stance per 100 kg of seed grains
Compounds according to the invention	

2-Ethylsulphinyl-5-methyl- sulphonyl-1,3,4-thiadiazole	49	20
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2-Ethylsulphinyl-5-ethyl- sulphonyl-1,3,4-thiadiazole	96	25
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25 *Agents for comparison* 25

2,5-Bis-(methane-1- sulphonyl)-1,3,4-thiadiazole	0	30
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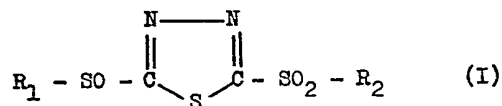
2-(Ethane-1-sulphonyl)-5- (methane-1-sulphonyl)-1,3,4- thiadiazole	0	30
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35 35

## CLAIMS

1. A 2-sulphinyl-5-sulphonyl-1,3,4-thiadiazole derivative of the general formula I

40 40



45 in which R<sub>1</sub> and R<sub>2</sub> each represents a C<sub>1</sub>-C<sub>6</sub>-alkyl, C<sub>2</sub>-C<sub>6</sub>-alkenyl, C<sub>2</sub>-C<sub>6</sub>-alkynyl or C<sub>3</sub>-C<sub>6</sub>-cycloalkyl group. 45

2. A compound as claimed in claim 1, wherein R<sub>1</sub> and R<sub>2</sub> each represents a methyl, ethyl, propyl, isopropyl, cyclopropyl, prop-2-enyl, prop-2-ynyl, *n*-butyl, isobutyl, sec.-butyl, *n*-pentyl, sec.-pentyl, isopentyl, *n*-hexyl, sec.-hexyl or isohexyl group.

50 3. 2-Ethylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole. 50

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

5. 2-Ethylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole.

6. 2-Ethylsulphinyl-5-ethylsulphonyl-1,3,4-thiadiazole.

7. 2-Ethylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole.

8. 2-Ethylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole.

55 9. 2-Ethylsulphinyl-5-sec.-butylsulphonyl-1,3,4-thiadiazole. 55

10. 2-Methylsulphinyl-5-propylsulphonyl-1,3,4-thiadiazole.

11. 2-Isopropylsulphonyl-5-propylsulphonyl-1,3,4-thiadiazole.

12. 2-Butylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole.

13. 2-Isobutylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole.

60 14. 2-Hexylsulphinyl-5-isopropylsulphonyl-1,3,4-thiadiazole. 60

15. 2-Isopropylsulphonyl-5-methylsulphonyl-1,3,4-thiadiazole.

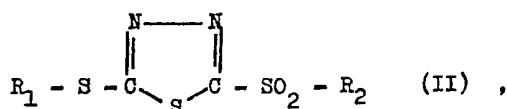
16. 2-Ethylsulphonyl-5-isopropylsulphonyl-1,3,4-thiadiazole.

17. 2-Ethylsulphonyl-5-(1-methylbutylsulphonyl)-1,3,4-thiadiazole.

18. 2-(1-Ethylbutylsulphonyl)-5-ethylsulphonyl-1,3,4-thiadiazole.

65 19. 2-(1-Methylbutylsulphonyl)-5-propylsulphonyl-1,3,4-thiadiazole. 65

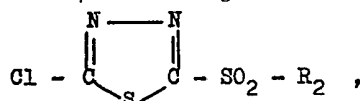
20. 2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole.  
 21. 2-Butylsulphonyl-5-(1-methylbutylsulphinyl)-1,3,4-thiadiazole.  
 22. 2-(1-Methylbutylsulphinyl)-5-pentylsulphonyl-1,3,4-thiadiazole.  
 23. 2-(1-Methylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole.  
 5 24. 2-(1-Methylbutylsulphinyl)-5-methylsulphonyl-1,3,4-thiadiazole. 5  
 25. 2-(1-Ethylbutylsulphinyl)-5-butylsulphonyl-1,3,4-thiadiazole.  
 26. 2-(1-Ethylbutylsulphinyl)-5-pentylsulphonyl-1,3,4-thiadiazole.  
 27. 2-(1-Ethylbutylsulphinyl)-5-propylsulphonyl-1,3,4-thiadiazole.  
 28. 2-(1-Ethylbutylsulphinyl)-5-(2-methylpropylsulphonyl)-1,3,4-thiadiazole.  
 10 29. 2-(1-Ethylbutylsulphinyl)-5-methylsulphonyl-1,3,4-thiadiazole. 10  
 30. 2-Methylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole.  
 31. 2-Methylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole.  
 32. 2-Isopropylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole.  
 33. 2-Ethylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole.  
 15 34. 2-Ethylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole. 15  
 35. 2-Ethylsulphonyl-5-butylsulphinyl-1,3,4-thiadiazole.  
 36. 2-Ethylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole.  
 37. 2-Ethylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole.  
 38. 2-Ethylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole.  
 20 39. 2-Ethylsulphonyl-5-sec.-butylsulphinyl-1,3,4-thiadiazole. 20  
 40. 2-Butylsulphonyl-5-methylsulphinyl-1,3,4-thiadiazole.  
 41. 2-sec.-Butylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole.  
 42. 2-sec.-Butylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole.  
 43. 2-Ethylsulphonyl-5-tert.-butylsulphinyl-1,3,4-thiadiazole.  
 25 44. 2-Butylsulphonyl-5-propylsulphinyl-1,3,4-thiadiazole. 25  
 45. 2-Butylsulphonyl-5-isopropylsulphinyl-1,3,4-thiadiazole.  
 46. 2-Butylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole.  
 47. 2-Butylsulphonyl-5-isobutylsulphinyl-1,3,4-thiadiazole.  
 48. 2-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole.  
 30 49. 2-tert.-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole. 30  
 50. 2-Isobutylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole.  
 51. 2-tert.-Butylsulphinyl-5-butylsulphonyl-1,3,4-thiadiazole.  
 52. 2-Butylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole.  
 53. 2-Butylsulphonyl-5-hexylsulphinyl-1,3,4-thiadiazole.  
 35 54. 2-Hexylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole. 35  
 55. 2-Methylsulphonyl-5-pentylsulphinyl-1,3,4-thiadiazole.  
 56. 2-sec.-Butylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole.  
 57. 2-Isopentylsulphinyl-5-methylsulphonyl-1,3,4-thiadiazole.  
 58. A process for the manufacture of a 1,3,4-thiadiazole derivative of the general formula I given in claim  
 40 1, in which R<sub>1</sub> and R<sub>2</sub> have the meanings given in claim 1, wherein a compound of the general formula II 40



- 45 in which R<sub>1</sub> and R<sub>2</sub> have the meanings given above, is treated in an inert solvent with an oxidizing agent.  
 59. A process as claimed in claim 58, wherein the oxidizing agent is an organic hydroperoxide, a peracid  
 or an inorganic oxidizing agent.  
 50 60. A process as claimed in claim 58 or 59, wherein the oxidizing agent is used in an equimolar amount. 50  
 61. A process as claimed in any one of claims 58 to 60, wherein the compound of the general formula II  
 has been prepared by the reaction of a compound of the general formula



- 55 in which R<sub>1</sub> has the meaning given in claim 1, either in the free form in the presence of an organic base or in  
 the form of an alkali salt thereof with a compound of the general formula



- 60 in which R<sub>2</sub> has the meaning given in claim 1.  
 62. A process as claimed in claim 61, wherein the preparation of the compound of the general formula II  
 has been carried out substantially as described in Example 3 herein.  
 65 63. A process as claimed in claim 58, conducted substantially as described herein. 65



64. A process as claimed in claim 58, conducted substantially as described in Example 1 or 2 herein.
65. A fungicidal preparation which comprises a compound of the general formula I given in claim 1, in which  $R_1$  and  $R_2$  have the meanings given in claim 1, the admixture or conjunction with a suitable carrier.
66. A fungicidal preparation which comprises a compound as claimed in claim 2, in admixture or conjunction with a suitable carrier. 5
67. A fungicidal preparation which comprises the compound claimed in any one of claims 3 to 29, in admixture or conjunction with a suitable carrier.
68. A fungicidal preparation which comprises the compound claimed in any one of claims 30 to 57, in admixture or conjunction with a suitable carrier.
- 10 69. A preparation as claimed in any one of claims 65 to 68, which is in the form of a powder, a strewable preparation, granules, a solution, an emulsion or a suspension. 10
70. A preparation as claimed in any one of claims 65 to 69, containing a single compound of the general formula I.
71. A preparation as claimed in any one of claims 65 to 69, containing two or more compounds of the general formula I. 15
72. A preparation as claimed in any one of claims 65 to 71, which also contains one or more active substances selected from fungicides, nematocides, insecticides and other pesticides other than compounds of the general formula I.
73. A preparation as claimed in any one of claims 65 to 72, wherein the total amount present of active substance or substances is 1 to 95% by weight. 20
74. A preparation as claimed in claim 73, wherein the total amount present of active substance or substances is 20 to 50% by weight.
75. A preparation as claimed in any one of claims 65 to 74, containing a single surface-active agent in an amount of up to 20% by weight.
- 25 76. A preparation as claimed in any one of claims 65 to 74, containing two or more surface-active agents in a total amount of up to 20% by weight. 25
77. A preparation as claimed in any one of claims 65 to 76, which also contains colouring matter.
78. Any one of the fungicidal preparations as claimed in claim 65 and substantially as described in Examples 4 to 8, 10 and 14 to 17 herein.
- 30 79. Any one of the fungicidal preparations as claimed in claim 65 and substantially as described in Examples 9, 11, 12 and 13 herein. 30
80. A method of protecting a living plant against phytopathogenic fungi, wherein the living plant and/or the area in the vicinity of the living plant is/are treated with a compound of the general formula I given in claim 1, in which  $R_1$  and  $R_2$  have the meanings given in claim 1.
- 35 81. A method as claimed in claim 80, wherein the treatment is carried out with a compound as claimed in claim 2. 35
82. A method as claimed in claim 80, wherein the treatment is carried out with the compound claimed in any one of claims 3 to 29.
83. A method as claimed in claim 80, wherein the treatment is carried out with the compound claimed in any one of claims 30 to 57. 40
84. A method as claimed in claim 80, wherein the treatment is carried out with a fungicidal preparation as claimed in any one of claims 65 to 76, 87 and 79.
85. A method as claimed in claim 80, conducted substantially as described in Example 9 or 11 herein.
86. A method as claimed in claim 80, conducted substantially as described in Example 10 herein.
- 45 87. A method of protecting a crop area against phytopathogenic fungi, wherein the crop area is treated with a compound of the general formula I given in claim 1, in which  $R_1$  and  $R_2$  have the meanings given in claim 1. 45
88. A method as claimed in claim 87, wherein the crop area is treated with a compound as claimed in claim 2.
- 50 89. A method as claimed in claim 87, wherein the crop area is treated with the compound claimed in any one of claims 3 to 29. 50
90. A method as claimed in claim 87, wherein the crop area is treated with the compound claimed in any one of claims 30 to 57.
91. A method as claimed in claim 87, wherein the crop area is treated with a fungicidal preparation as claimed in any one of claims 65 to 76, 78 and 79. 55
92. A method as claimed in any one of claims 87 to 91, wherein the crop is a cereal crop.
93. A method as claimed in claim 92, wherein the cereal crop is a barley, oat, rye or wheat crop.
94. A method as claimed in claim 87, conducted substantially as described in any one of Examples 4, 5, 7, 8, 16 and 17 herein.
- 60 95. A method of dressing seeds, wherein the seeds are treated with a compound of the general formula I given in claim 1, in which  $R_1$  and  $R_2$  have the meanings given in claim 1. 60
96. A method as claimed in claim 95, wherein the seeds are treated with a compound as claimed in claim 2.
97. A method as claimed in claim 95, wherein the seeds are treated with the compound claimed in any one of claims 3 to 29. 65

98. A method as claimed in claim 95, wherein the seeds are treated with the compound claimed in any one of claims 30 to 57.
99. A method as claimed in claim 95, wherein the seeds are treated with a fungicidal preparation as claimed in any one of claims 65 to 79.
- 5 100. A method as claimed in claim 95, conducted substantially as described in Example 12 or 13 herein. 5
101. A method as claimed in claim 95, conducted substantially as described in any one of Examples 14, 15 and 18 herein.
102. A pack which comprises a compound of the general formula I given in claim 1, in which  $R_1$  and  $R_2$  have the meanings given in claim 1, together with instructions for its use for controlling phytopathogenic  
10 fungi. 10
103. A pack as claimed in claim 102, wherein the compound of the general formula I is a compound as claimed in claim 2.
104. A pack as claimed in claim 102, wherein the compound of the general formula I is the compound claimed in any one of claims 3 to 29.
- 15 105. A pack as claimed in claim 102, wherein the compound of the general formula I is the compound  
claimed in any one of claims 30 to 57. 15