

PATENT SPECIFICATION

(11) 1 377 458

1 377 458

- (21) Application No. 23108/73 (22) Filed 15 May 1973
 (31) Convention Application No. 2 224 244 (32) Filed 18 May 1972
 (31) Convention Application No. 2 308 067 (32) Filed 19 Feb. 1973 in
 (33) Germany (DT)
 (44) Complete Specification published 18 Dec. 1974
 (51) International Classification C07D 49/38; A01N 9/36; C07D 55/12,
 87/22, 5/14; C07F 9/28
 (52) Index at acceptance

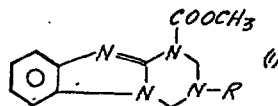
C2C 1173 1175 1177 1178 1182 1202 1222 142X 1470 1562
 200 202 213 214 215 220 221 222 225 226 22X
 22Y 246 247 250 252 253 255 25Y 28X 305 30Y
 311 313 31Y 323 32Y 338 360 361 362 364 365
 366 368 36Y 373 37X 37Y 463 464 552 612 620
 623 624 628 634 638 650 652 658 65X 660 662
 678 680 688 694 699 790 79Y BC LS QU
 C2P 3B13 3B14B 3B19B 7 B1 B



(54) TRIAZINO-BENZIMIDAZOLES

(71) We, FARBERWERKE HOECHST AKTIENGESELLSCHAFT, vormals Meister Lucius & Brüning, a body corporate organised according to the laws of Germany, of 6230 Frankfurt (Main) 80, Postfach 80 03 20, 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 provides a triazino-benzimidazole of the formula I

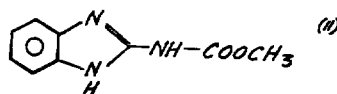


wherein R represents an alkyl group having from 1 to 18 carbon atoms; an alkenyl group having from 3 to 18 carbon atoms, an alkynyl group having from 2 to 8 carbon atoms, a cycloalkyl group having from 3 to 12 carbon atoms, which may be substituted by one or more alkyl groups having from 1 to 4 carbon atoms or by a hydroxy group;

a cyclohexylalkyl, cyclohexylalkenyl, or cyclohexylalkynyl group each having from 1 to 3 carbon atoms in the aliphatic chain, an endomethylene-cyclohexylmethyl, endomethylene-cyclohexenylmethyl, tricyclodecyl or tricyclodecenyl group; a phenylalkyl, diphenylalkyl or triphenylalkyl group each having from 1 to 6 carbon atoms in the alkyl radical, the phenyl nucleus being unsubstituted or substituted by a halogen atom or an alkyl, alkoxy or alkylthio group each having from 1 to 4 carbon atoms or a di-(C₁—C₄)-alkylamino group;

a phenyl or naphthyl group, which may be substituted by an alkyl group having from 1 to 4 carbon atoms, a halogen atom, a halogeno-alkyl group having from 1 to 4 carbon atoms, a trifluoromethyl or hydroxyl group, an alkoxy group having from 1 to 4 carbon atoms, a phenoxy or (C₁—C₄)-alkylthio group, a di-(C₁—C₄)-alkyl-amino-(C₂—C₆)-alkyl group; a hydroxy-(C₂—C₁₂)-alkyl, (C₂—C₁₈)-alkoxyalkyl or dialkoxyalkyl group, a (C₂—C₁₈)-alkylmercaptoalkyl, (C₃—C₉)-di-alkylphosphinylalkyl, furfuryl-alkyl, morpholino-(C₁—C₄)-alkyl, pyrrolidino-(C₁—C₄)-alkyl, piperidino-(C₁—C₄)-alkyl or (C₂—C₁₂)-carbalkoxyalkyl group.

The present invention provides a process for the preparation of a compound of formula I, which comprises reacting 2-methoxy-carbonylamino-benzimidazole of the formula II



with a primary amine of the formula H_2NR (III) wherein R is defined as above and formaldehyde.

A preferred embodiment of the process of the present invention is the following: 2-Methoxycarbonylamino-benzimidazole (II) in suspended or dissolved in a solvent, a molar to twice molar amount of the amine is added and subsequently, with agitation, a two to four times molar amount of an aqueous formaldehyde solution is added. The operational temperature is advantageously kept at 0° to $80^\circ C$, especially from 20° to $40^\circ C$, but the temperature range is not critical. The reaction product normally dissolves and may be separated by filtering the solution from a 2-methoxycarbonylamine-benzimidazole residue; concentration of the solution and treatment with an inert solvent, for example, benzene, or reprecipitation, for example, from methylene chloride/benzene, yields the triazinobenzimidazole in purified form.

The reaction always proceeds with formation of the final product I, even when there is a deficiency of formaldehyde.

Preferred amines of formula III for the reaction are those in which R is a straight-chain or branched-chain alkyl group having from 1 to 15 carbon atoms; an alkenyl group having from 3 to 18 carbon atoms; a cycloalkyl group having from 3 to 12 carbon atoms, which may be substituted by an alkyl group having from 1 to 4 carbon atoms, especially by methyl or ethyl; a tricyclodecyl, phenyl or naphthyl group; a phenyl or naphthyl group mono- or di-substituted by one or two methyl, ethyl, tert-butyl or hydroxy groups or a chlorine atom; a phenylalkyl group having from 7 to 9 carbon atoms, especially a benzyl group, or a diphenylalkyl group having from 13 to 14 carbon atoms the phenyl groups of which may be substituted by a chlorine atom or a methyl group; an alkoxy-alkyl, dialkoxyalkyl or alkylmercapto-alkyl group having from 3 to 8, especially from 3 to 4 carbon atoms; a hydroxyalkyl group having from 3 to 7, especially from 3 to 6 carbon atoms; a dialkyl-phosphinylalkyl group having from 3 to 9, especially from 3 to 5 carbon atoms; a morpholino-alkyl group having from 5 to 8, especially from 6 to 7 carbon atoms, or a carbalkoxy group having from 3 to 12, especially from 4 to 8 carbon atoms.

In addition to the amines used in the examples, the following amines may advantageously be used: iso-amylamine, iso-octylamine, nonyl amine, *n*-decylamine, iso-decylamine, *n*-undecylamine, pentadecylamine, hexadecylamine, octadecylamine, *n*-octadecen-9-ylamine, cyclobutylamine, 2-methyl-cyclopentylamine, *N,N*-dimethyl-, *N,N*-diethyl-, *N,N*-dibutyl-, *N,N*-methylethyl-, *N*-methyl-*N*-propyl-, *N*-ethyl-*N*-isobutyl-ethylene-diamine or the corresponding propylenediamines, tetramethylene-diamines and hexamethylene-diamines, 3-amino-hexahydro-toluene, 4-amino-hexahydro-*m*-xylene, 4-isopropyl-cyclohexylamine, 4-ethyl-cyclohexylamine, 2,6-diethylaniline, 4-tert.-butyl-aniline, 2-, 3- and 4-chloroaniline, 2-, 3- and 4-aminophenol, α - and β -naphthylamine, 3-phenylpropylamine, 2-phenylethylamine, 4-phenyl-butylamine, diphenylmethylaniline, 2,2-diphenylethylamine, 2-, 3- and 4-chlorobenzylamine, 2-(2'-chlorophenyl)-ethylamine, 2-, 3- and 4-methylbenzylamine, 2-ethylthio-ethylamine, 4-methylthio-butylamine, 1- and 4-amino-hexanol, dimethyl-(2-amino-ethyl)-phosphine oxide, diethyl-(4-aminobutyl)-phosphine oxide, *N*-aminomethyl-morpholine, *N*-(3-aminopropyl)-morpholine, *N*-aminoethyl-pyrrolidine, *N*-aminomethyl- and *N*-aminoethyl-piperidine, furfurylamine, aminoacetic acid methyl- and -ethyl ester, 2-aminopropionic acid methyl ester, 3-aminobutyric acid ethyl ester, 6-aminocaproic acid methyl- and -ethyl ester, alanine methyl ester γ -aminovaleic acid methyl- and -ethyl ester, 4-methoxybenzylamine, 4-tert.-butyl-cyclohexylamine, 2-amino-1,3,5-trimethylbenzene, 2-aminobutane, 2-ethylhexylamine, *n*-tridecylamine and tetradecylamine, or iso-tetradecylamine.

Suitable solvents for the reaction are especially moderately or weakly polar solvents, preferably those having a low boiling point, for example, methylene chloride, chloroform, carbon tetrachloride, benzene; ethers, for example, diethyl ether, di-isopropyl ether or tetrahydrofuran; esters, for example, methyl acetate or ethyl acetate; or ketones, for example, acetone or methylethyl ketone. Preferably, chloroform or methylene chloride is used.

2-Methoxycarbonylamine-benzimidazole may be prepared according to the method described in J. Am. Chem. Soc. 56, 144 (1934), by reaction of *o*-phenylene-diamine with *S*-methyl-isothiurea dicarboxylic acid dimethyl ester. The preparation of the amines required for the reaction is also known from the literature.

The compounds of the invention have an excellent fungicidal action.

The present invention therefore provides a pesticide, especially a fungicide, comprising a triazino-benzimidazole of formula I as active substance, especially in concentrations, of from 2 to 95%, in admixture or conjunction with one or more known formulation additives, for example, solid or liquid inert carriers, adhesives, wetting and dispersing agents and grinding auxiliaries, in the form of wettable powders, emulsions, suspensions, dusting powders or granules. The compounds of formula I may be mixed with other fungicides with which they form compatible mixtures.

As carrier material, mineral substances, for example, aluminium silicates, argillaceous earths, kaolin, chalks, siliceous chalks, talcum, kieselguhr or hydrated silicic acids can be used, or preparations of these mineral substances with special additives, for example, chalk with sodium stearate. As carrier material for liquid preparations, any suitable organic solvents may be employed, for example, toluene, xylene, diacetone alcohol, isophorone, gasolines, paraffin oils, dioxan, dimethyl formamide, dimethyl sulphoxide, ethyl acetate, tetrahydrofuran and chlorobenzene.

Suitable adhesives are glue-like cellulose products or polyvinyl alcohols.

As wetting agents, any suitable emulsifiers may be used, for example, ethoxylated alkylphenols, salts of aryl- or alkyl-aryl-sulphonic acids, salts of oleyl-methyl-taurine or of ethoxylated benzenesulphonic acids, or soaps.

Suitable dispersing agents are cellulose pitch (salts of ligninsulphonic acid), salts of naphthalenesulphonic acid or salts of oleyl-methyl-taurine.

As grinding auxiliaries, suitable inorganic or organic salts, for example sodium sulphate, ammonium sulphate, sodium carbonate and sodium bicarbonate, sodium thiosulphate, sodium stearate, or sodium acetate may be used.

The invention also provides a method for preventing or combating a fungal disease in a plant or plant product, plant habitat or potential plant habitat which comprises applying to a plant, plant product, plant habitat or potential plant habitat a compound or a preparation of the invention. The plant product may be, for example, a fruit, vegetable or seed, or paper, wood or a fibre. The plant habitat or potential plant habitat may be soil, or a soil-less or soil-containing compost, for example, a seeding or potting compost. The compound or preparation may be sprayed onto or mixed with the object to be treated.

The compounds of the invention have a good systemic fungicidal action and so are particularly useful for combating fungi which have entered plant tissues. This is especially important in the case of those fungus diseases which have a long incubation period and, after the outbreak of the infection, cannot be combated by the usual fungicides. The activity range of compounds of the invention is very broad and they are effective against a number of fungi important in crop farming, fruit growing, viticulture, hop growing, and horticulture, for example, *Fusicladium* Spp, *Gloeosporium* Spp, *Septoria* Spp, *Mycosphaerella* Spp, *Cladosporium* Spp, *Colletotrichum* Spp, *Rhizoctonia* Spp, *Fusarium* Spp, *Cercospora* Spp, *Ustilagineae*, *Erysiphaceae*, *Aspergillaceae* or *Sclerotinaceae*. It may also be used to treat Dutch Elm disease.

Furthermore, a number of the compounds of the invention, especially those having long-chain groups as the substituent R have an excellent activity against phycomycetes, for example, the *Peronospora* or *Phytophthora* species. Their degree of efficiency in this particular respect is equal to that of the metal salts of dithiocarbamic acid or the N-trichloromethylthio-phthalimide derivatives, and in many cases is even superior to them.

The compounds of the invention are useful for protecting stored fruits or vegetables against fungus infection, for example, by species of *Fusarium* or *Penicillium*.

The invention also provides a method for protecting a textile, dye, coating or paint against fungal infestation, which comprises applying a compound or preparation of the invention to a textile, dye, coating or paint.

The invention further provides an antihelmintic or fungicidal preparation for use in animals which comprises a compound of the invention in admixture or conjunction with a pharmaceutically suitable carrier.

The invention also provides a method of treating a commercially reared animal to combat a fungal or helminthic infection which comprises administering to an animal or a compound or veterinary preparation of the invention.

The following Examples of preparation and application illustrate the invention.

A) EXAMPLES OF PREPARATION

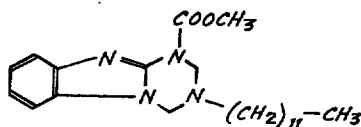
Example 1.

57.3 g (0.3 mole) of 2-methoxycarbonylamino-benzimidazole were suspended in 550 ml of methylene chloride, 55.5 g (0.3 mole) of dodecylamine were added and the mixture was heated to 35°C. At this temperature, 68 ml (0.8 mole) of aqueous 35%

formaldehyde solution were added dropwise with agitation, which was continued for 1 hour at 38°C, before the mixture was allowed to cool, also with agitation.

The non-converted 2-methoxycarbonylamino-benzimidazole was suction-filtered off, the aqueous layer was separated and the methylene chloride solution was dried over magnesium sulphate and concentrated, yielding 122.7 g of a crystalline substance having a melting point of 75°C.

In order to eliminate adhering amine, this substance was stirred with 200 ml of gasoline (30/85°C); thus obtaining 95 g (79% of the theoretical yield) of 1-methoxycarbonyl-3-dodecyl-s-hexahydrotriazino-benzimidazole having a melting point of 86° to 87°C.



$C_{23}H_{36}N_4O_2$ molecular weight: 400

calc: C 69.0%; H 9.0%; N 14.0%

found: C 69.3%; H 9.2%; N 14.0%

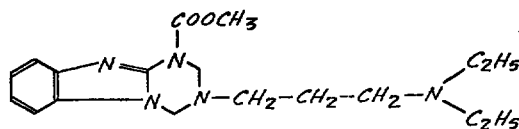
In the infrared spectrum, the compound had a characteristic carbonyl absorption at 1720 cm^{-1} , as well as double bond bands at 1620 cm^{-1} and 1595 cm^{-1} .

Example 1a.

57.3 g (0.3 mole) of 2-methoxycarbonylamino-benzimidazole were suspended in 900 ml of methylene chloride, and 39 g (0.3 mole) of 3-diethylamino-1-propylamine were added. The suspension was heated to 35°C. At this temperature, 60 ml (0.7 mole) of 35% formaldehyde solution were added dropwise with agitation, which was then continued at 38°C for 2 hours, before the mixture was allowed to cool, also with agitation.

The non-converted 2-methoxycarbonylamino-benzimidazole was suction-filtered off, the aqueous layer was separated, and the methylene chloride solution was dried over magnesium sulfate and concentrated, yielding an oily residue which was stirred at 30° to 85°C with gasoline. After decanting, the gasoline solution was concentrated, the oily residue obtained was redissolved in methylene chloride and washed twice with water. The methylene chloride solution was then dried over $MgSO_4$, concentrated, and the oily residue was degassed at room temperature under highly reduced pressure.

Yield: 37 g (36% of the theoretical yield) of a non-distillable oil.



$C_{23}H_{27}N_5O_2$ MW: 345

calc: C 62.6%; H 7.8%; N 20.2%

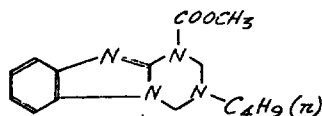
found: C 63.0%; H 8.5%; N 19.8%

Example 2.

38.2 g (0.2 mole) of 2-methoxycarbonylamino-benzimidazole were suspended in 600 ml of chloroform, 14.6 g (0.2 mole) of *n*-butylamine were added, and the whole was heated to 35°C. At this temperature, 68 ml (0.8 mole) of 35% aqueous formaldehyde solution was added dropwise, with agitation, which was then continued at 38°C for 1 hour. The benzimidazole dissolved while reacting. The mixture was allowed to cool, the aqueous layer was eliminated, and the organic phase was dried over magnesium sulfate.

After filtration and concentration, an oil was obtained which solidified after trituration with *n*-hexane.

Yield: 41 g (71% of the theoretical yield) of 1-methoxy-3-*n*-butyl-s-hexahydrotriazino-benzimidazole, melting point 109°C.



$C_{15}H_{20}N_4O_2$ MW 288

calc.: C 62.5%; H 6.94%; N 19.45%
found: C 62.8%; H 7.2 %; N 19.5 %

In the infrared spectrum, the compound showed a carbonyl absorption at 1745 cm^{-1} , and double bond bands at 1620 cm^{-1} .

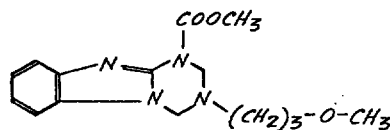
Example 3.

57.3 g (0.3 mole) of 2-methoxycarbonylamino-benzimidazole were suspended in 900 ml of methylene chloride, 26.7 g (0.3 mole) of 3-methoxy-propylamine were added and the whole was heated to 35°C . At this temperature, 68 ml (0.8 mole) of aqueous 35% formaldehyde solution were added dropwise, with agitation, which was subsequently continued at 38°C for 1 hour.

After cooling, the mixture was filtered off a small amount of non-converted starting benzimidazole. The aqueous phase was separated, and the methylene chloride solution was dried over magnesium sulfate.

After filtration and concentration, an oil was obtained which solidifies on trituration with n-hexane.

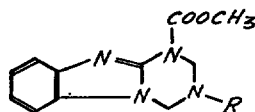
Yield: 63 g (69% of the theoretical yield) of 1-methoxycarbonyl-3-(3'-methoxypropyl)-s-hexahydro-triazino-benzimidazole. Melting point: 73° to 74°C .



$C_{15}H_{20}N_4O_3$ MW 304

calc.: C 59.2%; H 6.6%; N 18.7%
found: C 59.3%; H 6.9%; N 18.7%

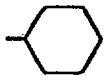
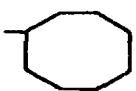
In the infrared spectrum, the compound showed a carbonyl absorption at 1750 cm^{-1} , and double bond bands at 1625 cm^{-1} and 1600 cm^{-1} . The substances of the formula

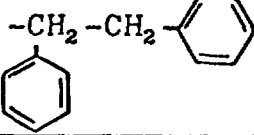
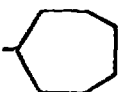
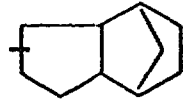


as indicated in the following Table are prepared according to Examples 1 to 3.

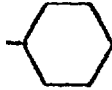
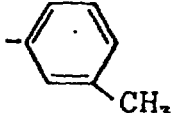
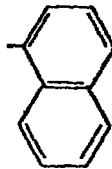
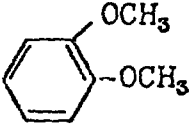
Table

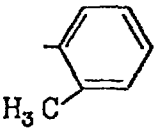
Example	R	Melting point °C
4	$-\text{CH}_3$	138
5	$-\text{C}_2\text{H}_5$	167-168
6	$-\text{C}_3\text{H}_7$ (n)	130-132
7	$-\text{C}_3\text{H}_7$ (iso)	112-114
8	$-\text{CH}-\text{CH}=\text{CH}_2$	106-108
9	$-\text{C}(\text{CH}_3)_3$	143
10	$ \begin{array}{c} \text{CH}_3 \\ \diagup \\ -\text{CH} \\ \diagdown \\ \text{CH}_2-\text{CH}_3 \end{array} $	136
11	$-\text{C}_4\text{H}_9$ (iso)	138
12	$-\text{C}_8\text{H}_{17}$ (n)	76-78
13	$-\text{C}_9\text{H}_{19}$ (iso)	139
14	$-\text{C}_{13}\text{H}_{27}$ (iso)	non-distill- able oil
15	$-\text{C}_8\text{H}_{13}$ (n)	75-76

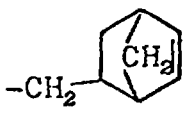
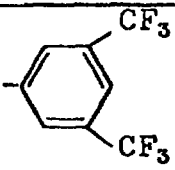
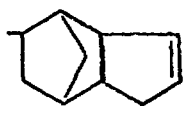
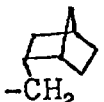
Example	R	M.p. °C
16	$-(\text{CH}_2)_3-\text{OH}$	154
17	$-\text{CH}_2-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$	110-112
18	$-\underset{\text{CH}_2-\text{CH}_3}{\text{CH}}-\text{CH}_2\text{OH}$	128-130
19	$-(\text{CH}_2)_5-\text{OH}$	86-88
20		130-132
21		165
22		155-156
23		171
24	$-\text{CH}_2-\text{C}_6\text{H}_5$	145-146
25	$-(\text{CH}_2)_2-\text{S}-\text{CH}_3$	107-109
26	$-(\text{CH}_2)_3-\text{S}-\text{CH}_3$	120-121
27	$-(\text{CH}_2)_3-\text{O}-\text{C}_2\text{H}_5$	84-85
28	$-(\text{CH}_2)_3-\text{O}-\text{C}_3\text{H}_7$	66-67

Example	R	M.p. °C.
29	$-(\text{CH}_2)_2-\text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{O}$	66-68
30	$-\text{CH}_2-\text{CH}_2-$ 	40-45
31	$-\text{CH}_2-\text{CH}-\text{CH}_3$ 	non-distill- able oil
32	$-(\text{CH}_2)_3-\text{CH} \begin{array}{l} \diagup \text{OC}_2\text{H}_5 \\ \diagdown \text{OC}_2\text{H}_5 \end{array}$	non-distill- able oil
33	$-\text{C}_7\text{H}_{15} \text{ (n)}$	73-74
34		118-120
35		133-134
36	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ -\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	151-152
37	$-\text{CH} \begin{array}{l} \diagup (\text{CH}_2)_5 \diagdown \\ \diagdown (\text{CH}_2)_5 \diagup \end{array} \text{CH}_2$	125-126
38	$-(\text{CH}_2)_2-\text{O}-\text{CH}_3$	99
39	$-\text{C}_9\text{H}_{19} \text{ (n)}$	106-107
40	$-\text{C}_9\text{H}_{19} \text{ (n)}$	100-102

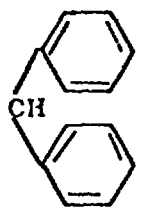
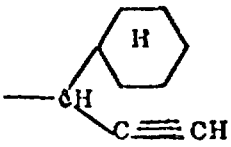
Example	R	M.p. °C
41	$-(\text{CH}_2)_3-\text{O}-\text{C}_4\text{H}_9$	non-distill- able oil
42	$-(\text{CH}_2)_3-\overset{\text{O}}{\underset{\text{CH}_3}{\underset{\text{CH}_3}{\text{P}}}}$	126-127
43	$-\text{C}_6\text{H}_{11}-\text{CH}_3$	152-153
44	$\text{H}_3\text{C}-\text{C}_6\text{H}_{11}$	112-114
45	$\text{H}_3\text{C}-\text{C}_6\text{H}_4-\text{H}_3\text{C}$	55-56
46	$-\text{C}_6\text{H}_5$	196-197
47	$-(\text{CH}_2)_2-\text{C}_6\text{H}_4-\text{Cl}$	158-159
48	$-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2-\text{COOCH}_3$	77-79
49	$-(\text{CH}_2)_3-\text{N}(\text{CH}_3)_2$	non-distill- able oil
50	$-(\text{CH}_2)_2-\text{N}(\text{CH}_3)_2$	110-114
51	$-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{CH}}}-\text{CH}_2-\text{N}(\text{CH}_3)_2$	non-distill- able oil

Example	R	M.p. °C
52	$-\text{CH}_2-$ 	154
53	 $-\text{C}(\text{CH}_3)_3$	132-134
54	$-\text{C}_{18}\text{H}_{35}$ (oleyl)	46-48
55	$-\text{C}_{16}\text{H}_{33}$	88-89
56		210 (decomp)
57	$-\text{C}_{18}\text{H}_{37}$ (stearyl)	89-90
58		70-73
59	$-\text{C}_{11}\text{H}_{23}$	92
60	$-\text{CH}_2-$  $-\text{Cl}$	140-142
61	$-\text{CH}_2-\text{CH}_2-$ 	142-143
62	$-\text{C}_{10}\text{H}_{21}$	85
63	$-\text{CH}_2-$  $-\text{OCH}_3$	146-148

Example	R	M _c p.
64	$-\text{CH}_2-\text{CH}_2-\text{CH} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	114-115
65	$-\text{C}_{15}\text{H}_{31}$ mixture with $-\text{C}_{13}\text{H}_{27}$	60-62
66		158
67	$-\text{C}_6\text{H}_{11}-\text{OH}$	179 (decomp.)
68	$-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5$	147
69	$-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_{11}$	137
70	$-\text{C}_6\text{H}_4-\text{CH}_3$	204-205
71	$-\text{C}_{13}\text{H}_{27}$	88
72	$-\text{C}_6\text{H}_4-\text{OH}$	245 (decomp.)
73	$-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{C}_4\text{H}_9$	84-87
74	$-\text{C}_{10}\text{H}_{21}$ (iso)	non-distill- able oil
75	$-(\text{CH}_2)_3-\text{O}-\text{CH} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$	60

Example	R	M.p. °C
76		190
77	$-(CH_2)_3-O-CH_2-\underset{\substack{ \\ C_2H_5}}{CH}-C_4H_9$	70-73
78		310-311
79	$-\underset{\substack{ \\ CH_3}}{CH}-CH_2-\underset{\substack{ \\ CH_3}}{CH}-CH_3$	73
80	$-C_7H_{13}$ mixture with C_9H_{17}	non-distill- able oil
81	$-C_{12}H_{25}$ mixture with $C_{18}H_{37}$	76-77
82		71-74
83	 (endo)	210-212
84	$-CH_2-$  (exo)	178-179
85	$-(CH_2)_3-O-(CH_2)_7-CH_3$ (mixture with 9)	non-distill- able oil
86	$-C_{14}H_{29}$	89-90

Example	R	M.p. °C
87	$-(\text{CH}_2)_3-\text{O}-\text{C}_{12}\text{H}_{25}$ (iso)	non-distillable oil
88	$-\text{CH}_2-\underset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}}(\text{C}_6\text{H}_4)-\text{CH}_2-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$	85-93
89	$-\text{CH}_2-\underset{\text{CH}_2-\text{C}_6\text{H}_3\text{Cl}_2}{\underset{\text{CH}_2-\text{C}_6\text{H}_3\text{Cl}_2}{\text{CH}}}(\text{C}_6\text{H}_4)-\text{CH}_2-\text{C}_6\text{H}_4-\text{N}(\text{CH}_3)_2$	95-105
90	$-\text{CH}_2-\text{CH}_2-\text{C}(\text{C}_6\text{H}_4\text{Cl})_3$	180-182

Example	R	M.p. °C
91	$-\text{CH}_2-\text{CH}_2-\text{CH}$ 	102 - 105 (decomp.)
92	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{CH}_3 \end{array}$	186 - 187
93	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ -\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{C}_2\text{H}_5 \end{array}$	130 - 132 (decomp.)
94		160 - 162 (decomp.)
95	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	143 - 144

B) EXAMPLES OF APPLICATION

Example I.

Cucumber plants were grown in pots, and in the 2-leaf stage treated, until drip-off, with aqueous suspensions of the compounds of Examples 1, 2 and 4 to 15. Before the treatment, newly grown leaves of the plants and the soil were carefully covered with plastic sheets in such a manner that they were not touched by the spray liquor.

The application concentrations were 2000, 1000, 500, 250 and 125 mg of active substance per liter of spray liquor. As comparative agent, benomyl (1-N-butyl-carbamoyl-2-methoxycarbonyl-amino-benzimidazole) was used.

After drying of the sprayed layer, the protective sheets were removed and the plants placed in a greenhouse. When the 4th and 5th leaves had developed, the plants were heavily infested with conidia of cucumber mildew (*Erysiphe cichoracearum*) and subsequently placed in a moisture chamber at a temperature of 22°C and a relative atmospheric humidity of 100%. After a residence time of 24 hours, the plants were

transferred to a greenhouse having a high relative atmospheric humidity (80 to 90%) and a temperature of from 22° to 23°C, where they were kept until the outbreak of the disease.

5 The evaluation of the infection was carried out visibly, as usual, and the infection degree is expressed in % of infested leaf area as compared to untreated, infested control plants. The results are shown in Table I. 5

Example II.

10 Garden earth was mixed in a shaking machine for 10 minutes with the compounds of the invention cited in Example I in application amounts of 10, 5, 2.5, 1.25, 0.6 and 0.3 mg of active substance/kg of earth. As comparative agent, benomyl was used in the same application amounts as the preparations of the invention. 10

15 Pots were charged with the earth so treated and 10 grains each of winter wheat of the brand Heine VII were sown, before the pots were placed in a greenhouse having a high atmospheric humidity and a temperature of 22°C for germination. After emergence of the wheat, the plants, in the 4- to 5- leaf stage, were heavily infested with conidia of the powdery mildew of cereals (*Erysiphe graminis*). After an incubation period of 14 days, the plants were visually examined for infection with mildew. The degree of infection was expressed in % of infested leaf area as compared to untreated, infested control plants. The results are indicated in Table II. 15

Example III.

20 Sugar beet plants in the 6-leaf stage were heavily infested with conidia of the beet leaf spot organism (*Cercospora beticola*) and placed dripping wet in a moisture chamber at 25°C and a 100% relative atmospheric humidity, where they were kept for 24 hours. Subsequently, they were placed in a greenhouse having a relative atmospheric humidity of from 85 to 90% and a temperature of from 24° to 25°C. After an infection time of 7 days, the plants were sprayed, until drip-off, with aqueous suspensions of the compounds cited in Example I. 20

25 The application concentrations were 60, 30, 15 and 7.5 mg/l of spray liquor. As comparative agent, benomyl was used in the same application concentrations. 25

30 After drying of the spray liquor, the plants were placed again in the greenhouse. After an incubation period of 3 weeks, the plants were examined for infection with beet leaf spot. The evaluation was carried out visually, and the degree of infection expressed in % of infested leaf area, as compared to untreated, infested control plants. The results are shown in Table III. 30

Example IV.

35 Tomato plants, in the stage of completely grown 3 leaves, were heavily infested with conidia of the leaf mould of tomatoes (*Cladosporium fulvum*), and placed dripping wet for one day in a moisture chamber having a temperature of 25°C and a relative atmospheric humidity of 100%. They were then transferred to a greenhouse having a relative atmospheric humidity of from 85 to 90%, and a temperature of from 23° to 25°C. After 7 days, the plants were treated with aqueous suspensions of the compounds according to Examples 16 to 24 in concentrations of 60, 30, 15 and 7.5 mg/l of spray liquor. As comparative agent, benomyl was used. 35

40 After drying of the sprayed layer, the plants were again placed in the greenhouse and, after an incubation period of 21 days, examined for infection with leaf mould. The infection was examined visually, as usual, and the degree of infection was expressed in % of infested leaf area relative to untreated, infested control plants. 40

The results are shown in Table IV. 45

Example V.

5 50 Wheat plants were grown in pots and in the 2-leaf stage treated, until drip-off, with the compounds cited in Example IV. The application concentrations were 2000, 1000, 500, 250 and 125 mg/l of spray liquor. As comparative agent, benomyl was used in the same concentrations of active substance as cited. 50

10 55 After drying of the layer of spray liquor, the plants were placed in a greenhouse, where they were kept until the 4th and 5th leaves were fully developed. In this stage, the plants were heavily infested with conidia of the powdery mildew of cereals (*Erysiphe graminis*), the temperature of the greenhouse was adjusted to 22° to 23°C, and the relative atmospheric humidity to 80 to 90%, in order to create optimum infection conditions for the mildew. 55

15 60 After incubation period of 10 days, the plants were visibly examined for infection, 60

and the degree of infection was expressed in % of infested area, relative to untreated, infested control plants. The results are indicated in Table V.

Example VI.

5 Winter wheat of the Heine VII brand was homogeneously seed-treated for 10 minutes in a shaking machine with the compounds cited in Example IV and benomyl, in application amounts of 200, 100, 50 and 25 g of active substance per 100 kg of seeds. 5

Subsequently, 5 times 10 grains each of the treated seeds were sown in pots filled with earth, and placed in a greenhouse for germination.

10 When the 4th and 5th leaves of the plants had developed, the plants were heavily infested with conidia of the powdery mildew of cereals (*Erysiphe graminis*) and the greenhouse adjusted to a relative atmospheric humidity of from 80 to 90% and a temperature of from 22° to 23°C. 10

15 After an incubation period of 10 days, the plants were examined for infection with mildew, and the degree of infection was expressed in % of infested leaf area, relative to untreated, infested control plants. The results are shown in Table VI. 15

Example VII.

20 Wheat plants of the Heine VII brand, in the 3-leaf stage, were infested with conidia of the powdery mildew of cereals (*Erysiphe graminis*) and, 3 days after the infection, treated with aqueous suspensions of the compounds according to Examples 3 and 25 to 32, until they were dripping wet. The application concentrations were 120, 60, 30 and 15 mg of active substance/l of spray liquor. As comparative agent, benomyl was used in the same application concentrations. 20

25 After drying of the sprayed layer the plants were placed in a greenhouse having a relative atmospheric humidity of from 80 to 90% and a temperature of from 22° to 23°C. 25

10 Days after the treatment, the plants were visually examined for infection with mildew. The degree of infection was expressed in % of infested leaf area, relative to untreated, infested control plants. The results of the test are indicated in Table VII.

Example VIII.

30 Cucumber plants in the 2-leaf stage were treated, until drip-off, with aqueous suspensions of the compounds cited in Example VII, in application concentrations of 2000, 1000, 500 and 250 mg of active substance/l of spray liquor; newly grown leaves and the soil being carefully protected by plastics sheets in such a manner that they were not touched by the spray liquor. The comparative agent was again benomyl. 30

35 After drying of the sprayed layer, the plants were placed in a greenhouse and were kept there until they had developed the 4th leaf. In this stage, all plants, including untreated control plants, were heavily infested with conidia of the cucumber mildew (*Erysiphe cichoracearum*), and placed in a moisture chamber having a temperature of 22°C and a relative atmospheric humidity of 100%. After 24 hours, the plants were transferred to a greenhouse having a high relative atmospheric humidity and a temperature of from 22° to 23°C. After an incubation period of 10 days, the plants were examined visually for infection with cucumber mildew. The degree of infection was expressed in % of infested leaf area, relative to untreated, infested control plants. The results are shown in Table VIII. 35

Example IX.

45 Rice plants in the 4-leaf stage were heavily infested with *Piricularia oryzae* and subsequently placed in a moisture chamber having a temperature of 25°C and a relative atmospheric humidity of 100%. After a residence time of 24 hours, the plants were transferred to a greenhouse having a relative atmospheric humidity of 85 to 90% and a temperature of 25° to 26°C. 4 Days after the infection, the plants were treated with the compounds cited in Example VII in application concentrations of 60, 30, 15 and 7.5 mg of active substance/l of spray liquor. As comparative agent, benomyl was used in the same application concentrations as above. 45

50 After drying of the sprayed layer, the plants were again placed in the greenhouse and, after an incubation period of 14 days, visually examined for infection with *Piricularia oryzae*. The degree of infection was expressed in % of infested leaf area, as compared to untreated, infested control plants. The results are shown in Table IX. 50

Example X.

60 Young vine plants of the *Peronospora* predisposed Müller-Thurgau brand, in the 4-leaf stage, were treated, until dripoff, with aqueous suspensions of the compounds of 60

ed,

10

in

ed

ily

he

n-

th

to

15

n-

c-

nd

30

as

a

to

th

to

30

d

ot

35

e

w

of

e

-

-

e

1

e

e

1

1

1

55

-

-

60

f

60

5

10

15

20

25

30

35

40

45

50

50

55

60

Examples 1 and 12 to 15. The application concentrations were 500, 250, 125 and 60 mg of active substance per liter of spray liquor. As comparative agents, benomyl (Comparative Agent I) and folpet (N-(trichloromethylthio)-phthalimide = Comparative Agent II) were used in the same concentrations of active substance as cited above.

After drying of the sprayed layer, the plants were heavily infested with a zoospore suspension of *Peronospora viticola* and placed dripping wet in a moisture chamber at a temperature of 20°C and a relative atmospheric humidity of 100%. After 24 hours, the infested plants were transferred to a greenhouse having a temperature of 23°C and an atmospheric humidity of from 80 to 90%. After an incubation period of 7 days, the plants, which had been wetted, were again placed in the moisture chamber overnight and thus the infection caused to appear. The evaluation of the infection was carried out visually, and the degree of infection was expressed in % of infested leaf area, as compared to untreated, infested control plants. The results are listed in Table X.

Example XI.

Vine plants grown from cuttings of the Müller-Thurgau brand, were sprayed in the 4-leaf stage, until drip-off, with aqueous suspensions of the compounds cited in Example X. The application concentrations were 20, 10, 5 and 2.5 mg of active substance/1 of spray liquor. As comparative agents, benomyl and folpet were used in the same concentrations of active substance as indicated above.

After drying of the sprayed layer, the plants were placed in a greenhouse having a relative atmospheric humidity of 85 to 90% and a temperature of 23° to 25°C, and heavily infested with conidia of the powdery mildew of vine (*Oidium tuckeri*).

After an incubation period of 14 days, the plants were examined for infection with *Oidium*, and the degree of infection was expressed in % of infested leaf area, as compared to untreated, infested control plants. The results are indicated in Table XI.

Example XII.

Tomato plants of the brand called Rheinlands Ruhm were sprayed in the 3-leaf stage with aqueous suspensions of the compounds indicated in Example X until drip-off. The application concentrations were 500, 250, 120, and 60 mg of active substance/1 of spray liquor. As comparative agents, benomyl (Comparative Agent I) and zineb (zinc-ethylene-bis-dithio-carbamate = Comparative Agent II) were used.

After drying of the sprayed layer, the plants were heavily infested with a zoospore suspension of *Phytophthora infestans* and placed dripping wet for 1 day in a moisture chamber having a temperature of 15°C and a relative atmospheric humidity of 100%. Subsequently, they were transferred to a greenhouse having a temperature of 15°C and a relative atmospheric humidity of 85 to 95%.

After an incubation time of 7 days, the plants were examined visually for infection with *Phytophthora*, and the degree of infection was expressed in % of infested leaf area, as compared to untreated, infested control plants. The results are indicated in Table XII.

Example XIII.

Barley plants in the 3-leaf stage were treated, until drip-off, with aqueous suspensions of the compounds of Examples 1a, 49, 50 and 51 in application concentrations of 60 and 30 mg of active substance per liter of spray liquor. As comparative agent, the commercial product benomyl was used.

After drying of the sprayed layer, the plants were infested with conidia of *Piricularia oryzae*, and placed dripping wet in a moisture chamber at 25°C and a relative atmospheric humidity of 100%. The plants were kept there for 1 day and then transferred to a greenhouse having a temperature of 25° to 26°C and a relative atmospheric humidity of 100%.

After an incubation period of 7 days, the plants were visibly examined for infection with *Piricularia*, and the degree of infection was expressed in % of infested leaf area, relative to untreated, infested control plants. The results are shown in Table XIII.

Example XIV.

Celery plants in the 6-leaf stage were heavily infested with germs of the celery leaf spot (*Septoria apii*), and subsequently placed in a moisture chamber having a temperature of 25°C and an atmospheric humidity of 100%. The plants were kept there for 1 day and were then transferred to a greenhouse having a temperature of 25° to 26°C and a relative humidity of 85 to 90%.

After an incubation time of 5 days, the plants were treated, until drip-off, with aqueous suspensions of the compounds indicated in Examples 1a, 49, 50 and 51 and the comparative agent benomyl in application concentrations of 125 and 60 mg of active

5

10

15

20

25

30

35

40

45

50

55

60

substance per liter of spray liquor. After drying of the spray liquor, the plants were placed again in the greenhouse and, after an incubation period of 21 days, visually examined for infection with the celery leaf spot. The degree of infection was expressed in % of infested leaf area, relative to untreated, infested control plants (Table XIII).

5

Example XV.

5

10

Dwarf bush bean seeds of the brand called Andreas were well mixed for 10 minutes in a shaking machine with the compounds of Examples 1a, 49, 50 and 51 and the comparative agent benomyl, in application amounts of 100 and 50 g of active substance per 100 kg of seeds, and, the following day, sown in earth which before had been infested with a very virulent culture of *Rhizoctonia solani*. Four times 100 beans each were sown in pots filled with this earth.

10

Three weeks after emergence of the bean plants, the number of emerged plants was counted and the plants were examined for infection with *Rhizoctonia*. The results of this test are indicated in Table XIII.

Table I

compound according to Example	% of leaf area infested with cucumber mildew at mg of active substance/liter of spray liquor				
	2000	1000	500	250	125
4	0	0	5	10	15
5	0	0	3	12	18
6	0	0	5	10	16
7	0	0	5	12	18
8	0	0	5	10	15
9	0	0	3	10	18
10	0	0	5	12	15
2	0	0	5	10	15
11	0	0	3	8	12
12	0	0	0	5	10
13	0	0	0	5	10
1	0	0	0	5	10
14	0	0	5	10	12
15	0	0	3	5	10
benomyl	0	5	8	15	20
control plants (un- treated)	100	100	100	100	100

Table II

compound
acc. to
Example

% of leaf area infested with powdery mildew of cereals
at mg of activesubstance/kg of earth

	10	5	2,5	1,25	0,6	0,3
4	0	0	0	5	12	25
5	0	0	0	5	15	20
6	0	0	0	5	12	20
7	0	0	0	5	10	20
8	0	0	0	5	10	25
9	0	0	0	5	12	20
2	0	0	0	5	10	20
10	0	0	0	5	12	18
11	0	0	0	5	10	15
12	0	0	0	0	5	12
13	0	0	0	0	5	10
1	0	0	0	0	3	10
14	0	0	0	3	5	12
15	0	0	0	5	8	15
benomyl	0	3	5	10	20	35
control plants (untreated)	100	100	100	100	100	100

Table III

% of leaf area infested with *Cercospora*
at mg of active substance/liter spray liquor

compound according to Example	60	30	15	7.5
4	0	0	8	15
5	0	0	8	15
6	0	0	5	10
7	0	0	5	10
8	0	0	5	12
9	0	0	8	15
2	0	0	5	10
10	0	0	5	12
11	0	0	8	12
12	0	0	5	10
13	0	0	3	8
1	0	0	0	5
14	0	0	5	10
15	0	0	8	15
benomyl	0	3	15	20
control plants (untreated)	100	100	100	100

b
co
(u
c
a
E

Table IV

compound acc. to Example	% of leaf area infested with <i>Cladosporium</i> at mg of active substance/liter of spray liquor			
	60	30	15	7.5
16	0	0	5	10
17	0	0	5	10
18	0	0	3	12
19	0	0	5	10
20	0	0	8	15
21	0	0	5	10
22	0	0	8	15
23	0	0	5	12
24	0	0	8	15
benomyl	5	12	20	28
control plants (untreated)	100	100	100	100

100

100

100

100

(untreated)

Table V

compound acc. to Example	% of infection with powdery mildew of cereals at mg of active substance/liter of spray liquor				
	2000	1000	500	250	125
16	0	0	5	10	18
17	0	0	3	8	15
18	0	0	0	10	15
19	0	0	0	5	12
20	0	0	0	8	15
21	0	0	0	5	10
22	0	0	0	5	12
23	0	0	0	3	10
24	0	0	0	5	15
benomyl	0	3	8	15	28
control plants (untreated)	100	100	100	100	100

Table VI

compound acc. to Example	% of mildew infection after seeds treatment with g of active substance/100 kg of seeds			
	200	100	50	25
16	0	0	5	12
17	0	0	5	10
18	0	0	3	10
19	0	0	0	5
20	0	0	5	10
21	0	0	0	5
22	0	0	3	8
23	0	0	0	5
24	0	0	3	10
benomyl	0	5	10	18
control plants (untreated)	100	100	100	100

Table VII

compound acc. to % of infestation with powdery mildew of cereals at mg
of active substance/liter of spray liquor

Example	120	60	30	15
25	0	0	0	8
26	0	0	5	10
3	0	0	3	8
27	0	0	5	10
28	0	0	5	8
29	0	0	8	10
30	0	0	5	10
31	0	0	5	8
32	0	0	3	5
benomyl	0	5	8	15
control plants (untreated)	100	100	100	100

Table VIII

compound
acc. to
Example

% of cucumber mildew infection at mg of active substance/
liter of spray liquor

	2000	1000	500	250
25	0	0	5	15
26	0	0	8	15
3	0	0	3	10
27	0	0	5	10
28	0	0	5	10
29	0	0	8	15
30	0	0	3	10
31	0	0	3	10
32	0	0	5	12
benomyl	3	10	15	28
control plants (untreated)	100	100	100	100

Table IX

compound acc. to	% of <i>piricularia</i> infection at mg of active substance/liter of spray liquor			
Example	60	30	15	7.5
25	0	0	3	10
26	0	0	5	12
3	0	0	3	10
27	0	0	5	15
28	0	0	3	12
29	0	0	8	18
30	0	0	5	18
31	0	0	0	5
32	0	0	3	10
benomyl	0	5	18	25
control plants (untreated)	100	100	100	100

Table X

compound acc. to	% of <i>Peronospora</i> infection at mg of active substance/liter of spray liquor			
Example	500	250	125	60
15	0	3	5	10
12	0	0	5	8
13	0	0	3	5
1	0	0	0	3
14	0	0	3	8
CA I	100	100	100	100
CA II	0	3	5	10
control plants (untreated)	100	100	100	100

Table XI

compound acc. to Example	% of <i>Oidium</i> infection of the vine at mg of active substance/liter of spray liquor			
	20	10	5	2.5
15	0	0	8	15
12	0	0	5	15
13	0	0	0	8
1	0	0	0	8
14	0	0	5	12
CA I	0	8	15	23
CA II	65	80	100	100
control plants (untreated)	100	100	100	100

Table XII

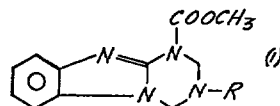
compound acc. to Example	% of <i>Phytophthora</i> infection at mg of active substance/liter of spray liquor			
	500	250	120	60
15	0	0	5	13
12	0	0	5	10
13	0	0	5	8
1	0	0	3	5
14	0	3	5	10
CA I	100	100	100	100
CA II	0	3	5	12
control plants (untreated)	100	100	100	100

Table XIII

compound acc. to Example	% of infested leaf area with <i>Piricularia</i> at mg of active subst./l. of spray liquor				% of <i>Rhizoctonia</i> infested plants at g of active substance/ 100 kg of seeds			
	60	30	125	with <i>Septoria</i> 60	100	50		
1a	0	8	0	8	0	8		
49	0	5	0	3	0	8		
50	0	5	0	5	0	5		
51	0	12	0	8	0	10		
comp. agent benomyl	0	10	0	5	0	10		
untreated infested plants	100	100	100	100	100	100		

WHAT WE CLAIM IS:—

1. A triazino-benzimidazole of the formula I

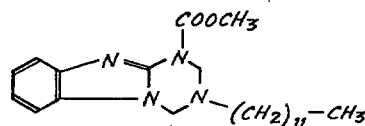


wherein R represents an alkyl group having from 1 to 18 carbon atoms; an alkenyl group having from 3 to 18 carbon atoms, an alkynyl group having from 2 to 8 carbon atoms, a cycloalkyl group having from 3 to 12 carbon atoms, which may be substituted by one or more alkyl groups having from 1 to 4 carbon atoms or by a hydroxy group;

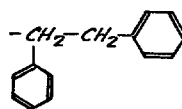
a cyclohexylalkyl, cyclohexylalkenyl, or cyclohexylalkinyl group each having from 1 to 3 carbon atoms in the aliphatic chain, an endomethylene-cyclohexylmethyl, endomethylene-cyclohexenylmethyl, tricyclodecyl, or tricyclodecenyl group; a phenylalkyl, diphenylalkyl or triphenylalkyl group each having from 1 to 6 carbon atoms in the alkyl radical, the phenyl nucleus being unsubstituted or substituted by a halogen atom or an alkyl, alkoxy or alkylthio group each having from 1 to 4 carbon atoms or a di-(C₁—C₄)-alkylamino group;

a phenyl or naphthyl group, which may be substituted by an alkyl group having from 1 to 4 carbon atoms, a halogen atom, a halogeno-alkyl group having from 1 to 4 carbon atoms, a trifluoromethyl or hydroxyl group, an alkoxy group having from 1 to 4 carbon atoms, a phenoxy or (C₁—C₄)-alkylthio group; a di-(C₁—C₄)-alkyl-amino-(C₂—C₆)-alkyl group; a hydroxy-(C₂—C₁₂)-alkyl, (C₂—C₁₈)-alkoxyalkyl or dialkoxyalkyl group, a (C₂—C₁₈)-alkylmercaptoalkyl, (C₃—C₉)-dialkylphosphinyl-alkyl, furfuryl-alkyl, morpholino-(C₁—C₄)-alkyl, pyrrolidino-(C₁—C₄)-alkyl, piperidino-(C₁—C₄)-alkyl or (C₂—C₁₂)-carbalkoxyalkyl group.

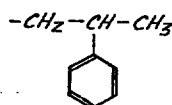
2. A compound as claimed in claim 1, having the formula



3. A compound as claimed in claim 1, wherein R represents the group



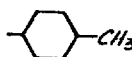
4. A compound as claimed in claim 1, wherein R represents the group



5. A compound as claimed in claim 1, wherein R represents the group



6. A compound as claimed in claim 1, wherein R represents the group





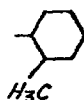
30

1,377,458

30

31

7. A compound as claimed in claim 1, wherein R represents the group



5

8. A compound as claimed in claim 1, wherein R represents the group

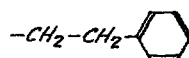


10

5

9. A compound as claimed in claim 1, wherein R represents the group

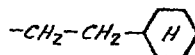
5



15

10. A compound as claimed in claim 1, wherein R represents the group

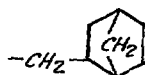
20



11. A compound as claimed in claim 1, wherein R represents the group

25

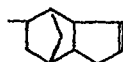
10



10

30

12. A compound as claimed in claim 1, wherein R represents the group



35

13. A compound as claimed in claim 1, wherein R represents the group

40



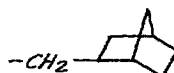
(endo)

45

15

14. A compound as claimed in claim 1, wherein R represents the group

15



(exo)

15. A compound as claimed in claim 1, wherein R represents the group



20

16. A compound as claimed in claim 1 and which is described in any one of Examples 1 to 95.

20

17. A process for the preparation of a triazino-benzimidazole of the formula I as claimed in claim 1, which comprises reacting 2-methoxy-carbonylamino-benzimidazole with a primary amine of the formula H_2N-R , wherein R is as defined in claim 1, and formaldehyde.

25

18. A process as claimed in claim 17, wherein the amine and the benzimidazole are used in a molar ratio of from 1:1 to 2:1.

25



30

31

1,377,458

31

19. A process as claimed in claim 17 or claim 18, wherein formaldehyde and the benzimidazole are used in a molar ratio of from 2:1 to 4:1.

20. A process as claimed in claim 17, conducted substantially as described in any one of Examples 1 to 95.

5 21. A compound as claimed in claim 1, whenever produced by a process as claimed in any one of claims 17 to 20. 5

22. A fungicidal preparation which comprises a compound as claimed in any one of claims 1 to 16 or claim 21 in admixture or conjunction with one or more known formulation additives.

10 23. A preparation as claimed in claim 22, wherein the additive is a solid or liquid carrier, an adhesive, a wetting or dispersing agent and/or a grinding auxiliary. 10

24. A preparation as claimed in claim 22 or claim 23, in the form of a wettable powder, emulsion, suspension, dusting powder or granules.

5 25. An antihelmintic preparation which comprises a compound as claimed in any one of claims 1 to 16 or claim 21 in admixture or conjunction with a pharmaceutically suitable carrier. 15

26. A method for preventing or combating a fungal disease in a plant or a plant product which comprises applying to a plant, plant product, plant habitat or potential plant habitat a compound as claimed in any one of claims 1 to 16 or claim 21 or a preparation as claimed in any one of claims 22 to 24. 20

27. A method as claimed in claim 26, wherein the plant product is a fruit, vegetable or seed.

28. A method as claimed in claim 26, wherein the plant product is paper, wood or a plant fibre. 25

29. A method as claimed in claim 26, wherein the plant habitat or potential plant habitat is soil or a soil-less or soil-containing compost. 25

30. A method as claimed in any one of claims 26 to 29, wherein the compound or preparation is sprayed onto or mixed with the plant, plant product, plant habitat or potential plant habitat. 10

31. A method as claimed in claim 26, wherein a compound as claimed in claim 1, wherein R represents a long-chain alkyl group or a preparation thereof is used to protect against or combat infection with a phycomycete. 30

32. A method as claimed in claim 31, wherein the phycomycete is of the *Peronospora* or *Phytophthora* species. 35

33. A method as claimed in claim 26, conducted substantially as described in any one of Examples I to XV herein. 35

34. A plant, plant product, plant habitat or potential plant habitat whenever protected against fungal infection by a process as claimed in any one of claims 26 to 33.

35. A method of treating a commercially reared animal to combat a helminthic or fungal infection which comprises administering to an animal a compound as claimed in any one of claims 1 to 16 or claim 21 or a preparation as claimed in claim 25. 40

36. A method of protecting a textile, dye, coating or paint against fungal infestation, which comprises applying to the textile, dye, coating or paint a compound as claimed in any one of claims 22 to 24. 45

37. A textile, dye, coating or paint whenever protected against fungal infestation by a method as claimed in claim 36. 45

15

ABEL & IMRAY,
Chartered Patent Agents,
Northumberland House,
303—306 High Holborn,
London, WC1V 7LH.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

x-

20

as
le
ad

le

25