

PATENT SPECIFICATION

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(54) FUNGICIDALLY ACTIVE CYCLOPROPANECARBOXYLIC ACID ANILIDES AND THEIR MANUFACTURE AND USE

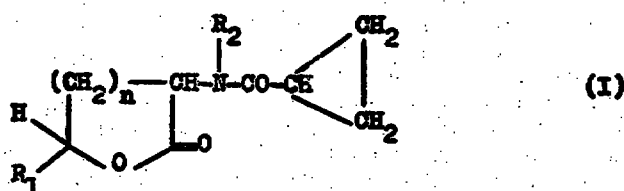
(71) We, SCHERING AKTIENGESellschaft, a Body Corporate organised according to the laws of the Federal Republic of Germany, of Berlin and Bergkamen, the Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to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

The present invention is concerned with new fungicidally active cyclopropanecarboxylic acid anilides, with the use of these compounds for controlling phytopathogenic fungi and also with a process for the manufacture of the new active compounds.

Agents that act against phytopathogenic fungi have already been known. Agents of this kind known in practice are, for example, 5 - ethoxy - 3 - trichloromethyl - 1,2,4 - thiadiazole (United States Patent Specification Nos. 3,260,588 and 3,260,725) and tetramethylthiuram disulphide (German Patent Specification No. 642,532). These agents, however, do not always have a satisfactory action against phytopathogenic fungi.

The problem upon which the present invention is based has been to provide an agent having an outstanding action against phytopathogenic fungi. This problem is now solved in accordance with the present invention by the compounds of the general formula I, as defined below.

The present invention provides compounds of the general formula I



in which

R₁ represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms,

R₂ represents an unsubstituted aromatic hydrocarbon group or an aromatic hydrocarbon group substituted by one or more substituents selected from alkyl groups containing 1 to 4 carbon atoms, alkoxy groups containing 1 to 4 carbon atoms, alkylthio groups containing 1 to 4 carbon atoms, halogen atoms, trifluoromethyl groups, nitro groups, alkoxycarbonyl groups containing 1 to 4 carbon atoms in the alkoxy part, alkylcarbonyl groups containing 1 to 4 carbon atoms in the alkyl part and cyano groups, and

n represents 1 or 2.

When the substituted aromatic hydrocarbon group represented by R₂ contains two or more substituents these substituents may be the same or different.

It is to be understood herein that when the unsubstituted or substituted aromatic hydrocarbon group represented by R₂ contains more than one aromatic ring, these rings may be fused together in the ortho-positions or may be isolated as in, for example, biphenyl.

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The action of the compounds of the present invention against phytopathogenic fungi is surprisingly superior to that of known agents having the same direction of action and, moreover, these compounds are distinguished by a good plant tolerance and a sufficient duration of action. Since, in addition, they do not act phytotoxically when applied in the quantities that come into consideration in practice, they may accordingly be used advantageously in agriculture and in horticulture for controlling phytopathogenic fungi.

The compounds of the present invention have outstanding fungicidal properties against pathogenic fungi, for example false mildew fungi.

In contrast to known fungicidal agents having only a preventive action such as, for example, N-trichloromethyl thiophthalimide (United States Patent Specifications Nos. 2,553,770, 2,553,771 and 2,553,776) and manganese ethylene bisdithiocarbamate (United States Patent Specifications Nos. 2,504,404 and 2,710,822), the compounds of the present invention surprisingly also have the additional advantage of a curative and systemic action which, therefore, makes it possible also to control pathogenic agents that have already penetrated into the plants.

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 contain one or more compounds of the general formula I.

The present invention further provides a method of protecting a living plant against phytopathogenic fungi, wherein the living plant is treated with a compound of the general formula I.

The present invention further provides a method of protecting a crop area against phytopathogenic fungi, wherein the crop area is treated with a compound of the general formula I.

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.

The compounds of the present invention that are especially distinguished by an outstanding fungicidal action are those of the general formula I given above in which R₁ represents a hydrogen atom or a methyl or ethyl group and R₂ represents a phenyl, methylphenyl, dimethylphenyl, ethylphenyl, isopropylphenyl, methoxyphenyl, ethoxyphenyl, methylthiophenyl, fluorophenyl, chlorophenyl, bromophenyl, dichlorophenyl, trifluoromethylphenyl, nitrophenyl, cyanophenyl, methoxycarbonylphenyl, acetylphenyl or biphenyl group.

The new active compounds may be applied singly or, alternatively, mixtures of at least two constitutionally different compounds of the general formula I may be applied. If desired, other fungicides, nematocides, herbicides or other types of pest-controlling agents may be added, depending on the purpose.

The active substances are advantageously applied 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 wetting, adhesive, emulsifying and/or dispersing agents.

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

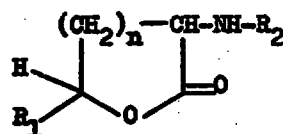
As surface-active agents there may be mentioned, for example, salts of ligninsulphonic acids, salts of alkylated benzenesulphonic acids, sulphonated acid amides and salts thereof, polyethoxylated amines and alcohols.

When the active substances are to be used for dressing seeds, they may also be admixed with dyestuffs in order to give the dressed seeds a clearly visible colour.

The proportion of active substance(s) in the fungicidal preparations may vary within wide limits, the exact concentration of the active substances used for the preparations being primarily dependent on the quantity in which the preparations *inter alia* are to be used for treating soil or seeds or for spraying leaves. The preparations may contain, for example, approximately 1 to 80% by weight, preferably between 20 and 50% by weight, of active compound(s), approximately 99 to 20% by weight of liquid or solid carrier and also, if desired, up to 20% by weight of surface-active agent(s).

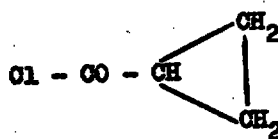
The new compounds of the general formula I may be produced by the process of the present invention, as defined below.

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



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in which R_1 , R_2 and n have the meanings given above, is reacted in the presence of an acid-binding agent and, if desired, a solvent with cyclopropanecarboxylic acid chloride of the formula III



(III)

The compound of the general formula II and the compound of the formula III are preferably used in equimolar proportions.

As acid-binding agents there may be used, for example, organic bases, for example pyridine, triethylamine or N,N-dimethylaniline, or inorganic bases, for example hydroxides, oxides and carbonates of alkali metals and alkaline earth metals, for example sodium, potassium or calcium.

As a solvent that may optionally be used, there may be mentioned, for example, ether, tetrahydrofuran, benzene or ethyl acetate. Liquid acid-binding agents, for example pyridine, may serve simultaneously as solvents.

The reaction is advantageously carried out at a temperature within the range of from -10°C to 120°C .

The products of the process of the present invention may be isolated in a manner known *per se*.

Some specific compounds of the present invention are listed in the following Table.

Compound No.	Name	Physical constant
1	Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 104°C
2	Cyclopropanecarboxylic acid [2,6-diethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: $102-103^\circ\text{C}$
3	Cyclopropanecarboxylic acid [2-methoxy-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: $175-176^\circ\text{C}$
4	Cyclopropanecarboxylic acid [2-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: $108-109^\circ\text{C}$
5	Cyclopropanecarboxylic acid [2,6-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: $114-116^\circ\text{C}$
6	Cyclopropanecarboxylic acid [2,5-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 84°C

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Compound No.	Name	Physical constant	
5	7 Cyclopropanecarboxylic acid [3-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 109°C	5
	8 Cyclopropanecarboxylic acid [4-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 123°C	
10	9 Cyclopropanecarboxylic acid [3,4-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 99—100°C	10
	10 Cyclopropanecarboxylic acid [2,3-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 153°C	
15	11 Cyclopropanecarboxylic acid [2,4-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 85—86°C	15
20	12 Cyclopropanecarboxylic acid [3,5-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 103°C	20
	13 Cyclopropanecarboxylic acid [2,4,6-trimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 119—121°C	
25	14 Cyclopropanecarboxylic acid [4-chloro-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 149—150°C	25
	15 Cyclopropanecarboxylic acid [3-chloro-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 99—100°C	
30	16 Cyclopropanecarboxylic acid [4-isopropyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 108—110°C	30
35	17 Cyclopropanecarboxylic acid [3-trifluoromethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 104—105°C	35
	18 Cyclopropanecarboxylic acid [3-fluoro-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 89°C	
40	19 Cyclopropanecarboxylic acid [3-bromo-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 93—94°C	40
	20 Cyclopropanecarboxylic acid [2,6-diisopropyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 215—216°C	
45	21 Cyclopropanecarboxylic acid [2-ethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 103°C	45
50	22 Cyclopropanecarboxylic acid [4-ethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 107°C	50

Compound No.	Name	Physical constant	
5	23 Cyclopropanecarboxylic acid [4-methoxy-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 75°C	5
	24 Cyclopropanecarboxylic acid [4-bromo-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 144—145°C	
10	25 Cyclopropanecarboxylic acid [4-fluoro-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 138—139°C	10
	26 Cyclopropanecarboxylic acid [2-ethoxy-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 143—145°C	
15	27 Cyclopropanecarboxylic acid [3-chloro-2-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 121—124°C	15
	28 Cyclopropanecarboxylic acid [5-chloro-2-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 114—116°C	
20	29 Cyclopropanecarboxylic acid [4-methoxy-2-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	$n_D^{20}=1.5520$	20
	30 Cyclopropanecarboxylic acid [4-ethoxy-N-(2-oxoperhydro-3-furyl)-anilide]	$n_D^{20}=1.4579$	
25	31 Cyclopropanecarboxylic acid [5-chloro-2-methoxy-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 163—164°C	25
	32 Cyclopropanecarboxylic acid [3-chloro-N-(5-methyl-2-oxoperhydro-3-furyl)-anilide]	M.p.: 95—97°C	
30	33 Cyclopropanecarboxylic acid [3-ethyl-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 69—70°C	30
	34 Cyclopropanecarboxylic acid [3-cyano-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 142—143°C	
35	35 Cyclopropanecarboxylic acid [3-thiomethyl-N-(2-oxoperhydro-3-furyl)-anilide]	$n_D^{20}=1.5888$	35
	36 Cyclopropanecarboxylic acid [2,3-dichloro-N-(2-oxoperhydro-3-furyl)-anilide]	M.p.: 136—137°C	
40	37 Cyclopropanecarboxylic acid [3-chloro-N-(5-methyl-2-oxoperhydro-3-furyl)-anilide]	M.p.: 95—97°C	40
45			45

The compounds of the present invention are in general almost colourless, odourless, crystalline substances which are practically insoluble in water and

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benzine, but, in contrast, are very readily soluble in polar organic solvents, for example acetone, dimethylformamide and dimethyl sulphoxide.

The starting compounds for the manufacture of the compounds of the present invention are known *per se* or may be produced according to processes known *per se*.

The following Examples illustrate the invention. Example 1 illustrates the manufacture of the compounds of the present invention and Examples 2 to 9 illustrate the possibilities of application of the compounds of the present invention.

Example 1

Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]

(Compound No. 1)

6.30 g (0.06 mole) of cyclopropanecarboxylic acid chloride were added dropwise, at a 5 to 10°C internal temperature, while stirring, to a solution of 10.62 g (0.06 mole) of 3-anilinoperhydrofuran-2-one in 50 ml of pyridine. The mixture was then stirred for $\frac{1}{2}$ hour at room temperature and then poured on to 200 g of water/ice and stirred well. After filtering with suction, the mixture was carefully washed with water and dried in a drying cupboard.

Yield: 10.25 g=70% of the theoretical yield; m.p.: 104°C.

Each of the other compounds of the present invention listed in the Table above may be produced in an analogous manner.

Example 2

Limiting Concentration Test in the Control of *Pythium Ultimum*

In a series of tests 20% pulverulent active substance preparations were mixed uniformly with soil which was severely infected with *Pythium ultimum*. The treated soil was placed in clay dishes each having a capacity of 0.5 litre and, without a waiting period, 20 marrowfat peas of the "Kelvedon Wonder" variety were sown in each dish. After a cultivation period of three weeks at 20 to 24°C the number of healthy peas was determined and an assessment (1—4 as defined below) of the roots was carried out.

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

Compound according to the invention	Active substance concentration in mg/l soil	Number of healthy peas	Root assessment (1—4)
Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	10 20 40	17 17 18	4 4 4
Cyclopropanecarboxylic acid [2,6-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	10 20 40	16 20 19	4 4 4
Cyclopropanecarboxylic acid [3-chloro-N-(2-oxoperhydro-3-furyl)-anilide]	10 20 40	19 17 17	4 4 4
Cyclopropanecarboxylic acid [3-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	10 20 40	10 16 16	1 2 4
Cyclopropanecarboxylic acid [2-methoxy-N-(2-oxoperhydro-3-furyl)-anilide]	10 20 40	10 16 20	1 2 4
Agent for comparison 5-Ethoxy-3-trichloromethyl-1,2,4-thiadiazole	10 20 40	2 5 12	1 1 3

	Compound according to the invention	Active substance concentration in mg/l soil	Number of healthy peas	Root assessment (1-4)	
5	Control I (3 repetitions) Infected soil	a) b) c)	1 0 0	1 — —	5
10	Control II (3 repetitions) Steamed soil	a) b) c)	19 18 18	4 4 4	10
15	Root assessment: 4=white roots without fungal necroses; 3=white roots, slight fungal necroses; 2=brown roots, considerably severe fungal necroses; 1=severe fungal necroses, mouldy roots.				15

20 Example 3 Dressing of Sugarbeet 20

In a series of tests graded sugarbeet seeds of the variety "Dieckmann Suprapoly" were dressed with 20% pulverulent active substance preparations. Clay dishes each of 2 litres capacity (20×20×5 cm) were filled with normal compost soil (damping-off) and 100 of the sugarbeet seeds were sown in each dish. After a cultivation period of 18 days at 19 to 21°C in a greenhouse the number of healthy seedlings was determined.

25 25

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

	Compound according to the invention	Active substance in g/kg seed	Number of healthy seedlings from 100 seeds	
30	Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	0.4 0.8 1.6	79 79 75	30
35	Cyclopropanecarboxylic acid [2,6-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	0.4 0.8 1.6	70 76 83	35
40	Cyclopropanecarboxylic acid [3-chloro-N-(2-oxoperhydro-3-furyl)-anilide]	0.4 0.8 1.6	83 82 93	40
45	Cyclopropanecarboxylic acid [3-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	0.4 0.8 1.6	77 71 85	45
50	Cyclopropanecarboxylic acid [2-methoxy-N-(2-oxoperhydro-3-furyl)-anilide]	0.4 0.8 1.6	83 87 87	50
	Agents for comparison 5-Ethoxy-3-trichloromethyl-1,2,4-thiadiazole	0.4 0.8 1.6	26 44 53	50
	Tetramethylthiuram disulphide	4.8 9.6	21 50	

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	Compound according to the invention	Active substance in g/kg seed	Number of healthy seedlings from 100 seeds	
5	Control I (3 repetitions) Infected soil	a) b) c)	5 7 6	5
10	Control II (3 repetitions) Steamed soil	a) b) c)	83 86 81	10

Example 4

15.	Effect of Prophylactic Leaf Treatment against <i>Plasmopara viticola</i> on Vines in a Greenhouse	15
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20	In a series of tests young vines having approximately 5 to 8 leaves were sprayed until dripping wet with the concentration of active substance indicated in the Table below and, after the spray coating had dried on, were sprayed on the undersides of the leaves with an aqueous suspension of sporangia of the fungus indicated in the heading above (approximately 20,000 per ml), and 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 (approximately 30 to 70% saturation) and then maintained at water vapour saturation for a further day. The percentage proportion of the surface attacked by fungi of each leaf was then recorded and the average per treatment was calculated as follows to determine the fungicidal effect:	20
25		25

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

	Compound according to the invention	% Effect against <i>Plasmopara viticola</i> +)	Concentration (% active substance)	
30	Cyclopropanecarboxylic acid [2,6-diethyl-N-(2-oxoperhydro-3-furyl)-anilide]	40	0.025	30
35	Cyclopropanecarboxylic acid [3-fluoro-N-(2-oxoperhydro-3-furyl)-anilide]	100	0.025	35
40	Cyclopropanecarboxylic acid [3-bromo-N-(2-oxoperhydro-3-furyl)-anilide]	100	0.025	40
	Cyclopropanecarboxylic acid [2,6-diisopropyl-N-(2-oxoperhydro-3-furyl)-anilide]	84	0.025	
45	Cyclopropanecarboxylic acid [2-ethyl-N-(2-oxoperhydro-3-furyl)-anilide]	83	0.025	45
	Cyclopropanecarboxylic acid [4-ethyl-N-(2-oxoperhydro-3-furyl)-anilide]	40	0.025	
50	Cyclopropanecarboxylic acid [4-fluoro-N-(2-oxoperhydro-3-furyl)-anilide]	100	0.025	50

	Compound according to the invention	% Effect against <i>Plasmopara viticola</i> +)	Concentration (% active substance)	
5	Cyclopropanecarboxylic acid [2-ethoxy-N-(2-oxoperhydro-3-furyl)-anilide]	70	0.025	5
	Cyclopropanecarboxylic acid [3-chloro-2-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	98	0.025	
10	Cyclopropanecarboxylic acid [3-ethyl-N-(2-oxoperhydro-3-furyl)-anilide]	100	0.025	10
15	Cyclopropanecarboxylic acid [3-cyano-N-(2-oxoperhydro-3-furyl)-anilide]	100	0.025	15
	Cyclopropanecarboxylic acid [3-thiomethyl-N-(2-oxoperhydro-3-furyl)-anilide]	70	0.025	
20	Cyclopropanecarboxylic acid [2,3-dichloro-N-(2-oxoperhydro-3-furyl)-anilide]	100	0.025	20
	Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	100	0.001	
25	Cyclopropanecarboxylic acid [3-chloro-N-(2-oxoperhydro-3-furyl)-anilide]	100	0.001	25

+) Effect was calculated on 100% attack in the untreated control.

Example 5

30 Effect of prophylactic leaf treatment against *Phytophthora infestans* in tomato plants or potato plants in a greenhouse 30

35 In a series of tests young tomato plants having at least two developed foliage leaves and potato plants (for example from eye cuttings) at least 10 cm tall were sprayed until dripping wet with the concentration of active substance indicated in the Table below and, after the spray coating had dried on, were sprayed with an aqueous suspension which contained per millilitre 50,000 to 80,000 sporangia of the fungus indicated in the heading above and which had been incubated in a refrigerator at 11°C for approximately 2 hours. The plants were incubated at a high level of air humidity and at approximately 15 to 18°C in a greenhouse and, after approximately 5 days, the percentage proportion of leaf surface that had been attacked was assessed. The fungicidal effect was calculated as follows: 40

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

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% Effect against *Phytophthora infestans*
in potatoes +)

5	Compound according to the invention	Concentration (% active substance) 0.005	5
	Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	95	
10	Cyclopropanecarboxylic acid [2,6-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	80	10
	Agent for comparison Manganeses ethylene bisdithiocarbamate	50	

15

% Effect against *Phytophthora infestans*
in tomatoes +)

15

	Compound according to the invention	Concentration (% active substance) 0.005	
20	Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	100	20
25	Cyclopropanecarboxylic acid [3-methyl-N-(2-oxoperhydro-3-furyl)-anilide]	81	25
	Cyclopropanecarboxylic acid [3-chloro-N-(2-oxoperhydro-3-furyl)-anilide]	91	
30	Agent for comparison Manganese ethylene bisdithiocarbamate	67	30

+) Effect was calculated on 100% attack in the untreated control.

Example 6

Systemic effect of soil treatment against *Phytophthora infestans* in tomato plants in a greenhouse

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In a series of tests the substances to be tested, which had been weighed out (weight by volume), were mixed with arable soil which was then placed in plant pots, and young tomato plants having at least two developed foliage leaves were placed in these pots. After the desired pre-dose time (for example after 4 or 18 days) had expired, the plants were sprayed with an aqueous suspension which contained per millilitre 50,000 to 80,000 sporangia of the fungus indicated in the heading above and which had been incubated in a refrigerator at 11°C for approximately 2 hours. The plants were incubated at a high level of air humidity and at approximately 15 to 18°C in a greenhouse and, after approximately 5 days, the percentage proportion of leaf surface that had been attacked was assessed. The fungicidal effect was calculated as follows:

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

Systemic effect of soil treatment against *Phytophthora infestans* in tomato plants

5	Compound according to the invention	ppm active substance	% Effect +) of treatment		5
			4 days before inoculation	18 days before inoculation	
	Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	25 5	89 70	85 89	
10	Cyclopropanecarboxylic acid [2,6-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	25 5	92 40	82 71	10

+) Effect was calculated on 100% attack in the untreated control.

Example 7

Curative effect of leaf treatment against *Phytophthora infestans* in tomato plants in a greenhouse

15	In a series of tests young tomato plants having at least two developed foliage leaves were sprayed with an aqueous suspension which contained per millilitre 50,000 to 80,000 sporangia of the fungus indicated in the heading above and which had been incubated in a refrigerator at 11°C for approximately 2 hours. The plants were incubated at a high level of air humidity. After the desired pre-dose time had expired, the plants were sprayed until dripping wet, within the period of latent fungal attack, with the concentration to be tested of the fungicide indicated in the Table below. After the outbreak of fungal attack in the untreated control plants the percentage proportion of leaf surface that had been attacked was assessed. The fungicidal effect was calculated as follows:	15
20		20
25		25

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

	Compound according to the invention	% Active substance sprayed	% Effect +) of treatment before inoculation	1 day after inoculation	
30	Cyclopropanecarboxylic acid [N-(2-oxoperhydro-3-furyl)-anilide]	0.004	100	68	30
35	Cyclopropanecarboxylic acid [2,6-dimethyl-N-(2-oxoperhydro-3-furyl)-anilide]	0.004	100	60	35
	Agent for comparison Manganese ethylene bisdithiocarbamate	0.004	91	0	

+) Effect was calculated on 100% attack in the untreated control.

Example 8

Effect of treatment of barley grains against *Helminthosporium spec.*

40	In a series of tests barley grains that had been attacked by <i>Helminthosporium spec.</i> were treated with 50 mg of active substance per 100 g of grains. The grains were then sown in soil and incubated in an air-conditioned chamber at +15°C. The tests were evaluated after 6 weeks and the resulting seedlings exhibited a markedly reduced attack as compared with plants of an untreated control group. The results are given in the following Table.	40
45		45

Compound according to the invention % Effect

	Cyclopropanecarboxylic acid [4 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide]	40
5	Cyclopropanecarboxylic acid [2,4 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide]	40
	Cyclopropanecarboxylic acid [4 - ethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide]	40
	Untreated control	0

Example 9

Limiting concentration test in the control

of *Pythium ultimum*

In a series of tests 20% pulverulent active substance preparations were mixed uniformly with soil which was severely infected with *Pythium ultimum*. The treated soil was placed in clay dishes each having a capacity of 0.5 litre and, without a waiting period, 20 marrowfat peas (*Pisum sativum* L. *conv.* *medullare* Alef.) of the "Kelvedon Wonder" variety were sown in each dish. After a cultivation period of 3 weeks at 20 to 24°C the number of healthy peas was determined and an assessment (1—4 as defined below) of the roots was carried out.

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

Compound according to the invention	Active substance concentration in mg/l soil	Number of healthy peas	Root assessment (1—4)
Cyclopropanecarboxylic acid [3-fluoro-N-(2-oxoperhydro-3-furyl)-anilide]	20 mg 40 mg 80 mg	18 20 19	4 4 4
Cyclopropanecarboxylic acid [3-bromo-N-(2-oxoperhydro-3-furyl)-anilide]	20 mg 40 mg 80 mg	17 19 20	4 4 4
Cyclopropanecarboxylic acid [4-fluoro-N-(2-oxoperhydro-3-furyl)-anilide]	20 mg 40 mg 80 mg	18 19 18	4 4 4
Cyclopropanecarboxylic acid [2-ethoxy-N-(2-oxoperhydro-3-furyl)-anilide]	20 mg 40 mg 80 mg	7 17 19	2 2 4
Cyclopropanecarboxylic acid [3-chloro-N-(5-methyl-2-oxoperhydro-3-furyl)-anilide]	20 mg 40 mg 80 mg	15 19 19	1 4 4
Cyclopropanecarboxylic acid [3-cyano-N-(2-oxoperhydro-3-furyl)-anilide]	20 mg 40 mg 80 mg	20 18 18	4 4 4
Cyclopropanecarboxylic acid [2,3-dichloro-N-(2-oxoperhydro-3-furyl)-anilide]	20 mg 40 mg 80 mg	— 10 11	— 3 3
Agent for comparison Manganese ethylene 1,2-bis-[dithiocarbamate]	20 mg 40 mg 80 mg	3 8 10	1 1 1
Control I (3 repetitions)	a)	1	1
Infected soil	b)	0	1
	c)	0	1

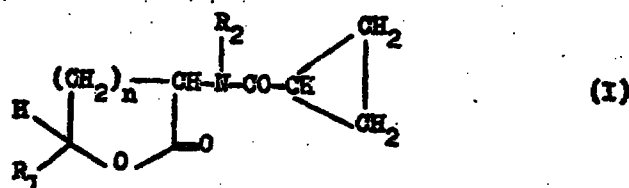
Compound according to the invention	Active substance concentration in mg/l soil	Number of healthy peas	Root assessment (1-4)
Control II (3 repetitions)	a)	19	4
Steamed soil	b)	17	4
	c)	18	4

Root assessment:

- 4=white roots without fungal necroses;
 3=white roots, slight fungal necroses;
 2=brown roots, considerably severe fungal necroses;
 1=severe fungal necroses, mouldy roots.

WHAT WE CLAIM IS:—

1. A compound of the general formula I



in which

R_1 represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms,

R_2 represents an unsubstituted aromatic hydrocarbon group or an aromatic hydrocarbon group substituted by one or more substituents selected from alkyl groups containing 1 to 4 carbon atoms, alkoxy groups containing 1 to 4 carbon atoms, alkylthio groups containing 1 to 4 carbon atoms, halogen atoms, trifluoromethyl groups, nitro groups, alkoxycarbonyl groups containing 1 to 4 carbon atoms in the alkoxy part, alkylcarbonyl groups containing 1 to 4 carbon atoms in the alkyl part and cyano groups, and

n represents 1 or 2.

2. A compound as claimed in claim 1, wherein R_1 represents a hydrogen atom or a methyl or ethyl group and R_2 represents a phenyl, methylphenyl, dimethylphenyl, ethylphenyl, isopropylphenyl, methoxyphenyl, ethoxyphenyl, methylthiophenyl, fluorophenyl, chlorophenyl, bromophenyl, dichlorophenyl, trifluoromethylphenyl, nitrophenyl, cyanophenyl, methoxycarbonylphenyl, acetylphenyl or biphenyl group.

3. Cyclopropanecarboxylic acid [N - (2 - oxoperhydro - 3 - furyl) - anilide].

4. Cyclopropanecarboxylic acid [2,6 - diethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

5. Cyclopropanecarboxylic acid [2 - methoxy - N - (2 - oxoperhydro - 3 - furyl) - anilide].

6. Cyclopropanecarboxylic acid [2 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

7. Cyclopropanecarboxylic acid [2,6 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

8. Cyclopropanecarboxylic acid [2,5 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

9. Cyclopropanecarboxylic acid [3 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

10. Cyclopropanecarboxylic acid [4 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

11. Cyclopropanecarboxylic acid [3,4 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

12. Cyclopropanecarboxylic acid [2,3 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

13. Cyclopropanecarboxylic acid [2,4 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].



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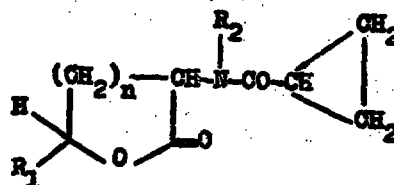
Compound according to the invention	Active substance concentration in mg/l soil	Number of healthy peas	Root assessment (1-4)
Control II (3 repetitions)	a)	19	4
Steamed soil	b)	17	4
	c)	18	4

Root assessment:

- 4=white roots without fungal necroses;
 3=white roots, slight fungal necroses;
 2=brown roots, considerably severe fungal necroses;
 1=severe fungal necroses, mouldy roots.

WHAT WE CLAIM IS:—

1. A compound of the general formula I



(I)

in which

R_1 represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms,

R_2 represents an unsubstituted aromatic hydrocarbon group or an aromatic hydrocarbon group substituted by one or more substituents selected from alkyl groups containing 1 to 4 carbon atoms, alkoxy groups containing 1 to 4 carbon atoms, alkylthio groups containing 1 to 4 carbon atoms, halogen atoms, trifluoromethyl groups, nitro groups, alkoxycarbonyl groups containing 1 to 4 carbon atoms in the alkoxy part, alkylcarbonyl groups containing 1 to 4 carbon atoms in the alkyl part and cyano groups, and

n represents 1 or 2.

2. A compound as claimed in claim 1, wherein R_1 represents a hydrogen atom or a methyl or ethyl group and R_2 represents a phenyl, methylphenyl, dimethylphenyl, ethylphenyl, isopropylphenyl, methoxyphenyl, ethoxyphenyl, methylthiophenyl, fluorophenyl, chlorophenyl, bromophenyl, dichlorophenyl, trifluoromethylphenyl, nitrophenyl, cyanophenyl, methoxycarbonylphenyl, acetylphenyl or biphenyl group.

3. Cyclopropanecarboxylic acid [N - (2 - oxoperhydro - 3 - furyl) - anilide].

4. Cyclopropanecarboxylic acid [2,6 - diethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

5. Cyclopropanecarboxylic acid [2 - methoxy - N - (2 - oxoperhydro - 3 - furyl) - anilide].

6. Cyclopropanecarboxylic acid [2 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

7. Cyclopropanecarboxylic acid [2,6 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

8. Cyclopropanecarboxylic acid [2,5 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

9. Cyclopropanecarboxylic acid [3 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

10. Cyclopropanecarboxylic acid [4 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

11. Cyclopropanecarboxylic acid [3,4 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

12. Cyclopropanecarboxylic acid [2,3 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

13. Cyclopropanecarboxylic acid [2,4 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].

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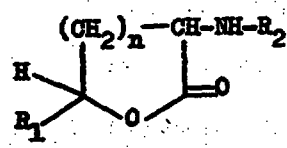
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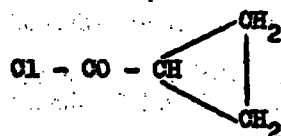
14. Cyclopropanecarboxylic acid [3,5 - dimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
15. Cyclopropanecarboxylic acid [2,4,6 - trimethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
16. Cyclopropanecarboxylic acid [4 - chloro - N - (2 - oxoperhydro - 3 - furyl) - anilide].
17. Cyclopropanecarboxylic acid [3 - chloro - N - (2 - oxoperhydro - 3 - furyl) - anilide].
18. Cyclopropanecarboxylic acid [4 - isopropyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
19. Cyclopropanecarboxylic acid [3 - trifluoromethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
20. Cyclopropanecarboxylic acid [3 - fluoro - N - (2 - oxoperhydro - 3 - furyl) - anilide].
21. Cyclopropanecarboxylic acid [3 - bromo - N - (2 - oxoperhydro - 3 - furyl) - anilide].
22. Cyclopropanecarboxylic acid [2,6 - diisopropyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
23. Cyclopropanecarboxylic acid [2 - ethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
24. Cyclopropanecarboxylic acid [4 - ethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
25. Cyclopropanecarboxylic acid [4 - methoxy - N - (2 - oxoperhydro - 3 - furyl) - anilide].
26. Cyclopropanecarboxylic acid [4 - bromo - N - (2 - oxoperhydro - 3 - furyl) - anilide].
27. Cyclopropanecarboxylic acid [4 - fluoro - N - (2 - oxoperhydro - 3 - furyl) - anilide].
28. Cyclopropanecarboxylic acid [2 - ethoxy - N - (2 - oxoperhydro - 3 - furyl) - anilide].
29. Cyclopropanecarboxylic acid [3 - chloro - 2 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
30. Cyclopropanecarboxylic acid [5 - chloro - 2 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
31. Cyclopropanecarboxylic acid [4 - methoxy - 2 - methyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
32. Cyclopropanecarboxylic acid [4 - ethoxy - N - (2 - oxoperhydro - 3 - furyl) - anilide].
33. Cyclopropanecarboxylic acid [5 - chloro - 2 - methoxy - N - (2 - oxoperhydro - 3 - furyl) - anilide].
34. Cyclopropanecarboxylic acid [3 - chloro - N - (5 - methyl - 2 - oxoperhydro - 3 - furyl) - anilide].
35. Cyclopropanecarboxylic acid [3 - ethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
36. Cyclopropanecarboxylic acid [3 - cyano - N - (2 - oxoperhydro - 3 - furyl) - anilide].
37. Cyclopropanecarboxylic acid [3 - thiomethyl - N - (2 - oxoperhydro - 3 - furyl) - anilide].
38. Cyclopropanecarboxylic acid [2,3 - dichloro - N - (2 - oxoperhydro - 3 - furyl) - anilide].
39. Cyclopropanecarboxylic acid [3 - chloro - N - (5 - methyl - 2 - oxoperhydro - 3 - furyl) - anilide].

40. A process for the manufacture of a compound as claimed in claim 1, wherein a compound of the general formula II



(II)

in which R₁, R₂ and n have the meanings given above, is reacted in the presence of an acid-binding agent with cyclopropanecarboxylic acid chloride of the formula III



(III)

41. A process as claimed in claim 40, wherein the reaction is carried out in the presence of a solvent.

42. A process as claimed in claim 40 or 41, wherein the compound of the general formula II and the compound of the formula III are used in equimolar proportions.

43. A process as claimed in claim 40, conducted substantially as described herein.

44. A process as claimed in claim 40, conducted substantially as described in Example 1 herein.

45. A fungicidal preparation which comprises a compound of the general formula I given in claim 1, in which R_1 , R_2 and n have the meanings given in claim 1, in admixture or conjunction with a suitable carrier.

46. A fungicidal preparation which comprises a compound as claimed in claim 2, in admixture or conjunction with a suitable carrier.

47. A fungicidal preparation which comprises the compound claimed in any one of claims 3 to 39, in admixture or conjunction with a suitable carrier.

48. A preparation as claimed in any one of claims 45 to 47, which is in the form of a powder, a strewable preparation, granules, a solution, an emulsion or a suspension.

49. A preparation as claimed in any one of claims 45 to 48, containing a single compound of the general formula I in an amount of approximately 1 to 80% by weight.

50. A preparation as claimed in any one of claims 45 to 48, containing two or more compounds of the general formula I in a total amount of approximately 1 to 80% by weight.

51. A preparation as claimed in any one of claims 45 to 50, which also contains a single surface-active agent in an amount of up to 20% by weight.

52. A preparation as claimed in any one of claims 45 to 50, which also contains two or more surface-active agents in a total amount of up to 20% by weight.

53. A preparation as claimed in any one of claims 45 to 52, which also contains a dyestuff.

54. Any one of the fungicidal preparations as claimed in claim 45 and substantially as described in Examples 2, 3, 5 and 7 herein.

55. Any one of the fungicidal preparations as claimed in claim 45 and substantially as described in Examples 4 and 9 herein.

56. A method of protecting a living plant against phytopathogenic fungi, wherein the living plant is treated with a compound of the general formula I given in claim 1, in which R_1 , R_2 and n have the meanings given in claim 1.

57. A method as claimed in claim 56, wherein the living plant is treated with a compound as claimed in claim 2.

58. A method as claimed in claim 56, wherein the living plant is treated with the compound claimed in any one of claims 3 to 39.

59. A method as claimed in claim 56, wherein the living plant is treated with a fungicidal preparation as claimed in any one of claims 45 to 52, 54 and 55.

60. A method as claimed in claim 56, conducted substantially as described in Example 4 herein.

61. A method as claimed in claim 56, conducted substantially as described in Example 5 or 7 herein.

62. 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 , R_2 and n have the meanings given in claim 1.

63. A method as claimed in claim 62, wherein the crop area is treated with a compound as claimed in claim 2.

64. A method as claimed in claim 62, wherein the crop area is treated with the compound claimed in any one of claims 3 to 39.

65. A method as claimed in claim 62, wherein the crop area is treated with a fungicidal preparation as claimed in any one of claims 45 to 52, 54 and 55.

66. A method as claimed in claim 62, conducted substantially as described in Example 2 or 6 herein.

67. A method as claimed in claim 62, conducted substantially as described in Example 9 herein.

68. 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 , R_2 and n have the meanings given in claim 1.

69. A method as claimed in claim 68, wherein the seeds are treated with a compound as claimed in claim 2.

70. A method as claimed in claim 68, wherein the seeds are treated with the compound claimed in any one of claims 3 to 39.

71. A method as claimed in claim 68, wherein the seeds are treated with a fungicidal preparation as claimed in any one of claims 45 to 55.

72. A method as claimed in claim 68, conducted substantially as described in Example 3 herein.

73. A method as claimed in claim 68, conducted substantially as described in Example 8 herein.

74. A pack which comprises a compound of the general formula I given in claim 1, in which R_1 , R_2 and n have the meanings given in claim 1, together with instructions for its use for controlling phytopathogenic fungi.

75. A pack as claimed in claim 74, wherein the compound of the general formula I is a compound as claimed in claim 2.

76. A pack as claimed in claim 74, wherein the compound of the general formula I is the compound claimed in any one of claims 3 to 39.

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