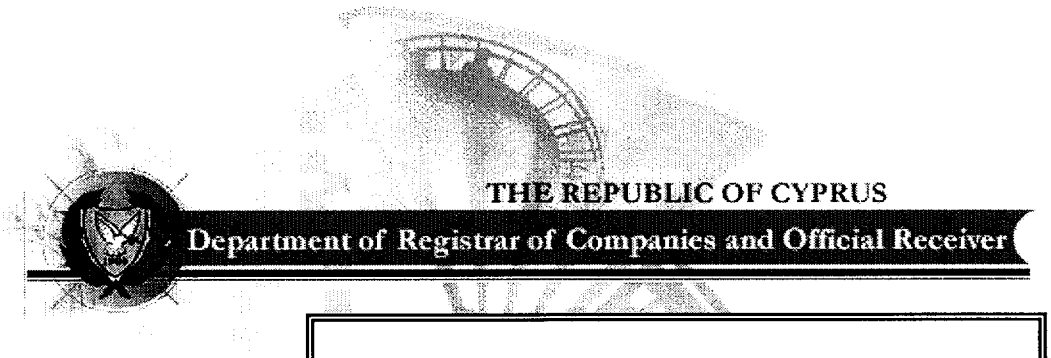

ΚΥΠΡΙΑΚΟ ΓΡΑΦΕΙΟ ΔΙΠΛΩΜΑΤΩΝ ΕΥΡΕΣΙΤΕΧΝΙΑΣ

THE PATENT OFFICE OF CYPRUS

ΑΡΙΘΜΟΣ ΔΗΜΟΣΙΕΥΣΗΣ **CY1173**
PUBLICATION NUMBER

ΑΡΙΘΜΟΣ ΔΗΜΟΣΙΕΥΣΗΣ
ΓΡΑΦΕΙΟΥ ΔΙΠΛΩΜΑΤΩΝ ΕΥΡΕΣΙΤΕΧΝΙΑΣ
ΗΝΩΜΕΝΟΥ ΒΑΣΙΛΕΙΟΥ
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GB 1500581
GB 1500576
GB 1498199
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(74) Agents
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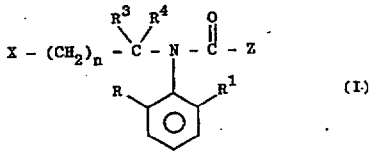
(54) Acyl anilines exerting a fungicidal action

(57) Compounds endowed with fungicidal activity and low phytoxicity having the general formula:

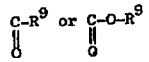


(I)

in which R and R^1 may be the same or different and each represent a hydrogen atom or a CH_3, C_2H_5, n–C_3H_7, $-CH_2-CH=CH_2$ or $-CH=CH-CH_3$ group,

R^3 and R^4 may be the same or different and each represent a hydrogen, chlorine or fluorine atom, an alkyl group having 1 to 3 carbon atoms or a halomethyl, alkoxymethyl, CN, O–alkyl or S–alkyl group, or R^3 and R^4 together represent $CH_2=$,

X represents



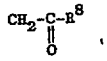
(in which R^9 represents an alkyl group having 1 to 3 carbon atoms), CN, $-CH(OR^5)_2$ (in which R^5 represents an alkyl or alkylidene group) or

(in which R^6 and R^7 may be the same or different and each represent a hydrogen atom or an alkyl group),

n is 0 or 1,

Z represents an optionally substituted phenyl group,

(in which R^2 represents a hydrogen atom or CH_3 group, m is 1 or 2 and Y represents an alkynyl group having 2 to 8 carbon atoms, an optionally substituted phenyl group, a cycloalkyl group having 3 to 8 carbon atoms, a phenylacetyl, furyl, thienyl or pyridyl group or a heterocyclic group containing 2 or 3 heteroatoms one of which is other than nitrogen) or



(in which R^8 represents a CH_3, alkoxymethyl, halomethyl or O-alkyl group).

GB 2 023 132 A

SPECIFICATION

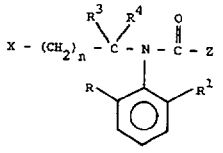
Acyl anilines exerting a fungicidal action

The present invention relates to acyl anilines and in particular to acyl anilines having a fungicidal action, to their use and to their preparation.

The bactericidal and fungicidal activity of some derivatives of aniline and of glycine having, on the nitrogen atom, a substituted phenyl and an acyl group has been recently disclosed. For example, German Offenlegungsschrift No. 2 513 789 discloses such compounds in which the acyl group comprises an alpha or beta - haloalkanoyl group, French Patent Application No. 7 510 722 discloses such compounds in which the acyl group comprises an acetyl group substituted in the alpha position by an oxygen or sulphur atom bound to various groups and German Offenlegungsschrift Nos. 2 513 732 and 2 513 788 disclose compounds in which the acyl group comprises a 2 - furoyl group, a 2 - thienoyl group or a pyridyl 2 - carboxylic group. The microbicidal activity of methylalaninates carrying, on the nitrogen atom, a 2, 6 - dialkyl - phenyl and one of the following groups, cyclopropanoyl, acryloyl, crotonoyl, has been disclosed in Swiss Patent Application Nos. 4998/74 and 2906/75. The interest in the research of new derivatives of acyl anilines having a fungicidal action is due to the desirability of finding compounds having a high fungicidal activity combined with the absence of phytotoxicity. Several known products though exhibiting an excellent fungicidal activity, are also toxic on the plants it is desired to protect from infections due to fungi.

We have now found new series of compounds which are endowed with a high fungicidal activity and a low phytotoxicity.

Therefore according to the invention there is provided a compound of the general formula:



(I)

in which:

R and R¹ may be the same or different and each represent a hydrogen atom or a CH_3, C_2H_5, n - C_3H_7, - CH_2 - CH=CH_2 or - CH=CH - CH_3 group,

R^3 and R^4 may be the same or different and each represent hydrogen, chlorine or fluorine atom, an alkyl group having 1 to 3 carbon atoms or a halomethyl, alkoxymethyl, CN, O - alkyl or S - alkyl group, or R^3 and R^4 together represent CH_2=,

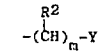
X represents C - R^9 or C - O - R^9 (in which R^9

represents an alkyl group having 1 to 3 carbon atoms), CN, - $CH(OR^5)_2$, (in which R^5 represents an alkyl or alkylidene group) or

(in which R^6 and R^7 may be the same or different and each represent a hydrogen atom or an alkyl group),

n is 0 or 1,

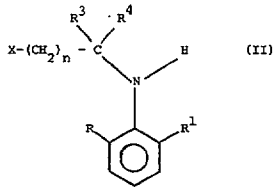
Z represents an optionally substituted phenyl group,



(in which R^2 represents a hydrogen atom or CH_3 group, m is 1 or 2 and Y represents an alkynyl group having 2 to 8 carbon atoms, an optionally substituted phenyl group, a cycloalkyl group having 3 to 8 carbon atoms, a phenylacetyl, furyl, thienyl or pyridyl group or a heterocyclic group containing 2 or 3 heteroatoms one of which is other than nitrogen) or

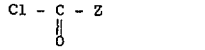
(in which R^8 represents a CH_3, alkoxymethyl, halomethyl or O-alkyl group).

The synthesis of the acyl anilines of formula (I) may be carried out by condensing anilines of the general formula:



(II)

in which X, R, R¹, R^3, R^4 and n are as defined above, with a compound of the formula:



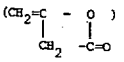
(III)

in which Z is as defined above, in the presence of a halogenhydric acid-accepting base or dimethylformamide.

Some of the anilines of formula (II) are commercially available and others are readily obtained by known reactions starting from 2, 6 - disubstituted anilines. The anilines substituted in one or both of the 2 and 6 positions by alkenyl groups have been described in Italian Patent Application Nos. 23809 A/77 and 28817 A/77.

Examples of compounds of formula (III) include benzoyl chloride, phenylacetylchloride, the monochloride of a malonic ester (Cl - CO - CH_2 - COO - alkyl) and the chloride of chloro - acetoacetic acid (Cl - CO - CH_2 - CO - CH_2 - Cl).

The synthesis of compounds of formula (I) in which Z represents CH_2 - CO - R^8 and R^8 represents CH_3, can also be carried out by reacting an aniline of the general formula (II) with diketene



The compounds reported on Table 1 have been pre-

Certain of the chemical formula (e) appearing in the printed specification were submitted in formal form after the date of filing

Table 1

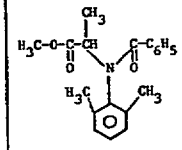
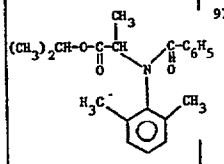
Compound	Formula	(a) Melting point °C	Elemental analysis (%) calculated C	H	N	found C	H	N	(b) IR Max (cm^{-1})	(c) NMR (δ.ppm) [TMS]
1		96-100	73.29	6.80	4.50	73.8	7.0	4.4	1635 1730 1745	1.04 (d, 3H, $\underline{CH_3}$-CH) 2.23 (s, 3H, CH_3-ø) 2.29 (s, 3H, CH_3-ø) 3.79 (s, 3H, CH_3-O) 4.30 (q, 1H, CH) 6.83-7.33 (m, 8H, aromatic protons)
2		97-100	74.31	7.42	4.13	74.45	7.77	4.25	1630 1715 1720	1.2 (d, 3H, $\underline{CH_3}$-CH) 1.3 [d, 6H, $(\underline{CH_3})_2$-CH] 2.3 (s, 3H, CH_3-ø) 2.32 (s, 3H, CH_3-ø) 4.4 (q, 1H, CH_3-CH) 5.2 [m, 1H, $(CH_3)_2\underline{CH}$] 6.8-7.5 (m, 8H, aromatic protons)

Table 1 Contd.

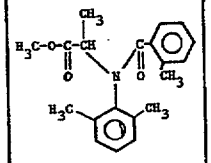
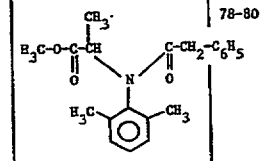
3		114-115								1.20 (d, 3H, $\underline{CH_3}$-CH) 2.27 (s, 3H, CH_3-ø) 2.37 (s, 3H, CH_3-ø) 2.47 (s, 3H, CH_3-ø) 3.83 (s, 3H, CH_3-O) 4.30 (q, 1H, CH_3-$\underline{CH}$) 6.63-7.20 (m, 7H, aromatic protons)
4		78-80	78.32	7.12	4.30	75.34	7.47	4.67	1660 1750	0.98 (d, 3H, $\underline{CH_3}$-CH) 1.85 (s, 3H, CH_3-ø) 2.40 (s, 3H, CH_3-ø) 3.25 (s, 2H, CH_2) 3.80 (s, 3H, CH_3-O) 4.45 (q, 1H, CH_3-$\underline{CH}$) 6.85-7.3 (m, 8H, aromatic protons)

Table 1 Contd.

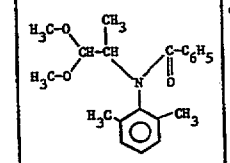
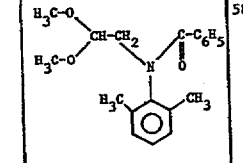
5		oil	73.37	7.70	4.18	75.4	8.4	4.3		
6		58-59	72.81	7.40	4.47	73.14	7.66	4.69		2.2 (s, 6H, CH_3-ø) 3.3 (s, 6H, CH_3-O) 3.9 (d, 2H, CH_2-N) 4.95 (t, 1H, CH) 7-7.3 (m, 8H, aromatic protons)

Table 1 Contd

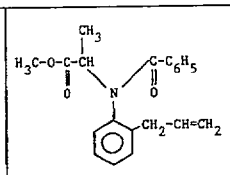
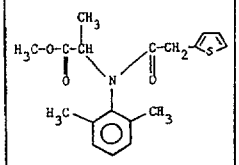
7		oil	74.28	6.54	4.33	73.6	6.6	4.6		1.35; 1.65 (d,d,3H,$\underline{CH}_3$-CH) 3.3 (m, 2H, $\underline{CH}_2$-CH=CH_2) 3.8 (s, 3H, CH_3-O) 4.8 (q, 1H, CH_3-$\underline{CH}$) 4.9; 5.15 (m,m,2H, -CH=$\underline{CH}_2$) 5.6 (m, 1H, $\underline{CH}$=CH_2) 7.1-7.35 (m, 9H, aromatic protons)
8		63.64	65.23	6.39	4.23	66.53	6.74	4.54	1655 1745	1.0 (d, 3H, $\underline{CH}_3$-CH) 2.0 (s, 3H, $\underline{CH}_3$-Ø) 2.45 (s, 3H, $\underline{CH}_3$-Ø) 3.4 (s, 2H, CH_2) 3.8 (s, 3H, $COOCH_3$) 4.5 (q, 1H, CH_3-$\underline{CH}$) 6.5-7.3 (m, 6H)

Table 1 Contd.

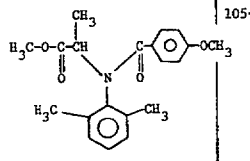
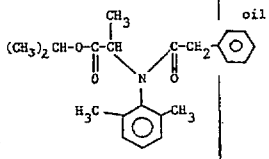
9		105-108	70.36	6.79	4.10	70.5	6.9	4.0	1630 1750	1.3 (d, 3H, $\underline{CH}_3$-CH) 2.3 (s, 6H, $\underline{CH}_3$-Ø) 3.7 (s, 3H, $\underline{CH}_3$-O-Ø) 3.85 (s, 3H, $COOCH_3$) 4.45 (q, 1H, CH_3-$\underline{CH}$) 6.75-7.6 (m, 7H, aromatic protons)
10		oil	74.76	7.70	3.96	73.84	7.91	3.99	1650 1730	1.2-1.45 (9H) 2.3 (s, 6H, CH_3-Ø) 4.4 (q, 1H. N-CH) 5.2 (m, 1H, COOCH) 6.8-7.5 (m, 8H, aromatic protons)

Table 1 Contd

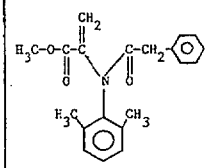
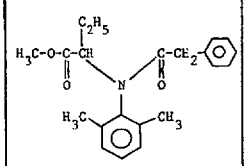
11		56-57								2.05 (s, 6H, CH_3-Ø) 3.4 (s, 2H, CH_2-Ø) 3.85 (s, 3H, $COOCH_3$) 4.6-5.4 (d,d, 2H, CH_2=C) 7.1-7.3 (m, 8H, aromatic protons)
12		51-52	74.31	7.42	4.13	74.03	7.52	4.07		

Table 1 Contd.

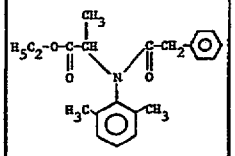
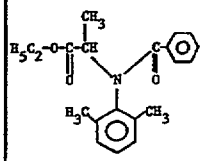
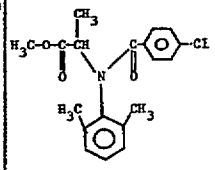
13		oil	74.31	7.42	4.13	72.96	7.16	4.34		
14		69-70	73.82	7.12	4.30	73.41	7.28	4.31		
15[d]		97-100	65.99	5.83	4.05	67.0	5.9	3.7	1630 1730 1745	1.27 (d, 3H, $\underline{CH_3}$-CH 2.3 (s, 6H, $\underline{CH_3}$-Ø) 3.8 (s, 3H, $COOCH_3$) 4.45 (q, 1H, CH_3-$\underline{CH}$) 6.9-7.4 (m, 7H, aromatic protons)

Table 1 Contd.

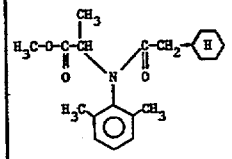
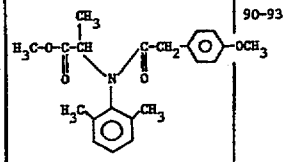
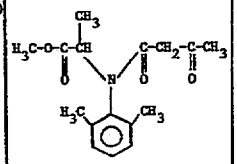
16		60-64	72.47	8.82	4.22	71.75	9.12	3.81	1650 1750	
17		90-93	70.96	7.09	3.94	70.59	7.28	3.70	1655 1745	
18[e]		oil								0.98 (d, 3H, $\underline{CH_3}$-CH) 2.12) 2.15) (6H, CH_3-Ø) 2.39) 2.43) 1.71) (3H, CH_3-CO) 2.09) 2.92 (CH_2) 3.70 (s, 3H, CH_3O) 4.33 ($\underline{CH}$=C-OH) 4.40 (CH_3-$\underline{CH}$)

Table 1 Contd.

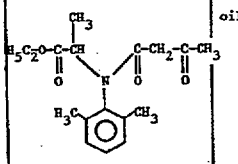
18 Contd.										6.96-7.26 (3H aromatic protons) 13.93 (s, OH)
19[e]		oil								0.99 (d, 3H, $\underline{CH_3}$-CH) 1.29 (t, 3H, $\underline{CH_3}$-CH_2) 2.08) 2.25) (CH_3-Ø + CH_3-C(=O)) 2.40) 2.43) 2.08 - 2.25 (CH_3-C(=O)) 1.71 (CH_3-C(OH)=) 2.91 (CO-$\underline{CH_2}$-CO) 4.16 (CH_3-$\underline{CH_2}$) 4.37 (CH_3-$\underline{CH}$) 6.93-7.24 (m, 3H, aromatic protons) 13.90 (OH) 4.30 (CH=C-OH)

Table 1 Contd.

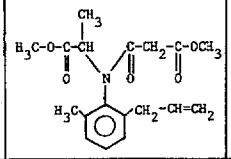
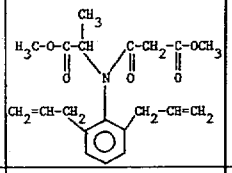
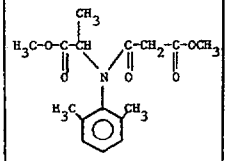
20		oil	64.85	6.95	4.20	64.84	7.24	4.51	1660 1745	
21		oil	66.83	7.01	3.90	67.93	7.72	4.67	1660 1745	
22		oil								0.97 (3H, d, $\underline{CH_3}$-CH) 4.36 (1H, q, CH_3-$\underline{CH}$) 2.87 (2H, s, CH_2) 3.60) 3.73) (6H, s, s, OCH_3) 2.20 (3H, s, CH_3-Ø) 2.45 (3H, s, CH_3-Ø) 7.0-7.2 (3H, m, aromatic protons)

Table 1 Contd.

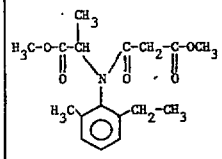
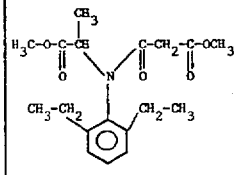
23										0.97-0.99 (3H,d,d,$\underline{CH_3}$-CH) 1.27 (3H, t, $\underline{CH_3}$-CH_2) 2.27-2.46 (3H, s,s, CH_3-Ø) 2.85 (2H, s, CH_2-CO) 2.27-3.17 (2H, m $\underline{CH_2}$-CH_3) 3.60-3.72 (6H, s, s, OCH_3) 4.37 (1H, m, CH_3-$\underline{CH}$) 6.93-7.30 (3H, m, aromatic protons)
24										0.97 (3H, d, CH_3-CH) 1.23 (6H, t, $\underline{CH_3}$-CH_2) 2.83 (2H, s, CH_2-CO) 2.13-3.17 (4H, m, $\underline{CH_2}$-CH_3) 3.57-3.70 (6H, s,s, OCH_3) 4.33 (1H, m, $\underline{CH}$-CH_3) 4.97-7.37 (3H, m, aromatic protons)

Table 1 Contd.

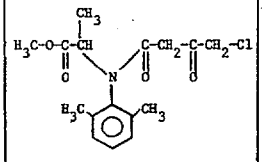
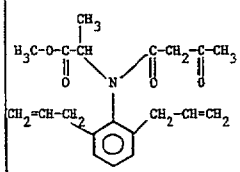
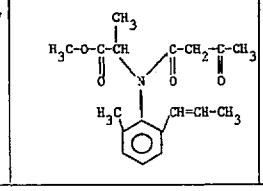
25		105-110							
26		oil	69.95	7.34	4.08	68.60	7.30	4.32	1630 1650 1720 1745
27		oil	68.12	7.30	4.41	65.85	7.49	4.35	1630 1650 1715 1745

Table 1 Contd.

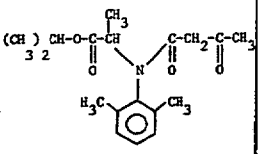
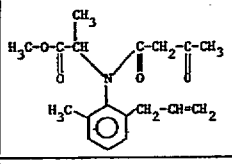
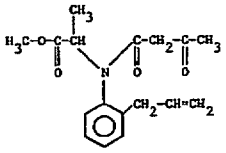
28		oil	67.69	7.89	4.38	67.71	8.32	4.40	1630 1655 1740	
29		oil	68.12	7.30	4.41	67.70	7.33	4.36	1630 1750	
30		oil	67.31	6.98	4.62	66.2	6.90	4.90	1630 1650 1720 1740	

Table 1 Contd.

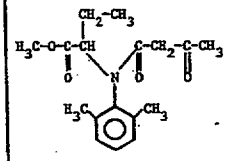
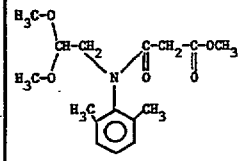
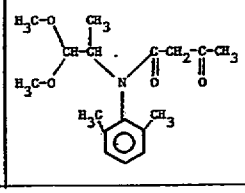
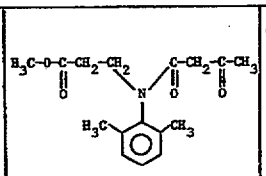
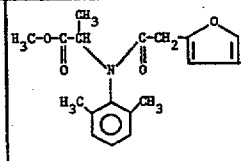
31		84-87								
32		oil	62.12	7.49	4.53	61.06	7.84	4.47	1660 1745	
33		oil	66.43	8.20	4.56	65.76	8.43	4.89		

Table 1 Contd.

34(e)		65.68							2.19 (s, 3H, CH_3-ø) 2.22 (s, 3H, CH_3-ø) 2.65 (t, 2H, CH_2) 3.78 (t, 2H, CH_2) 2.10 (s, CH_3-CO) 1.73 (s, CH_3-C(OH)=) 2.89 (s, CH_2-CO) 4.27 (s, CH=C(OH)-) 4.99-7.20 (m, 3H, aromatic protons) 14.25 (OH) 3.55 (s, 3H, OCH_3)
35		oil	68.55	6.71	4.44	67.61	6.70	4.57	1655 1740	1.0 (d, 3H, $\underline{CH_3}$-CH) 2.1 (s, 3H, CH_3-ø) 2.4 (s, 3H, CH_3-ø) 3.3 (s, 2H, CH_2CO) 3.8 (s, 3H, OCH_3) 4.4 (q, 1H, CH_3-$\underline{CH}$) 5.9-7.5 (m, 6H, aromatic protons)

Notes to Table 1

(a) The melting points have not been corrected.
(b) Only the most meaningful bands are recorded.
(c) The NMR spectra of compounds 1 and 3 have been recorded by using CCl_4 as a solvent, the other spectra by using $CDCl_3$;
s = singlet,
d = doublet,
t = triplet,
q = quadruplet,
m = multiplet.
(d) Elemental analysis: calculated chlorine = 10.25; found chlorine = 9.68
(e) Mixture of tautomers.

The compounds of general formula (I) are endowed with an excellent fungicidal activity towards phytopathogenous fungi, and the action exerted by same is both preventive, as it prevents the disease from arising, and curative, as it combats infection already present.

Furthermore the compounds possess good systemic characteristics, i.e. they are transported to the various parts of the plant and therefore the compounds may be applied to the leaves of the plant or to the soil in which the plants are grown.

The invention will be illustrated by the following Examples.

Example 1

Preparation of N - (2, 6 - dimethylphenyl) - N - acetoacetyl - α - amino - methylpropionate (Compound 18, Table 1)

7.06 g of just distilled diketene were added to 14.5 g of N - (2, 6 - dimethylphenyl) - 2 - amino - propionate of methyl in 25 ml of toluene. The reaction mixture was heated at reflux for 24 hours. After cooling and evaporation of the solvent, the residue was purified by chromatography on a silica gel column using chloroform as an eluent.

20g of the desired product were obtained in the form of oil, with a yield of 98% in respect of the theoretical yield.

The structure ascribed to the product was confirmed by NMR spectroscopy. Under the operative conditions adopted, the compound appears as a mixture of tautomers, as will be seen from the signals corresponding to the various protons listed in Table 1.

Example 2

Preparation of N - (2, 6 - diallylphenyl) - N - acetoacetyl - α - amino - methylpropionate (Compound 26, Table 1)

0.02 mole of methyl ester of N - (2, 6 - diallylphenyl) - α - amino propionic acid were dissolved in toluene (10ml). 0.025 mole of just distilled diketene were added to the solution and the mixture was heated at reflux temperature for 24 hours. After cooling and evaporation of the solvent, the residue was purified by chromatography on a silica gel column using a mixture of hexane and ethyl - acetate (4:1) as eluent.

3 g of the desired product were obtained in the form of oil.

Example 3

Preparation of N - (2 - allyl - phenyl) - N - acetoacetyl - α - aminomethylpropionate (Compound 30, Table 1)

0.02 mole of methyl ester of N - (2 - allyl - phenyl) - α - amino - methylpropionic acid were dissolved in 20 ml of benzene. 0.5 mole of pyridine and 0.25 mole of just distilled diketene were added to the solution and the reaction mixture was heated at reflux for 10 hours. After cooling the mixture was diluted with benzene, washed with a hydrogen chloride solution (1% conc.) and with water. The organic phase was separated, anhydrified with Na_2SO_4 and the solvent was evaporated. The residue was purified by chromatography on a silica gel column using hexane - ethylacetate (4:1) as eluent.

3 g of the desired product were obtained in the form of an oil.

Example 4

Starting from the corresponding intermediates and following the procedures described in Examples 1, 2 or 3, compounds 19, 27, 28, 29, 31, 33 and 34 (Table 1) were prepared.

Example 5

Preparation of N - (2 - methyl - 6 - allyl - phenyl) - N - (carboxy - methyl - acetal) - α - amino - methyl-propionate (Compound 20, Table 1)

5g (0.021 mole) of a methyl ester of N - (2 - methyl - 6 - allyl - phenyl) - α - amino propionic acid were dissolved in toluene (120 ml). 3.5 g (0.027 mole) of malonic acid methyl ester monochloride (ClCO - CH_2 - $COOCH_3$) were added to the solution under stirring, dropwise, over a period of 15 minutes at room temperature. The reaction mixture was then stirred at room temperature for 1 hour followed by heating at reflux for 5 hours.

After cooling the solution was filtered and the solvent evaporated. The oily residue was purified by chromatography on a silica gel column using hexane-ethyl acetate (3:1) as eluent.

4.6 g of the desired product were obtained in the form of a red oil.

Example 6

Preparation of N - (2, 6 - dimethyl - phenyl) - N - (2, 2 - dimethoxyethyl) - carbomethoxyacetamide (Compound 32, Table 1)

Malonic acid methyl ester monochloride (2.1 ml, 0.02 mole) was added dropwise over a period of 15 minutes at 0 to 5°C under stirring to a solution of N - (2, 2 - dimethoxyethyl) - 2, 6 - dimethyl aniline (4.45 g, 0.02 mole), triethylamine (2.76 ml, 0.02 mole) in ethyl ether (25 ml).

The reaction mixture was then stirred for 1 hour at 0°C and 10 minutes at room temperature, then it was filtered, washed twice with 10 ml of a hydrogen chloride solution (5%), then with water till a neutral pH (3 x 10 ml).

The organic phase was anhydrified on anhydrous Na_2SO_4 and the solvent was evaporated. The residue (yellow oil) was purified by chromatography on a silica gel column using hexane-ethyl acetate (7:3) as eluent.

2.1 g of the desired product in the form of an oil were obtained.

Example 7

Starting from the corresponding intermediates and adopting the procedures described in Examples 5 or 6, compounds 21, 22, 23, 24 and 25 were

obtained.

Example 8

Preparation of N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxyethyl) - phenylacetamide (Compound 4, Table 1)

17 g (0.11 mole) of phenylacetylchloride were added dropwise in 30 minutes and at room temperature, to a solution of N - (1 - carbomethoxy - ethyl) - 2, 6 - dimethylaniline (21.2 g at a purity of 95%, 0.1 mole) in toluene (150 ml) and dimethylformamide (1 ml).

The reaction mixture was stirred 1 hour at room temperature and 3 hours at reflux temperature, then it was cooled to room temperature and washed with an aqueous solution of $NaHCO_3$ at 5% and successively with water.

The organic phase was separated and anhydrified with anhydrouse Na_2SO_4. The solvent was evaporated and the rough product obtained was recrystallized from ligroin (75 to 120°C), to yield 26 g of the desired product as a white solid, melting at 78 to 80°C.

Example 9

Operating as described in Example 8 and starting from the corresponding intermediates, the compounds 1, 2, 3, 7, 8, 9, 10, 12, 13, 14, 15, 16, 17 and 34 of Table 1 were obtained. Compounds 10, 13 and 34 were obtained as oils at room temperature and were purified by chromatography on a silica gel column (eluent:hexane - ethyl acetate (3:1) instead of crystallization.

Example 10

Preparation of N - (2', 2' - dimethoxyethyl) - N - (2, 6 - dimethylphenyl) - benzamide (Compound 6, Table 1)

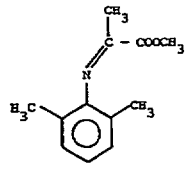
2.81 g (0.02 mole) of benzoyl chloride were added dropwise in 20 minutes at a temperature of 0 to 5°C to a solution of N - (2', 2' - dimethoxy - ethyl) - 2, 6 - dimethyl aniline (4.45 g, 0.02 mole) in ethyl ether (20 ml) containing triethylamine (2.76 ml, 0.02 mole). The reaction mixture was stirred at room temperature for 15 minutes. The resulting salt was filtered and the solution was washed with 8 ml of an aqueous solution of hydrochloric acid at 5% and then with water up to neutral pH. The organic phase was anhydrified with anhydrous Na_2SO_4 and the solvent was evaporated, to yield 5.2 g of a white solid which, recrystallized from petroleum ether (25 ml) provided 4.5 g of product (purity = 91% by GLC) with a yield of 65.5% as a white solid, melting at 58 to 59°C).

Example 11

Operating according to Example 10 and starting from N - (1' - methyl - 2', 2' - dimethoxy - ethyl) - 2, 6 - dimethyl - aniline and from benzoyl chloride, N - (1' - methyl - 2', 2' - dimethoxy - ethyl) - N - (2, 6 - dimethyl - phenyl) - benzamide (Compound 5, Table 1) was prepared in the form of clear oil.

Example 12

Preparation of N - (methyl - methoxycarbonyl - methylene) - 2, 6 - dimethyl aniline



A solution of 2, 6 - dimethyl aniline (37.2 ml, 0.3 mole) in benzene (200 ml) was mixed with 0.5 g of $ZnCl_2$ and added dropwise at room temperature to 33.2 ml (0.33 mole) of methyl pyruvate. The reaction mixture was heated at reflux for 7 hours whilst azeotropically distilling the water that formed during the reaction, then the solvent was evaporated, to yield 65 g of an oil, which was distilled, collecting the fraction that boiled at 87 to 88°C at a pressure of 0.07 mmHg.

42.5 g of product having a purity of 92% by GLC (yield = 63.5%) were obtained.

Example 13

Preparation of N - (2, 6 - dimethylphenyl) - N - (1' - carbomethoxyvinyl) - phenylacetamide (Compound 11, Table 1)

4.35 ml of phenyacetyl - chloride (0.033 mole) were added dropwise at room temperature to a solution of 6.7 g (0.03 mole) of N - (methyl - methoxycarbonyl - methylene) - 2, 6 - dimethyl aniline (prepared as described in Example 12 and at 92% purity) in toluene (100 ml). The reaction mixture was heated at reflux and kept under a nitrogen stream for 3 hours, whereupon the solvent was evaporated, to yield 10.8 g of a light yellow oil which solidified by rubbing. The rough product obtained was crystallized from petroleum ether, to yield 2 g of product (a white solid pure by TLC), the yield being of 21% (TLC = thin layer chromatography).

Example 14

Preventive activity on vine mildew. (Plasmopara viticola (B et C) Berl et de Toni).

Leaves of vines cv. Dolcetto, cultivated in pots in a conditioned environment at 25°C and 60% relative humidity, were treated by spraying onto both faces the products being tested in an aqueous solution of acetone (20% by volume of acetone). At different periods of time from the treatment the leaves were sprayed on their lower faces with an aqueous suspension of conids Plasmopara viticola (200,000 conids/cc); after a 24-hour residence time in a humidity-saturated environment, at 21°C, the plants were transferred to 70% relative humidity and 21°C for the incubation period (7 days). Finally, the intensity of the infection was evaluated according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (thoroughly infected plant). The results are reported in Table 2.

Example 15

Curative activity on vine mildew. (Plasmopara viticola (B et C) Berl et de Toni).

The leaves of vine plants cv. Dolcetto, cultivated in pots in a conditioned environment at 25°C and 60% relative humidity, were sprayed on their lower faces with an aqueous suspension of conids of *Plasmopara viticola* (200,000 conids/cc); after a 24-hour residence time in a humidity-saturated environment at 21°C, the plants were divided into three groups. The plants of each group were treated by spraying the leaf faces with the products being tested in an aqueous solution of acetone (20% of acetone vol./vol.) after 1, 2 and 3 days respectively from the infection.

At the conclusion of the incubation period (7 days) the seriousness of the infection was evaluated visually according to indexes of an evaluation scale rang-

ing from 100 (sound plant) to 0 (fully infected plant). The results are reported in Table 2).

Example 16

Immuninzing activity on vine mildew. (Plasmopara viticola (B et C) Berl et de Toni).

The leaves of vine plants cv. Dolcetto, cultivated in pots in a conditioned environment, were sprayed on their upper faces with the product being tested in an aqueous solution of acetone (20% acetone vol./vol.). The plants were then kept in a conditioned environment for 6 days; on the 7th day they were sprayed on their lower faces with a suspension of conids of *Plasmompara viticola* (200,000 conids/cc); after a 24-hour residence period in a humidity-saturated environment, the plants were brought again into a conditioned environment. At the conclusion of the incubation period (7 days) the seriousness of the infection was evaluated visually according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant.) The results are reported in Table 2.

Example 17

Preventive systemic activity on vine mildew. Plasmopara viticola (B et C) Berl et de Toni).

Vine plants cv. Dolcetto, cultivated in pots in a conditioned environment at 25°C and 60% relative humidity, were treated by introducing into the soil in an aqueous solution of acetone (10% acetone vol./vol.) the product being tested, at a concentration of 0.01% (referred to the earth volume).

The plants were maintained in a conditioned environment and at different time stretches from the treatment, the leaves were sprayed on their lower faces with an aqueous suspension of conids of *Plasmopara viticola* (200,000 conids/cc). After a 24-hour residence time in a humidity-saturated environment at 21°C, the plants were transferred to 70% relative humidity and 21°C for the duration of the incubation period (7 days). Finally, the intensity of the infection was evaluated according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (thoroughly infected plant). The results are reported in the following Table 2.

Table 2

Fungicidal activity against Plasmopara viticola on vine

Compound No.	Type of action	Preventive		Curative		Immunizing Systemic		Systemic	
	Treatment	on leaves		on leaves		on upper leaves		soil	
	Dose (%)	days (a) 1	7	days (a) 1	7	days (a) 1	7	days (a) 1	7
18(b)	1	100	100	100	100	100	100	100	100
	0.5	100	100	100		100	100	100	
	0.1	100	100	100		100	100		
19(c)	1	100	100			100			
	0.5	100							
	0.1	100							
Zineb (reference commerical fungicide)	1	90							
	0.5	70							
	0.1	30							

(a) days elapsed from the treatment to the infection or vice-versa.

(b) N - (2, 6 - dimethylphenyl) - N - acetacetyl - α - amino - methylproprionate.

(c) N - (2, 6 - dimethylphenyl) - N - acetacetyl - α - amino - ethylpropionate.

The data obtained from a comparison with Zineb, a commercial fungicide widely utilized prove that the compounds of the present invention are by far more active, the doses being equal.

Example 18

Preventive activity on tobacco mildew. (Peronospora tabacina Adam).

The leaves of tobacco plants cv. Burley, cultivated in pots in a conditioned environment, were treated by spraying onto both leaf faces the product being tested in an aqueous solution of acetone (20% acetone vol./vol.). 2 days after the treatment the leaves were sprayed on their lower faces with an aqueous suspension of conids of *Peronospora tabacina* (200,000 conids/cc). After a 6-hour residence period in a humidity-saturated environment, the plants were transferred to a conditioned environment at 20°C and 70% relative humidity for the incubation of the fungus. At the conclusion of the incubation period (6 days) the seriousness of the infection was evaluated visually according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant). The results are reported in Table 3.

Example 19

Curative activity on tobacco mildew. (Peronospora tabacina Adam).

The leaves of tobacco plants cv. Burley, cultivated in pots in a conditioned environment were sprayed on their lower faces with an aqueous suspension of conids of *Peronospora tabacina* (200,000 conids/cc). After a 6-hour residence in a humidity-saturated environment, the plants were divided into 2 groups and transferred into a conditioned environment at 20°C and 70% relative humidity for the incubation of the fungus. 24 and 48 hours after the infection the first and the second group respectively were treated by spraying the product being tested in an aqueous solution of acetone (20% acetone vol./vol.) on both leaf faces.

At the conclusion of the incubation period (6 days) the seriousness of the infection was evaluated visually according to an evaluation scale range from 100 (sound plant) to 0 (thoroughly infected plant). The results are reported in Table 3.

Table 3

Fungicidal activity against Peronospora tabacina

Compound No.	Type of action	Preventive	Curative
	Treatment	on leaves	on leaves
	Dose (%)	days(a) 2	days(a) 2
18(b)	1	100	100
	0.5	100	100

(a) days elapsed from the treatment to the infection or vice-versa.

(b) N-(2,6-dimethylphenyl)-N-acetacetyl-α-amino-methyl-propionate.

Example 20

Preventive activity on tomato mildew. (Phytophthora infestans (Mont) de Bary).

Leaves of tomato plants cv. Marmande, cultivated in pots in a conditioned environment at 26°C and 6% relative humidity, were sprayed with an aqueous solution of acetone (20% acetone vol./vol.) of the products being tested. After 1 day the infection was effected by spraying the lower faces of the leaves with an aqueous suspension of conids of *Phytophthora infestans* (200,000 conids/cc); after a 24-hour residence in a humidity-saturated environment at 21°C, the plants were transferred, for the incubation period (4 days), to another conditioned environment at 70% relative humidity and 21°C.

At the conclusion of such period, the seriousness of the infection was evaluated according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant). The results are reported in Table 4.

Example 21

Curative activity on tomato mildew. (Phytophthora infestans (Mont) de Bary).

Leaves of tomato plants cv. Marmande, cultivated in pots in a conditioned environment at 26°C and 60% relative humidity, were sprayed on their lower faces with an aqueous suspension of conids of *Phytophthora infestans* (200,000 conids/cc).

After a 24-hour residence period in a humidity-saturated environment, the leaves were treated with the product being tested in an aqueous solution of acetone (20% acetone vol./vol.) by spraying both leaf faces. At the conclusion of the incubation period (4 days) the seriousness of the infection was evaluated visually according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (fully infected plant). The results are reported in Table 4.

Example 22

Preventive systemic activity on tomato mildew. (Phytophthora infestans (Mont) de Bary).

Tomato plants cv. Marmande, cultivated in pots in a conditioned environment at 26°C and 60% relative humidity, were treated by adding to the soil in an aqueous solution of acetone (10% acetone vol./vol.) the product being tested, at a concentration of 0.01% (referred to the earth volume).

The plants were kept in a conditioned environment and, after 3 days from the treatment, the leaves were sprayed, on their lower faces, with an aqueous suspension of conids of *Phytophthora infestans* (200,000 conids/cc).

After a 24-hour residence in a humidity-saturated environment at 21°C, the plants were transferred into another conditioned environment at 70% relative humidity and 21°C, where they were left over the incubation period (4 days). At the end of the period, the intensity of the infection was evaluation according to indexes of an evaluation scale ranging from 100 (sound plant) to 0 (completely infected plant). The results are reported in the following Table 4.

Table 4

Fungicidal activity against Phytophthora infestans on tomato

Compound No.	Type of action	Preventive	Curative	Systemic
	Treatment	on leaves	on leaves	soil
	Dose (%)	days(a) 1	days(a) 1	days(a) 3
18(b)	1	100	100	100
	0.5	100	100	100
	0.1	-	-	100

(a) days elapsed from the treatment to the infection or vice-versa.

(b) N-(2,6-dimethylphenyl)-N-acetactyl-α-amino-methyl-propionate.

Example 23

Determination of the phytotoxicity

The leaves of vine plants cv. Dolcetto, cultivated in pots in a room conditioned at 25°C and 60% relative humidity, were treated by spraying both their faces with the products being tested in an aqueous solution of acetone (20% acetone vol./vol.).

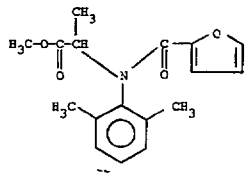
The seriousness of the phytotoxic symptoms was visually evaluated after 7 days according to indexes of an evaluation scale ranging from 100 (fully damaged plant) to 0 (sound plant).

Table 5 shows the fungicidal activity of compounds of the present invention and the phytotoxicity of same. Both these data are compared with those of "Furalaxyl". a known product disclosed in German Offenlegungsschrift No. 2 513 788 and "Ridomil" disclosed in German Offenlekungsschrift No. 2 515 091. The values concerning the fungicidal activity and the phytotoxicity have been determined as described in Examples 23 and 15. From the comparison between the recorded data it is clear that, with equal application does, the compounds of this invention exhibit a fungicidal activity equal to the one of "Furalaxyl" and "Ridomil", but possess a much lower phytotoxicity.

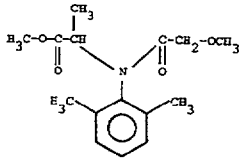
Table 5

Products	Curative activity against Plasmopara viticola on vine, by application to leaves effected 24 hours after infection, at doses of 0.1%.	Phytotoxicity index at doses of 3%.
Compound 1	100	25
Compound 2	100	0
Compound 3	100	5
Compound 4	100	10
Ridomil *	100	100
Furalaxyl *	100	100

* "Furalaxyl" = N - (2, 6 - dimethylpheny - N - (1' - carbomethoxy - ethyl) - 2 - furoylamide



* "Ridomil" = N - (2, 6 - dimethylphenyl) - N - (1' - carbomethoxy - ethyl) - methoxyacetamide



The damage caused by phytotoxicity to the plants cannot be avoided by using the dose of fungicidal product, which results to be the best compromise between the fungicidal activity of the product and its phytotoxicity.

In the practical application in agriculture, the amount of fungicidal product which actually remains on the plant varies markedly depending upon the weather conditions (especially frequency of precipitations) and the correctness and frequency of the treatments effected by the farmer. It is therefore necessary to have fungicidal products endowned with a good activity as well as with a wide margin of safety, so that even high doses of product cannot damage the plants.

The following Table 6 shows a comparison between the fungicidal activity of compounds according to the present invention and the activity of "Furalaxyl" and "Ridomil" at different application doses, and the phytotoxicity of the same compounds at increasing doses.

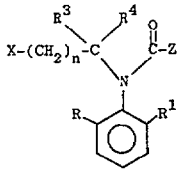
From the comparison between the data recorded on Table 6 it is evidence that the fungicidal activity of the compounds of this invention is of the same order of magnitude as the one of the comparison compounds, but the phytotoxicity is substantially lower as the application dose increases.

Table 6

Compound	Curative activity against Plasmopara viticola on vine at indicated doses (%).				Phytotoxicity index at the indicated doses (%).			
	0.1	0.05	0.01	0.005	0.75	1.5	3	9
1	100	98	76	41			25	
2	100	80	70	60			0	0
4	100	100	100	100	0	0	10	37
8	100	100	100	100			30	
Furalaxyl	100	100	100	100	32	53	100	100
Ridomil	100	100	100	100	30	54	100	100

CLAIMS

1. A compound of the general formula:



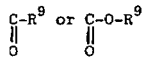
(I)

in which:

R and R^1 may be the same or different and each represent a hydrogen atom or a CH_3, C_2H_5, n - C_3H_7, - CH_2 - CH = CH_2 or - CH = CH - CH_3 group,

R^3 and R^4 may be the same or different and each represent a hydrogen, chlorine or fluorine atom, an alkyl group having 1 to 3 carbon atoms or a halomethyl, alkoxymethyl, CN, O-alkyl or S-alkyl group, or R^3 and R^4 together represent CH_2 =,

X represents



(in which R^9 represents an alkyl group having 1 to 3 carbon atoms), CN, - $CH(OR^5)_2$ (in which R^5 represents an alkyl or alkylidene group) or

(in which R^6 and R^7 may be the same or different and each represent a hydrogen atom or an alkyl group),

n is 0 or 1,

Z represents an optionally substituted phenyl group,

(in which R^2 represents a hydrogen atom or CH_3 group, m is 1 or 2 and Y represents an alkynyl group having 2 to 8 carbon atoms, an optionally substituted phenyl group, a cycloalkyl group having 3 to 8 carbon atoms, a phenylacetyl, furyl, thienyl or pyridyl group or a heterocyclic group containing 2 or 3 heteroatoms one of which is other than nitrogen) or

(in which R^8 represents a CH_3, alkoxymethyl, halomethyl or O-alkyl group).

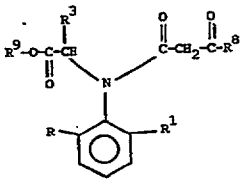
2. A compound as claimed in Claim 1 in which Z is

and R^8 is as defined in Claim 1.

3. A compound as claimed in Claim 1 or Claim 2 in which n is 0 and X is

in which R^9 is as defined in Claim 1.

4. A compound as claimed in Claim 1 having the formula:



in which R, R^1 and R^8 are as defined in Claim 1 and R^9 represents an alkyl group having 1 to 3 carbon atoms and R^3 represents CH_3 or C_2H_5.

5. N - (2, 6 - dimethylphenyl) - N - acetoacetyl - α - amino - methylpropionate.

6. N - (2, 6 - dimethylphenyl) - N - acetoacetyl - α - amino - ethylpropionate.

7. N - (2 - methyl - 6 - allyl - phenyl) - N - carboxymethylacetyl - α - amino - methylpropionate.

8. N - (2, 6 - diallyl - phenyl) - N - carboxymethyl - acetyl - α - amino - methylpropionate.

9. N - (2, 6 - dimethyl - phenyl) - N - carboxymethylacetyl - α - amino - methylpropionate.

10. N - (2 - methyl - 6 - ethylphenyl) - N - carboxymethylacetyl - α - amino - methylpropionate.

11. N - (2, 6 - diethylphenyl) - N - carboxymethylacetyl - α - amino - methylpropionate.

12. N - (2, 6 - dimethylphenyl) - N - chloroacetoacetyl - α - amino - methylpropionate.

13. N - (2, 6 - diallylphenyl) - N - acetoacetyl - α - amino - methylpropionate.

14. N - (2 - methyl 6 - allyl - phenyl) - N - acetoacetyl - α - amino - methylpropionate.

15. N - (2, 6 - dimethylphenyl) - N - acetoacetyl - α - amino - iso - propyl - propionate

16. N - [2 - methyl - 6 - (1' propenyl) - phenyl] - N - acetoacetyl - α - amino - methylpropionate.

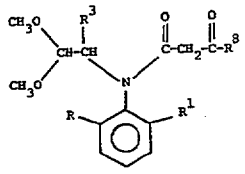
17. N - (2 - allyl - phenyl) - N - acetoacetyl - α - amino - methylpropionate.

18. N - (2, 6 - dimethyl - phenyl) - N - acetoacetyl - α - amino - methylbutyrate

19. A compound as claimed in Claim 2 in which X represents

in which R^5 represents an alkyl group.

20. A compound as claimed in Claim 19, having the formula:



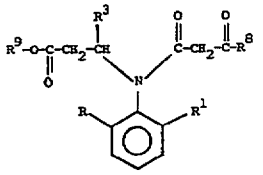
in which R, R^1 and R^8 are as defined in Claim 1 and R^3 represents a hydrogen atom or CH_3 group.

21. N - (2, 2 - dimethoxy - ethyl) - N - (2, 6 - dimethylphenyl) - carboxymethylacetamide.

22. N - (1 - methyl - 2, 2 - dimethoxy - ethyl) - N - (2, 6 - dimethylphenyl) - acetoacetamide.

23. A compound as claimed in Claim 2 in which n is 1.

24. A compound as claimed in Claim 23 having the formula:



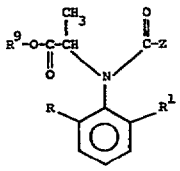
in which R, R^1 and R^8 are as defined in Claim 1, R^3 represents a hydrogen atom or CH_3 group, and R^9 represents an alkyl group having 1 to 3 carbon atoms.

25. N - (2, 6 - dimethylphenyl) - N - acetoacetyl - β - amino - methylpropionate.

26. A compound as claimed in Claim 1 in which Z is an optionally substituted phenyl group.

27. A compound as claimed in Claim 26 in which R^4 represents a hydrogen atom and n is 0.

28. A compound as claimed in Claim 27, having the formula:



in which R, R^1 and R^9 are as defined in Claim 1 and Z represents an optionally substituted phenyl group.

29. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxyethyl) - benzamide.

30. N - (2, 6 - dimethylphenyl) - N - (1 - carboisopropoxy - ethyl) - benzamide.

31. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - 2 - methyl - benzamide.

32. N - (2 - allyl - phenyl) - N - (1 - carbomethoxy - ethyl) - benzamide.

33. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - 4 - methoxy - benzamide.

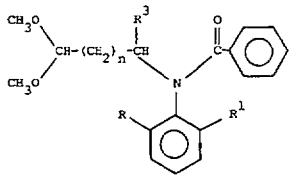
34. N - (2, 6 - dimethylphenyl) - N - (1 - carboethoxy - ethyl) - benzamide.

35. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - 4 - chloro - benzamide.

36. A compound as claimed in Claim 26 in which X represents

in which R^5 represents an alkyl group.

37. A compound as claimed in Claim 36 having the formula:



in which R, R^1, R^3 and n are as defined in Claim 1.

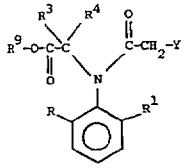
38. N - (1 - methyl - 2, 2 - dimethoxy - ethyl) - N - (2, 6 - dimethylphenyl) - benzamide.

39. N - (2,2 - dimethoxy - ethyl) - N - (2,6-dimethylphenyl) - benzamide.

40. A compound as claimed in Claim 1 in which Z is R^2 - $(CH)_m$ - Y in which R^2, Y and m are as defined in Claim 1.

41. A compound as claimed in Claim 40 in which n is 0.

42. A compound as claimed in Claim 41 having the formula:



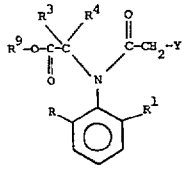
in which R, R^1, R^3, R^4 and R^9 are as defined in Claim 1 and Y represents a furyl or thienyl group or a cycloalkyl group having 3 to 8 carbon atoms.

43. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - (2) - furylacetamide.

44. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - (2) - thienylacetamide.

45. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - cyclohexylacetamide.

46. A compound as claimed in Claim 40 having the formula:



in which R, R^1, R^3, R^4 and R^9 are as defined in Claim 1 and Y is an optionally substituted phenyl group.

47. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - phenylacetamide.

48. N - (2, 6 - dimethylphenyl) - N - (1 - carboisopropoxy - ethyl) - phenylacetamide.

49. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - vinyl) - phenylacetamide.

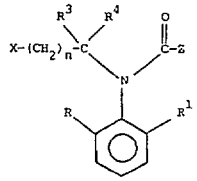
50. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - propyl) - phenylacetamide.

51. N - (2, 6 - dimethylphenyl) - N - (1 - carboethoxy - ethyl) phenylacetamide.

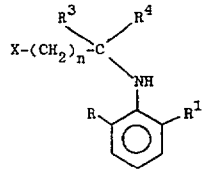
52. N - (2, 6 - dimethylphenyl) - N - (1 - carbomethoxy - ethyl) - 4 - methoxy - phenylacetamide.

53. A compound as claimed in Claim 1 substantially as herein described with reference to any one of the Examples.

54. A process for preparing a compound of the general formula:

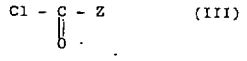


in which R, R^1, R^3, R^4, X, Y and n are as defined in Claim 1,
comprising reacting an aniline of the general formula:



(II)

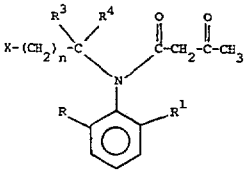
in which R, R^1, R^3, R^4, X and n are as defined in Claim 1,
in an inert solvent and in the presence of dimethylformamide or of a halogenhydric acid accepting base, with a compound of the formula:



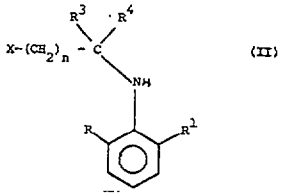
(III)

in which Z is defined in Claim 1.

55. A process for preparing a compound of the general formula:

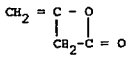


in which R, R^1, R^3, R^4, X and n are as defined in Claim 1,
comprising reacting an aniline of the formula:



(II)

in which R, R^1, R^3, R^4, X and n are as defined in Claim 1, in an inert solvent with diketene of the formula:



56. A process as claimed in Claim 54 or Claim 55 substantially as herein described with reference to any one of Examples 1 to 13.

57. A method for combatting infections of phytopathogenous fungi on plants, when the infection has not yet begun or when the infection is already in progress comprising applying to the plants or to the soil in which they are growing an effective amount of one or more of the compounds as claimed in any of claims 1 to 54.

58. A method as claimed in Claim 57 in which the phytopathogenous fungi is vine mildew *(Plasmopara viticola* (B et C) Berl et de Toni).

59. A method as claimed in Claim 57 in which the phytopathogenous fungi is tobacco mildew *(Peronospora tabacina* Adam).

60. A method as claimed in Claim 57 in which the phytopathogenous fungi is tomato mildew *(Phytophthora infestant* (Mont) de Bary).

61. A fungicidal composition containing as active principle one or more of the compounds as claimed in any of claims 1 to 54.

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