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(54) Title: FUNGICIDAL SUBSTITUTED THIOPHENES

(57) Abstract: The present invention relates to the use of substituted thiophenes and the salts thereof use of compounds for combating phytopathogenic fungi, and to seeds coated with at least one such compound. The invention also relates to novel substituted thiophenes, processes for preparing these compounds and to compositions comprising at least one such compound.

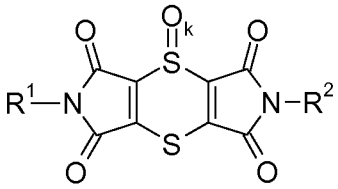
Fungicidal substituted thiophenes

Description

The present invention relates to the use of substituted thiophenes and the salts thereof use of compounds for combating phytopathogenic fungi, and to seeds coated with at least one such compound. The invention also relates to novel substituted thiophenes, processes for preparing these compounds and to compositions comprising at least one such compound.

The preparation of 2,3,5,6-tetracyano-[1,4]dithiine and its use to control bacteria and algae is disclosed in US 3,753,677. The use of this compound against *Sclerotinia fructigena* and *Stemphyllum sarcinaeforme* has been disclosed in US 3,265,565.

The use of certain substituted dithiine-tetracarboximides of formula



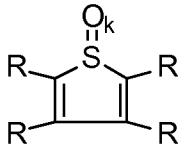
for controlling phytopathogenic fungi is known from WO 2010/043319 and 2011/029551.

The compounds according to the present invention differ from those described in the abovemention publications by the replacement of the dithiine moiety by a thiophene moiety.

In many cases, in particular at low application rates, the fungicidal activity of the known fungicidal compounds is unsatisfactory. Based on this, it was an object of the present invention to provide compounds having improved activity and/or a broader activity spectrum against phytopathogenic harmful fungi.

This object is achieved by certain substituted thiophenes having good fungicidal activity against phytopathogenic harmful fungi.

Accordingly, the present invention relates to the use of compounds of formula I:



I,

wherein:

k indicates the number of the oxygen atoms bound to the sulfur atom of the thiophene moiety and k is 0, 1 or 2;

R is CN, -(C=X)-R^C or -CH=N-O-R^E;

X is O or S;

R^C is hydrogen, C_1-C_4-alkyl, C_2-C_4-alkenyl, C_2-C_4-alkynyl, -O-R^E or NR^AR^B;

R^A,R^B independently of one another are hydrogen or C_1-C_4-alkyl;

R^E is hydrogen or C_1-C_4-alkyl;

provided that all four R substituents are identical;

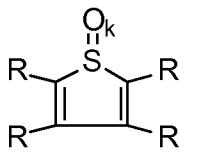
and the agriculturally acceptable salts thereof; for combating phytopathogenic harmful fungi.

The preparation of thiophene-2,3,4,5-tetracarbonitrile is disclosed in DE 1 163 849. Therein it is generally mentioned that this compound is suitable as a preventative herbicide against unwanted vegetation.

Further, the preparation of thiophene-2,3,4,5-tetracarbonitrile, 2,3,4,5-tetracarboxylic acid, thiophene-2,3,4,5-tetracarboxamide, tetramethyl thiophene-2,3,4,5-tetracarboxylate, tetraethyl thiophene-2,3,4,5-tetracarboxylate, tetra(tert.-butyl) thiophene-2,3,4,5-tetracarboxylate and thiophene-2,3,4,5-tetracarbaldehyde and thiophene-2,3,4,5-tetracarboximidic acid has been mentioned earlier in J. Am. Chem. Soc. (1962) 84, 4746-56; Chimia (1959), 13, 107-8; Synthesis (2009), 12, 1960-62; and C. R. Acad. Sci. Paris, Series C: Sci. Chimiques (1969), 269(1), 37-38.

The compounds according to the present invention differ from those described in the abovementioned publications by the specific definition of R and by the proviso that thiophene-2,3,4,5-tetracarbonitrile, thiophene-2,3,4,5-tetracarboxylic acid, thiophene-2,3,4,5-tetracarboxamide, tetramethyl thiophene-2,3,4,5-tetracarboxylate, tetraethyl thiophene-2,3,4,5-tetracarboxylate, tetra(tert.-butyl) thiophene-2,3,4,5-tetracarboxylate and thiophene-2,3,4,5-tetracarboximidic acid are being excluded.

Therefore, according to a second aspect, the invention provides compounds of formula I which are represented by formula I having good fungicidal activity against phytopathogenic harmful fungi:



I,

wherein:

k indicates the number of the oxygen atoms bound to the sulfur atom of the thiophene moiety and k is 0, 1 or 2;

R is CN, -(C=X)-R^C or -CH=N-O-R^E;

X is O or S;

R^C is hydrogen, C_1-C_4-alkyl, C_2-C_4-alkenyl, C_2-C_4-alkynyl, -O-R^E or NR^AR^B;

R^A,R^B independently of one another are hydrogen or C_1-C_4-alkyl;

R^E is hydrogen or C_1-C_4-alkyl;

provided that all four R substituents are identical;

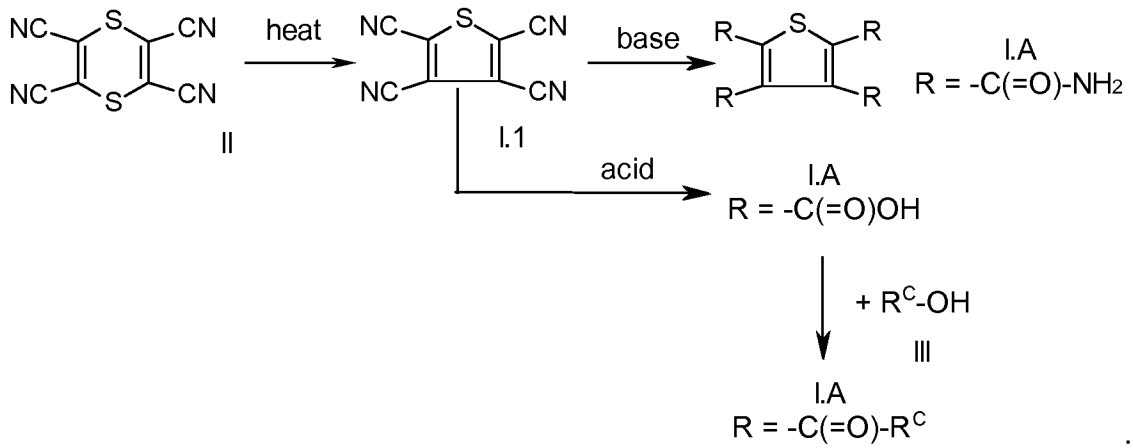
the agriculturally acceptable salts thereof;

except for thiophene-2,3,4,5-tetracarbonitrile, thiophene-2,3,4,5-tetracarbaldehyde, thiophene-2,3,4,5-tetracarboxylic acid, thiophene-2,3,4,5-tetracarboxamide, tetramethyl thiophene-2,3,4,5-tetracarboxylate, tetraethyl thiophene-2,3,4,5-tetracarboxylate, tetra(tert.-butyl) thiophene-2,3,4,5-tetracarboxylate and thiophene-2,3,4,5-tetracarboximidic acid.

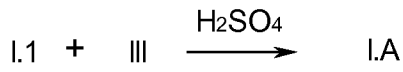
The term "compounds I" refers to compounds of formula I. Likewise, this terminology applies to all sub-formulae, e. g. "compounds I.A" refers to compounds of formula I.A or "compounds III" refers to compounds of formula III, etc..

The compounds I can be obtained from 2,3,5,6-tetracyano-[1,4]dithiine of formula II by various routes in analogy to prior art processes known (J. Am. Chem. Soc. (1962) 84, 4746-56; Chimia (1959), 13, 107-8; Synthesis (2009), 12, 1960-62; and C. R. Acad. Sci. Paris, Series C: Sci. Chimiques (1969), 269(1), 37-38) and, advantageously, by the synthesis shown in the following schemes and in the experimental part of this application.

In a first process, for example (cf. J. Am. Chem. Soc. (1962) 84, 4746-56), compound II is heated to its about its melting point, if appropriate in the presence of a diluent to obtain cyano compound I.1. Thereafter, compound I.1 may be hydrolysed in the presence of a base, preferably alkali metal hydroxide, at temperatures of about 0 to 150°C, preferably at at temperatures of about 10 to 60°C, to compound I, wherein k 0 0, which are of formula I.a as depicted below, and wherein R is -(C=O)-NH_2. Likewise, compound I.A, wherein R is –C(=O)OH, may be obtained by hydrolysis in the presence of an acid, preferably hydrochchloric acid; at temperatures of about 10 to 150°C, preferably at about 60 to 130 °C. Thereafter, the resulting thiophene-2,3,4,5-tetracarboxylic acid may be converted with alcohols of formula III, wherein R^C is as defined above, using standard procedures to obtain compounds I.A, and wherein R is -(C=O)-R^C:



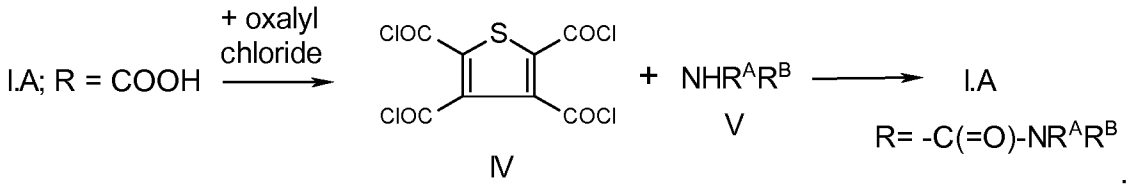
Alternatively, for example in analogy to Bioorg. Med. Chem. (2008 16, 2513, compound I.1 is reacted with H_2SO_4 and compounds III simultaneously, if appropriate in the presence of a diluent, to obtain compounds I.A, wherein R is -(C=O)-R^C:



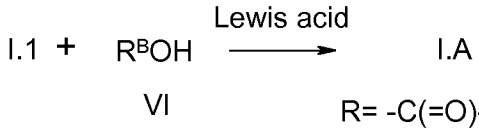
R = -(C=O)-R^C.

Alternatively, to obtain compounds I.A, wherein R is –C(=O)-R^C, R^C being –O-R^E, various routes are known. For example, in analogy to Synthesis (2009), 12, 1960-62), dialkyl acetylenedicarboxylates can be reacted with elemental sulfur in the presence of triethyl phosphite or an N-heteroaromatic catalyst like isoquinoline, pyridine, or N-methylimidazole proceeds preferably in anhydrous dichloromethane at ambient temperature to produce exclusively tetraalkyl 2,3,4,5-thiophenetetracarboxylate derivatives.

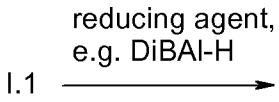
To obtain compounds of formula I, wherein R is -(C=O)-NR^AR^B, the following procedure may be used. For example, thiophene-2,3,4,5-tetracarboxylic acid is reacted in a first step with oxalyl chloride, to obtain the corresponding acid chloride IV. Compounds of formula I.A, wherein R is -(C=O)-NR^AR^B, are prepared from compound IV and the appropriate substituted amines of formula V, wherein R^A and R^B are as defined herein, if appropriate in the presence of a diluent and a suitable base such as triethylamine:



Alternatively, to obtain compounds of formula I.A, wherein R is -(C=O)-NHR^B and R^B is tertiary alkyl, cyano compound I.1 is reacted with tertiary alcohols of formula VI, using Ritter reaction conditions, preferably in the presence of a Lewis acid:



To obtain compound of formula I.A, wherein R is -CHO, various routes are known (e.g. C. R. Acad. Sci. Paris, Series C: Sci. Chimiques (1969), 269(1), 37-38). In a further process, cyano compound I.1 is reduced e.g. with diisobutyl aluminium hydride (DiBAl-H), using standard reducing conditions tocompounds of formula I.A, wherein R is -CHO:

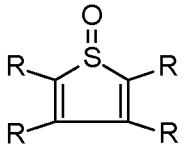


R= -CHO.

To obtain compound of formula I.A, wherein R is –CH=N-O-R^E, for example (cf. Bull. Korean Chem. Soc. (1994), 15, 1021) compound I.A, wherein R is -CHO, may be reacted with compounds VIII, wherein R^E is as defined herein, to obtain compounds I, wherein R is –CH=N-O-R^E:



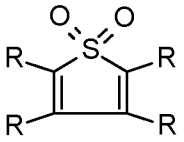
If appropriate, the compounds I, wherein k is 0, which are of formula I.A, can subsequently be oxidized e.g. with nitric acid to form compounds I, wherein k is 1, which are of formula I.B:



I.B

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If appropriate, the compounds I.B, wherein k is 1, can subsequently be further oxidized e.g. with nitric acid to form compounds I, wherein k is 2, which are of formula I.C:



I.C

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If individual compounds I cannot be obtained by the routes described above, they can be prepared by derivatization of other compounds I.

If the synthesis yields mixtures of isomers, a separation is generally not necessarily required since in some cases the individual isomers can be interconverted during work-up for use or during application (e. g. under the action of light, acids or bases). Such conversions may also take place after use, e. g. in the treatment of plants in the treated plant, or in the harmful fungus to be controlled.

In the definitions of the variables given above, collective terms are used which are generally representative for the substituents in question. The term "C_n-C_m" indicates the number of carbon atoms possible in each case in the substituent or substituent moiety in question.

The term "halogen" refers to fluorine, chlorine, bromine and iodine.

The term "C_1-C_4-alkyl" refers to a straight-chained or branched saturated hydrocarbon group having 1 to 6 carbon atoms, e.g. methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl and 1,1-dimethylethyl.

The term "C_2-C_4-alkenyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 4 carbon atoms and a double bond in any position, e.g. ethenyl, 1-propenyl, 2-propenyl (allyl), 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl.

The term "C_2-C_4-alkynyl" refers to a straight-chain or branched unsaturated hydrocarbon radical having 2 to 4 carbon atoms and containing at least one triple bond, such as ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl.

Agriculturally acceptable salts of compounds I encompass especially the salts of those cations or the acid addition salts of those acids whose cations and anions, respectively, have no adverse effect on the fungicidal action of the compounds I. Suitable cations are thus in particular the ions of the alkali metals, preferably sodium and potassium, of the alkaline earth metals, preferably calcium, magnesium and barium, of the transition metals, preferably manganese, copper, zinc and iron, and also the ammonium ion which, if desired, may carry one to four C_1-C_4-alkyl substituents and/or one phenyl or benzyl substituent, preferably diisopropylammonium, tetramethylammonium, tetrabutylammonium, trimethylbenzylammonium, furthermore phosphonium ions, sulfonium ions, preferably tri(C_1-C_4-alkyl)sulfonium, and sulfoxonium ions, preferably tri(C_1-C_4-alkyl)sulfoxonium. Anions of useful acid addition salts are primarily chloride, bromide, fluoride, hydrogensulfate, sulfate, dihydrogenphosphate, hydrogenphosphate, phosphate, ni-

trate, bicarbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate, and the anions of C_1-C_4-alkanoic acids, preferably formate, acetate, propionate and butyrate. They can be formed by reacting a compound of formula I with an acid of the corresponding anion, preferably of hydrochloric acid, hydrobromic acid, sulfuric acid, phosphoric acid or nitric acid.

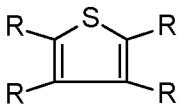
The compounds of formula I can be present in atropisomers arising from restricted rotation about a single bond of asymmetric groups. They also form part of the subject matter of the present invention.

Depending on the substitution pattern, the compounds I may have one or more centers of chirality, in which case they are present as pure enantiomers or pure diastereomers or as enantiomer or diastereomer mixtures. Both, the pure enantiomers or diastereomers and their mixtures are subject matter of the present invention.

In respect of the variables, the embodiments of the intermediates correspond to the embodiments of the compounds I.

Preference is given to the use of those compounds I and where applicable also to compounds I per se and of all sub-formulae provided herein, e. g. formulae I.A and I.B, wherein the substituents and variables (such as k, R, R^A, R^B, R^C and R^E) have independently of each other or more preferably in combination the following meanings:

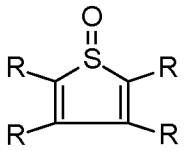
One embodiment relates to compounds I, wherein k is 0, which compounds are of formula I.A:



I.A

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Another embodiment relates to compounds I wherein k is 1, which compounds are of formula I.B:



I.B

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In a further embodiment, R is CN.

A further embodiment relates to compounds I, wherein R is -(C=X)-R^C. Amongst these compounds, X is preferably O.

Amongst compounds I, wherein wherein R is -(C=X)-R^C, R^C is preferably selected from hydrogen, C_1-C_4-alkyl, -O-R^E and NR^AR^B, more preferably from NR^AR^B and -O-R^E.

Amongst preferred compounds I, wherein R is –C(=O)-NR^AR^B, R^A and R^B are preferably selected from methyl, ethyl and hydrogen.

Amongst preferred compounds I, wherein R is –C(=O)-O-R^E, R^E is preferably from ethyl, methyl and hydrogen. According to a further embodiment, R is –C(=O)-O-R^E, wherein R^E is preferably propyl.

A further embodiment relates to compounds I, wherein R is -(C=X)-H. Amongst these compounds, X is preferably O.

A further embodiment relates to compounds I, wherein R is -CH=N-O-R^E, wherein R^E is preferably selected from hydrogen, methyl and ethyl, and in particular methyl.

A further embodiment relates to compounds I, wherein R^A and R^B are independently of each other hydrogen or C_1-C_4-alkyl.

A skilled person will readily understand that the preferences given in connection with compounds I apply for formulae I.A, I.B and I.C as defined above.

With respect to their use, particular preference is given to the compounds 1 to 78 of formulae I.A and I.B compiled in the tables 1 to 2 below. Here, the groups mentioned in the Tables for a substituent are furthermore, independently of the combination wherein they are mentioned, a particularly preferred embodiment of the substituent in question.

Table 1: Compounds 1 to 18 of formula I.A, wherein the meaning of R for each individual compound corresponds in each case to one line in Table A.

Table 2: Compounds 19 to 36 of formula I.B, wherein the meaning of R for each individual compound corresponds in each case to one line in Table A.

Table 2: Compounds 37 to 54 of formula I.C, wherein the meaning of R for each individual compound corresponds in each case to one line in Table A.

Table A.

No.	R
R-1	-CN
R-2	-CHO
R-3	-(C=O)CH_3
R-4	-(C=O)CH_2CH_3
R-5	-(C=O)$CH_2CH_2CH_3$
R-6	-(C=O)NH_2
R-7	-(C=O)NH(CH_3)
R-8	-(C=O)N(CH_3)$_2$
R-9	-(C=S)CH_3

No.	R
R-10	-(C=S)NH_2
R-11	-(C=O)-OH
R-12	-(C=O)-OCH_3
R-13	-(C=O)-OCH_2CH_3
R-14	-(C=O)-$OCH_2CH_2CH_3$
R-15	-CH-N-OH
R-16	-CH=N-OCH_3
R-17	-CH=N-OCH_2CH_3
R-18	-CH=N-$OCH_2CH_2CH_3$

The compounds I and the compositions according to the invention, respectively, are suitable as fungicides. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, including soil-borne fungi, which derive especially from the classes of the Plasmodiophoromycetes, Peronosporomycetes (syn. Oomycetes), Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes (syn. Fungi imperfecti). Some are systemically effective and they can be used in crop protection as foliar fungicides, fungicides for seed dressing and soil fungicides. Moreover, they are suitable for controlling harmful fungi, which inter alia occur in wood or roots of plants.

Preferably, the compounds of formula I are used for combating phytoapthogenic harmful fungi in an amount which is sufficient for controlling phytopathogenic harmful fungi on treated plants and which does not result in a substantial damage to the treated plants.

The compounds I and the compositions according to the invention are particularly important in the control of a multitude of phytopathogenic fungi on various cultivated plants, such as cereals, e. g. wheat, rye, barley, triticale, oats or rice; beet, e. g. sugar beet or fodder beet; fruits, such as pomes, stone fruits or soft fruits, e. g. apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries, blackberries or gooseberries; leguminous plants, such as lentils,

peas, alfalfa or soybeans; oil plants, such as rape, mustard, olives, sunflowers, coconut, cocoa beans, castor oil plants, oil palms, ground nuts or soybeans; cucurbits, such as squashes, cucumber or melons; fiber plants, such as cotton, flax, hemp or jute; citrus fruit, such as oranges, lemons, grapefruits or mandarins; vegetables, such as spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, cucurbits or paprika; lauraceous plants, such as avocados, cinnamon or camphor; energy and raw material plants, such as corn, soybean, rape, sugar cane or oil palm; corn; tobacco; nuts; coffee; tea; bananas; vines (table grapes and grape juice grape vines); hop; turf; sweet leaf (also called Stevia); natural rubber plants or ornamental and forestry plants, such as flowers, shrubs, broad-leaved trees or evergreens, e. g. conifers; and on the plant propagation material, such as seeds, and the crop material of these plants.

Preferably, compounds I and compositions thereof, respectively are used for controlling a multitude of fungi on field crops, such as potatoes sugar beets, tobacco, wheat, rye, barley, oats, rice, corn, cotton, soybeans, rape, legumes, sunflowers, coffee or sugar cane; fruits; vines; ornamentals; or vegetables, such as cucumbers, tomatoes, beans or squashes.

The term "plant propagation material" is to be understood to denote all the generative parts of the plant such as seeds and vegetative plant material such as cuttings and tubers (e. g. potatoes), which can be used for the multiplication of the plant. This includes seeds, roots, fruits, tubers, bulbs, rhizomes, shoots, sprouts and other parts of plants, including seedlings and young plants, which are to be transplanted after germination or after emergence from soil. These young plants may also be protected before transplantation by a total or partial treatment by immersion or pouring.

Preferably, treatment of plant propagation materials with compounds I and compositions thereof, respectively, is used for controlling a multitude of fungi on cereals, such as wheat, rye, barley and oats; rice, corn, cotton and soybeans.

The term "cultivated plants" is to be understood as including plants which have been modified by breeding, mutagenesis or genetic engineering including but not limiting to agricultural biotech products on the market or in development (cf. http://www.bio.org/speeches/pubs/er/agri_products.asp). Genetically modified plants are plants, which genetic material has been so modified by the use of recombinant DNA techniques that under natural circumstances cannot readily be obtained by cross breeding, mutations or natural recombination. Typically, one or more genes have been integrated into the genetic material of a genetically modified plant in order to improve certain properties of the plant. Such genetic modifications also include but are not limited to targeted post-translational modification of protein(s), oligo- or polypeptides e. g. by glycosylation or polymer additions such as prenylated, acetylated or farnesylated moieties or PEG moieties.

Plants that have been modified by breeding, mutagenesis or genetic engineering, e. g. have been rendered tolerant to applications of specific classes of herbicides, such as auxin herbicides such as dicamba or 2,4-D; bleacher herbicides such as hydroxylphenylpyruvate dioxygenase (HPPD) inhibitors or phytoene desaturase (PDS) inhibittors; acetolactate synthase (ALS) inhibitors such as sulfonyl ureas or imidazolinones; enolpyruvylshikimate-3-phosphate synthase (EPSPS) inhibitors, such as glyphosate; glutamine synthetase (GS) inhibitors such as glufosinate; protoporphyrinogen-IX oxidase inhibitors; lipid biosynthesis inhibitors such as acetyl CoA carboxylase (ACCase) inhibitors; or oxynil (i. e. bromoxynil or ioxynil) herbicides as a result

of conventional methods of breeding or genetic engineering. Furthermore, plants have been made resistant to multiple classes of herbicides through multiple genetic modifications, such as resistance to both glyphosate and glufosinate or to both glyphosate and a herbicide from another class such as ALS inhibitors, HPPD inhibitors, auxin herbicides, or ACCase inhibitors. These herbicide resistance technologies are e. g. described in Pest Managem. Sci. 61, 2005, 246; 61, 2005, 258; 61, 2005, 277; 61, 2005, 269; 61, 2005, 286; 64, 2008, 326; 64, 2008, 332; Weed Sci. 57, 2009, 108; Austral. J. Agricult. Res. 58, 2007, 708; Science 316, 2007, 1185; and references quoted therein. Several cultivated plants have been rendered tolerant to herbicides by conventional methods of breeding (mutagenesis), e. g. Clearfield® summer rape (Canola, BASF SE, Germany) being tolerant to imidazolinones, e. g. imazamox, or ExpressSun® sunflowers (DuPont, USA) being tolerant to sulfonyl ureas, e. g. tribenuron. Genetic engineering methods have been used to render cultivated plants such as soybean, cotton, corn, beets and rape, tolerant to herbicides such as glyphosate and glufosinate, some of which are commercially available under the trade names RoundupReady® (glyphosate-tolerant, Monsanto, U.S.A.), Cultivance® (imidazolinone tolerant, BASF SE, Germany) and LibertyLink® (glufosinate-tolerant, Bayer CropScience, Germany).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more insecticidal proteins, especially those known from the bacterial genus *Bacillus*, particularly from *Bacillus thuringiensis*, such as δ-endotoxins, e. g. CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) or Cry9c; vegetative insecticidal proteins (VIP), e. g. VIP1, VIP2, VIP3 or VIP3A; insecticidal proteins of bacteria colonizing nematodes, e. g. *Photorhabdus* spp. or *Xenorhabdus* spp.; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp toxins, or other insect-specific neurotoxins; toxins produced by fungi, such Streptomycetes toxins, plant lectins, such as pea or barley lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin or papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 3-hydroxysteroid oxidase, ecdysteroid-IDP-glycosyl-transferase, cholesterol oxidases, ecdysone inhibitors or HMG-CoA-reductase; ion channel blockers, such as blockers of sodium or calcium channels; juvenile hormone esterase; diuretic hormone receptors (helicokinin receptors); stilben synthase, bibenzyl synthase, chitinases or glucanases. In the context of the present invention these insecticidal proteins or toxins are to be understood expressly also as pre-toxins, hybrid proteins, truncated or otherwise modified proteins. Hybrid proteins are characterized by a new combination of protein domains, (see, e. g. WO 02/015701). Further examples of such toxins or genetically modified plants capable of synthesizing such toxins are disclosed, e. g., in EP-A 374 753, WO 93/007278, WO 95/34656, EP-A 427 529, EP-A 451 878, WO 03/18810 und WO 03/52073. The methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e. g. in the publications mentioned above. These insecticidal proteins contained in the genetically modified plants impart to the plants producing these proteins tolerance to harmful pests from all taxonomic groups of athropods, especially to beetles (Coleoptera), two-winged insects (Diptera), and moths (Lepidoptera) and to nematodes (Nematoda). Genetically modified plants capable to synthesize one or more insecticidal proteins are, e. g., described in the publications mentioned above, and some of which are commercially available

such as YieldGard® (corn cultivars producing the Cry1Ab toxin), YieldGard® Plus (corn cultivars producing Cry1Ab and Cry3Bb1 toxins), Starlink® (corn cultivars producing the Cry9c toxin), Herculex® RW (corn cultivars producing Cry34Ab1, Cry35Ab1 and the enzyme Phosphinothricin-N-Acetyltransferase [PAT]); NuCOTN® 33B (cotton cultivars producing the Cry1Ac toxin), Bollgard® I (cotton cultivars producing the Cry1Ac toxin), Bollgard® II (cotton cultivars producing Cry1Ac and Cry2Ab2 toxins); VIPCOT® (cotton cultivars producing a VIP-toxin); NewLeaf® (potato cultivars producing the Cry3A toxin); Bt-Xtra®, NatureGard®, KnockOut®, BiteGard®, Protecta®, Bt11 (e. g. Agrisure® CB) and Bt176 from Syngenta Seeds SAS, France, (corn cultivars producing the Cry1Ab toxin and PAT enyzme), MIR604 from Syngenta Seeds SAS, France (corn cultivars producing a modified version of the Cry3A toxin, c.f. WO 03/018810), MON 863 from Monsanto Europe S.A., Belgium (corn cultivars producing the Cry3Bb1 toxin), IPC 531 from Monsanto Europe S.A., Belgium (cotton cultivars producing a modified version of the Cry1Ac toxin) and 1507 from Pioneer Overseas Corporation, Belgium (corn cultivars producing the Cry1F toxin and PAT enzyme).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the resistance or tolerance of those plants to bacterial, viral or fungal pathogens. Examples of such proteins are the so-called "pathogenesis-related proteins" (PR proteins, see, e. g. EP-A 392 225), plant disease resistance genes (e. g. potato cultivars, which express resistance genes acting against *Phytophthora infestans* derived from the mexican wild potato *Solanum bulbocastanum*) or T4-lysozym (e. g. potato cultivars capable of synthesizing these proteins with increased resistance against bacteria such as *Erwinia amylvora*). The methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e. g. in the publications mentioned above.

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the productivity (e. g. bio mass production, grain yield, starch content, oil content or protein content), tolerance to drought, salinity or other growth-limiting environmental factors or tolerance to pests and fungal, bacterial or viral pathogens of those plants.

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve human or animal nutrition, e. g. oil crops that produce health-promoting long-chain omega-3 fatty acids or unsaturated omega-9 fatty acids (e. g. Nexera® rape, DOW Agro Sciences, Canada).

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve raw material production, e. g. potatoes that produce increased amounts of amylopectin (e. g. Amflora® potato, BASF SE, Germany).

The compounds I and compositions thereof, respectively, are particularly suitable for controlling the following plant diseases:

Albugo spp. (white rust) on ornamentals, vegetables (e. g. *A. candida*) and sunflowers (e. g. *A. tragopogonis*); *Alternaria* spp. (Alternaria leaf spot) on vegetables, rape (*A. brassicola* or *brassicae*), sugar beets (*A. tenuis*), fruits, rice, soybeans, potatoes (e. g. *A. solani* or *A. alternata*),

tomatoes (e. g. *A. solani* or *A. alternata*) and wheat; *Aphanomyces* spp. on sugar beets and vegetables; *Ascochyta* spp. on cereals and vegetables, e. g. *A. tritici* (anthracnose) on wheat and *A. hordei* on barley; *Bipolaris* and *Drechslera* spp. (teleomorph: *Cochliobolus* spp.), e. g. Southern leaf blight (*D. maydis)* or Northern leaf blight (*B. zeicola*) on corn, e. g. spot blotch (*B. sorokiniana*) on cereals and e.g. *B. oryzae* on rice and turfs; *Blumeria* (formerly *Erysiphe*) *graminis* (powdery mildew) on cereals (e. g. on wheat or barley); *Botrytis cinerea* (teleomorph: *Botryotinia fuckeliana*: grey mold) on fruits and berries (e. g. strawberries), vegetables (e. g. lettuce, carrots, celery and cabbages), rape, flowers, vines, forestry plants and wheat; *Bremia lactucae* (downy mildew) on lettuce; *Ceratocystis* (syn. *Ophiostoma*) spp. (rot or wilt) on broad-leaved trees and evergreens, e. g. *C. ulmi* (Dutch elm disease) on elms; *Cercospora* spp. (Cercospora leaf spots) on corn (e.g. Gray leaf spot: *C. zeae-maydis*), rice, sugar beets (e. g. *C. beticola*), sugar cane, vegetables, coffee, soybeans (e. g. *C. sojina* or *C. kikuchii*) and rice; *Cladosporium* spp. on tomatoes (e. g. *C. fulvum*: leaf mold) and cereals, e. g. *C. herbarum* (black ear) on wheat; *Claviceps purpurea* (ergot) on cereals; *Cochliobolus* (anamorph: *Helminthosporium* of *Bipolaris*) spp. (leaf spots) on corn (*C. carbonum*), cereals (e. g. *C. sativus*, anamorph: *B. sorokiniana*) and rice (e. g. *C. miyabeanus*, anamorph: *H. oryzae*); *Colletotrichum* (teleomorph: *Glomerella*) spp. (anthracnose) on cotton (e. g. *C. gossypii*), corn (e. g. *C. graminicola:* Anthracnose stalk rot), soft fruits, potatoes (e. g. *C. coccodes*: black dot), beans (e. g. *C. lindemuthianum*) and soybeans (e. g. *C. truncatum* or *C. gloeosporioides*); *Corticium* spp., e. g. *C. sasakii* (sheath blight) on rice; *Corynespora cassiicola* (leaf spots) on soybeans and ornamentals; *Cycloconium* spp., e. g. *C. oleaginum* on olive trees; *Cylindrocarpon* spp. (e. g. fruit tree canker or young vine decline, teleomorph: *Nectria* or *Neonectria* spp.) on fruit trees, vines (e. g. *C. liriodendri*, teleomorph: *Neonectria liriodendri*: Black Foot Disease) and ornamentals; *Dematophora* (teleomorph: *Rosellinia*) necatrix (root and stem rot) on soybeans; *Diaporthe* spp., e. g. *D. phaseolorum* (damping off) on soybeans; *Drechslera* (syn. *Helminthosporium*, teleomorph: *Pyrenophora*) spp. on corn, cereals, such as barley (e. g. *D. teres*, net blotch) and wheat (e. g. *D. tritici-repentis*: tan spot), rice and turf; Esca (dieback, apoplexy) on vines, caused by *Formitiporia* (syn. *Phellinus*) *punctata*, *F. mediterranea*, *Phaeomoniella chlamydospora* (earlier *Phaeoacremonium chlamydosporum*), *Phaeoacremonium aleophilum* and/or *Botryosphaeria obtusa*; *Elsinoe* spp. on pome fruits (*E. pyri*), soft fruits (*E. veneta*: anthracnose) and vines (*E. ampelina*: anthracnose); *Entyloma oryzae* (leaf smut) on rice; *Epicoccum* spp. (black mold) on wheat; *Erysiphe* spp. (powdery mildew) on sugar beets (*E. betae*), vegetables (e. g. *E. pisi*), such as cucurbits (e. g. *E. cichoracearum*), cabbages, rape (e. g. *E. cruciferarum*); *Eutypa lata* (Eutypa canker or dieback, anamorph: *Cytosporina lata*, syn. *Libertella blepharis*) on fruit trees, vines and ornamental woods; *Exserohilum* (syn. *Helminthosporium*) spp. on corn (e. g. *E. turcicum*); *Fusarium* (teleomorph: *Gibberella*) spp. (wilt, root or stem rot) on various plants, such as *F. graminearum* or *F. culmorum* (root rot, scab or head blight) on cereals (e. g. wheat or barley), *F. oxysporum* on tomatoes, *F. solani* on soybeans and *F. verticillioides* on corn; *Gaeumannomyces graminis* (take-all) on cereals (e. g. wheat or barley) and corn; *Gibberella* spp. on cereals (e. g. *G. zeae*) and rice (e. g. *G. fujikuroi*: Bakanae disease); *Glomerella cingulata* on vines, pome fruits and other plants and *G. gossypii* on cotton; Grainstaining complex on rice; *Guignardia bidwellii* (black rot) on vines; *Gymnosporangium* spp. on rosaceous plants and junipers, e. g. *G. sabinae* (rust) on pears; *Helminthosporium* spp. (syn. *Drechslera*, teleomorph: *Cochli-*

obolus) on corn, cereals and rice; *Hemileia* spp., e. g. *H. vastatrix* (coffee leaf rust) on coffee; *Isariopsis clavispora* (syn. *Cladosporium vitis*) on vines; *Macrophomina phaseolina* (syn. *phaseoli*) (root and stem rot) on soybeans and cotton; *Microdochium* (syn. *Fusarium*) *nivale* (pink snow mold) on cereals (e. g. wheat or barley); *Microsphaera diffusa* (powdery mildew) on soybeans; *Monilinia* spp., e. g. *M. laxa*, *M. fructicola* and *M. fructigena* (bloom and twig blight, brown rot) on stone fruits and other rosaceous plants; *Mycosphaerella* spp. on cereals, bananas, soft fruits and ground nuts, such as e. g. *M. graminicola* (anamorph: *Septoria tritici*, Septoria blotch) on wheat or *M. fijiensis* (black Sigatoka disease) on bananas; *Peronospora* spp. (downy mildew) on cabbage (e. g. *P. brassicae*), rape (e. g. *P. parasitica*), onions (e. g. *P. destructor*), tobacco (*P. tabacina*) and soybeans (e. g. *P. manshurica*); *Phakopsora pachyrhizi* and *P. meibomiae* (soybean rust) on soybeans; *Phialophora* spp. e. g. on vines (e. g. *P. tracheiphila* and *P. tetraspora*) and soybeans (e. g. *P. gregata*: stem rot); *Phoma lingam* (root and stem rot) on rape and cabbage and *P. betae* (root rot, leaf spot and damping-off) on sugar beets; *Phomopsis* spp. on sunflowers, vines (e. g. *P. viticola*: can and leaf spot) and soybeans (e. g. stem rot: *P. phaseoli*, teleomorph: *Diaporthe phaseolorum*); *Physoderma maydis* (brown spots) on corn; *Phytophthora* spp. (wilt, root, leaf, fruit and stem root) on various plants, such as paprika and cucurbits (e. g. *P. capsici*), soybeans (e. g. *P. megasperma*, syn. *P. sojae*), potatoes and tomatoes (e. g. *P. infestans*: late blight) and broad-leaved trees (e. g. *P. ramorum*: sudden oak death); *Plasmodiophora brassicae* (club root) on cabbage, rape, radish and other plants; *Plasmopara* spp., e. g. *P. viticola* (grapevine downy mildew) on vines and *P. halstedii* on sunflowers; *Podosphaera* spp. (powdery mildew) on rosaceous plants, hop, pome and soft fruits, e. g. *P. leucotricha* on apples; *Polymyxa* spp., e. g. on cereals, such as barley and wheat (*P. graminis*) and sugar beets (*P. betae*) and thereby transmitted viral diseases; *Pseudocercosporella herpotrichoides* (eyespot, teleomorph: *Tapesia yallundae*) on cereals, e. g. wheat or barley; *Pseudoperonospora* (downy mildew) on various plants, e. g. *P. cubensis* on cucurbits or *P. humili* on hop; *Pseudopezicula tracheiphila* (red fire disease or ‚rotbrenner', anamorph: *Phialophora*) on vines; *Puccinia* spp. (rusts) on various plants, e. g. *P. triticina* (brown or leaf rust), *P. striiformis* (stripe or yellow rust), *P. hordei* (dwarf rust), *P. graminis* (stem or black rust) or *P. recondita* (brown or leaf rust) on cereals, such as e. g. wheat, barley or rye, *P. kuehnii* (orange rust) on sugar cane and *P. asparagi* on asparagus; *Pyrenophora* (anamorph: *Drechslera*) *tritici-repentis* (tan spot) on wheat or *P. teres* (net blotch) on barley; *Pyricularia* spp., e. g. *P. oryzae* (teleomorph: *Magnaporthe grisea*, rice blast) on rice and *P. grisea* on turf and cereals; *Pythium* spp. (damping-off) on turf, rice, corn, wheat, cotton, rape, sunflowers, soybeans, sugar beets, vegetables and various other plants (e. g. *P. ultimum* or *P. aphanidermatum*); *Ramularia* spp., e. g. *R. collo-cygni* (Ramularia leaf spots, Physiological leaf spots) on barley and *R. beticola* on sugar beets; *Rhizoctonia* spp. on cotton, rice, potatoes, turf, corn, rape, potatoes, sugar beets, vegetables and various other plants, e. g. *R. solani* (root and stem rot) on soybeans, *R. solani* (sheath blight) on rice or *R. cerealis* (Rhizoctonia spring blight) on wheat or barley; *Rhizopus stolonifer* (black mold, soft rot) on strawberries, carrots, cabbage, vines and tomatoes; *Rhynchosporium secalis* (scald) on barley, rye and triticale; *Sarocladium oryzae* and *S. attenuatum* (sheath rot) on rice; *Sclerotinia* spp. (stem rot or white mold) on vegetables and field crops, such as rape, sunflowers (e. g. *S. sclerotiorum*) and soybeans (e. g. *S. rolfsii* or *S. sclerotiorum*); *Septoria* spp. on various plants, e. g. *S. glycines* (brown spot) on soybeans, *S. tritici* (Septoria

blotch) on wheat and *S.* (syn. *Stagonospora*) nodorum (Stagonospora blotch) on cereals; *Uncinula* (syn. *Erysiphe*) *necator* (powdery mildew, anamorph: *Oidium tuckeri*) on vines; *Setospaeria* spp. (leaf blight) on corn (e. g. *S. turcicum*, syn. *Helminthosporium turcicum*) and turf; *Sphacelotheca* spp. (smut) on corn, (e. g. *S. reiliana*: head smut), sorghum und sugar cane; *Sphaerotheca fuliginea* (powdery mildew) on cucurbits; *Spongospora subterranea* (powdery scab) on potatoes and thereby transmitted viral diseases; *Stagonospora* spp. on cereals, e. g. *S. nodorum* (Stagonospora blotch, teleomorph: *Leptosphaeria* [syn. *Phaeosphaeria*] *nodorum*) on wheat; *Synchytrium endobioticum* on potatoes (potato wart disease); *Taphrina* spp., e. g. *T. deformans* (leaf curl disease) on peaches and *T. pruni* (plum pocket) on plums; *Thielaviopsis* spp. (black root rot) on tobacco, pome fruits, vegetables, soybeans and cotton, e. g. *T. basicola* (syn. *Chalara elegans*); *Tilletia* spp. (common bunt or stinking smut) on cereals, such as e. g. *T. tritici* (syn. *T. caries*, wheat bunt) and *T. controversa* (dwarf bunt) on wheat; *Typhula incarnata* (grey snow mold) on barley or wheat; *Urocystis* spp., e. g. *U. occulta* (stem smut) on rye; *Uromyces* spp. (rust) on vegetables, such as beans (e. g. *U. appendiculatus*, syn. *U. phaseoli*) and sugar beets (e. g. *U. betae*); *Ustilago* spp. (loose smut) on cereals (e. g. *U. nuda* and *U. avaenae*), corn (e. g. *U. maydis*: corn smut) and sugar cane; *Venturia* spp. (scab) on apples (e. g. *V. inaequalis*) and pears; and *Verticillium* spp. (wilt) on various plants, such as fruits and ornamentals, vines, soft fruits, vegetables and field crops, e. g. *V. dahliae* on strawberries, rape, potatoes and tomatoes.

The compounds I and compositions thereof, respectively, are also suitable for controlling harmful fungi in the protection of stored products or harvest and in the protection of materials. The term "protection of materials" is to be understood to denote the protection of technical and non-living materials, such as adhesives, glues, wood, paper and paperboard, textiles, leather, paint dispersions, plastics, colling lubricants, fiber or fabrics, against the infestation and destruction by harmful microorganisms, such as fungi and bacteria. As to the protection of wood and other materials, the particular attention is paid to the following harmful fungi: Ascomycetes such as *Ophiostoma* spp., *Ceratocystis* spp., *Aureobasidium pullulans*, *Sclerophoma* spp., *Chaetomium* spp., *Humicola* spp., *Petriella* spp., *Trichurus* spp.; Basidiomycetes such as *Coniophora* spp., *Coriolus* spp., *Gloeophyllum* spp., *Lentinus* spp., *Pleurotus* spp., *Poria* spp., *Serpula* spp. and *Tyromyces* spp., Deuteromycetes such as *Aspergillus* spp., *Cladosporium* spp., *Penicillium* spp., *Trichorma* spp., *Alternaria* spp., *Paecilomyces* spp. and Zygomycetes such as *Mucor* spp., and in addition in the protection of stored products and harvest the following yeast fungi are worthy of note: *Candida* spp. and *Saccharomyces cerevisae*.

The compounds I and compositions thereof, resepectively, may be used for improving the health of a plant. The invention also relates to a method for improving plant health by treating a plant, its propagation material and/or the locus where the plant is growing or is to grow with an effective amount of compounds I and compositions thereof, respectively.

The term "plant health" is to be understood to denote a condition of the plant and/or its products which is determined by several indicators alone or in combination with each other such as yield (e. g. increased biomass and/or increased content of valuable ingredients), plant vigor (e. g. improved plant growth and/or greener leaves (“greening effect”)), quality (e. g. improved content or composition of certain ingredients) and tolerance to abiotic and/or biotic stress.The above identified indicators for the health condition of a plant may be interdependent or may re-

sult from each other.

The compounds of formula I can be present in different crystal modifications whose biological activity may differ. They are likewise subject matter of the present invention.

The compounds I are employed as such or in form of compositions by treating the fungi or the plants, plant propagation materials, such as seeds, soil, surfaces, materials or rooms to be protected from fungal attack with a fungicidally effective amount of the active substances. The application can be carried out both before and after the infection of the plants, plant propagation materials, such as seeds, soil, surfaces, materials or rooms by the fungi.

Plant propagation materials may be treated with compounds I as such or a composition comprising at least one compound I prophylactically either at or before planting or transplanting.

The invention also relates to agrochemical compositions comprising a solvent or solid carrier and at least one compound I and to the use for controlling harmful fungi.

An agrochemical composition comprises a fungicidally effective amount of a compound I. The term "effective amount" denotes an amount of the composition or of the compounds I, which is sufficient for controlling harmful fungi on cultivated plants or in the protection of materials and which does not result in a substantial damage to the treated plants. Such an amount can vary in a broad range and is dependent on various factors, such as the fungal species to be controlled, the treated cultivated plant or material, the climatic conditions and the specific compound I used.

The compounds I, their N-oxides and salts can be converted into customary types of agrochemical compositions, e. g. solutions, emulsions, suspensions, dusts, powders, pastes and granules. The composition type depends on the particular intended purpose; in each case, it should ensure a fine and uniform distribution of the compound according to the invention.

Examples for composition types are suspensions (SC, OD, FS), emulsifiable concentrates (EC), emulsions (EW, EO, ES), pastes, pastilles, wettable powders or dusts (WP, SP, SS, WS, DP, DS) or granules (GR, FG, GG, MG), which can be water-soluble or wettable, as well as gel formulations for the treatment of plant propagation materials such as seeds (GF).

Usually the composition types (e. g. SC, OD, FS, EC, WG, SG, WP, SP, SS, WS, GF) are employed diluted. Composition types such as DP, DS, GR, FG, GG and MG are usually used undiluted.

The compositions are prepared in a known manner (cf. US 3,060,084, EP-A 707 445 (for liquid concentrates), Browning: ”Agglomeration”, Chemical Engineering, Dec. 4, 1967, 147-48, Perry’s Chemical Engineer’s Handbook, 4th Ed., McGraw-Hill, New York, 1963, S. 8-57 und ff. WO 91/13546, US 4,172,714, US 4,144,050, US 3,920,442, US 5,180,587, US 5,232,701, US 5,208,030, GB 2,095,558, US 3,299,566, Klingman: Weed Control as a Science (J. Wiley & Sons, New York, 1961), Hance et al.: Weed Control Handbook (8th Ed., Blackwell Scientific, Oxford, 1989) and Mollet, H. and Grubemann, A.: Formulation technology (Wiley VCH Verlag, Weinheim, 2001).

The agrochemical compositions may also comprise auxiliaries which are customary in agrochemical compositions. The auxiliaries used depend on the particular application form and active substance, respectively.

Examples for suitable auxiliaries are solvents, solid carriers, dispersants or emulsifiers (such as further solubilizers, protective colloids, surfactants and adhesion agents), organic and anor-

ganic thickeners, bactericides, anti-freezing agents, anti-foaming agents, if appropriate colorants and tackifiers or binders (e. g. for seed treatment formulations).

Suitable solvents are water, organic solvents such as mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, e. g. toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, alcohols such as methanol, ethanol, propanol, butanol and cyclohexanol, glycols, ketones such as cyclohexanone and gamma-butyrolactone, fatty acid dimethylamides, fatty acids and fatty acid esters and strongly polar solvents, e. g. amines such as N-methylpyrrolidone.

Solid carriers are mineral earths such as silicates, silica gels, talc, kaolins, limestone, lime, chalk, bole, loess, clays, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, e. g., ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

Suitable surfactants (adjuvants, wtters, tackifiers, dispersants or emulsifiers) are alkali metal, alkaline earth metal and ammonium salts of aromatic sulfonic acids, such as ligninsoulfonic acid (Borresperse® types, Borregard, Norway) phenolsulfonic acid, naphthalenesulfonic acid (Morwet® types, Akzo Nobel, U.S.A.), dibutylnaphthalene-sulfonic acid (Nekal® types, BASF, Germany),and fatty acids, alkylsulfonates, alkylarylsulfonates, alkyl sulfates, laurylether sulfates, fatty alcohol sulfates, and sulfated hexa-, hepta- and octadecanolates, sulfated fatty alcohol glycol ethers, furthermore condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxy-ethylene octylphenyl ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenyl polyglycol ethers, tributylphenyl polyglycol ether, tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignin-sulfite waste liquors and proteins, denatured proteins, polysaccharides (e. g. methylcellulose), hydrophobically modified starches, polyvinyl alcohols (Mowiol® types, Clariant, Switzerland), polycarboxylates (Sokolan® types, BASF, Germany), polyalkoxylates, polyvinylamines (Lupasol® types, BASF, Germany), polyvinylpyrrolidone and the copolymers therof.

Examples for thickeners (i. e. compounds that impart a modified flowability to compositions, i. e. high viscosity under static conditions and low viscosity during agitation) are polysaccharides and organic and anorganic clays such as Xanthan gum (Kelzan®, CP Kelco, U.S.A.), Rhodopol® 23 (Rhodia, France), Veegum® (R.T. Vanderbilt, U.S.A.) or Attaclay® (Engelhard Corp., NJ, USA).

Bactericides may be added for preservation and stabilization of the composition. Examples for suitable bactericides are those based on dichlorophene and benzylalcohol hemi formal (Proxel® from ICI or Acticide® RS from Thor Chemie and Kathon® MK from Rohm & Haas) and isothiazolinone derivatives such as alkylisothiazolinones and benzisothiazolinones (Acticide® MBS from Thor Chemie).

Examples for suitable anti-freezing agents are ethylene glycol, propylene glycol, urea and glycerin.

Examples for anti-foaming agents are silicone emulsions (such as e. g. Silikon® SRE, Wacker, Germany or Rhodorsil®, Rhodia, France), long chain alcohols, fatty acids, salts of fatty acids, fluoroorganic compounds and mixtures thereof.

Suitable colorants are pigments of low water solubility and water-soluble dyes. Examples to be mentioned und the designations rhodamin B, C. I. pigment red 112, C. I. solvent red 1, pigment blue 15:4, pigment blue 15:3, pigment blue 15:2, pigment blue 15:1, pigment blue 80, pigment yellow 1, pigment yellow 13, pigment red 112, pigment red 48:2, pigment red 48:1, pigment red 57:1, pigment red 53:1, pigment orange 43, pigment orange 34, pigment orange 5, pigment green 36, pigment green 7, pigment white 6, pigment brown 25, basic violet 10, basic violet 49, acid red 51, acid red 52, acid red 14, acid blue 9, acid yellow 23, basic red 10, basic red 108.

Examples for tackifiers or binders are polyvinylpyrrolidons, polyvinylacetates, polyvinyl alcohols and cellulose ethers (Tylose®, Shin-Etsu, Japan).

Powders, materials for spreading and dusts can be prepared by mixing or concomitantly grinding the compounds I and, if appropriate, further active substances, with at least one solid carrier.

Granules, e. g. coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active substances to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, e. g., ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

Examples for composition types are:

1. Composition types for dilution with water

i) Water-soluble concentrates (SL, LS)

10 parts by weight of a compound I according to the invention are dissolved in 90 parts by weight of water or in a water-soluble solvent. As an alternative, wetting agents or other auxiliaries are added. The active substance dissolves upon dilution with water. In this way, a composition having a content of 10% by weight of active substance is obtained.

ii) Dispersible concentrates (DC)

20 parts by weight of a compound I according to the invention are dissolved in 70 parts by weight of cyclohexanone with addition of 10 parts by weight of a dispersant, e. g. polyvinylpyrrolidone. Dilution with water gives a dispersion. The active substance content is 20% by weight.

iii) Emulsifiable concentrates (EC)

15 parts by weight of a compound I according to the invention are dissolved in 75 parts by weight of xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5 parts by weight). Dilution with water gives an emulsion. The composition has an active substance content of 15% by weight.

iv) Emulsions (EW, EO, ES)

25 parts by weight of a compound I according to the invention are dissolved in 35 parts by weight of xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in

each case 5 parts by weight). This mixture is introduced into 30 parts by weight of water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion. The composition has an active substance content of 25% by weight.

v) Suspensions (SC, OD, FS)

In an agitated ball mill, 20 parts by weight of a compound I according to the invention are comminuted with addition of 10 parts by weight of dispersants and wetting agents and 70 parts by weight of water or an organic solvent to give a fine active substance suspension. Dilution with water gives a stable suspension of the active substance. The active substance content in the composition is 20% by weight.

vi)Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of a compound I according to the invention are ground finely with addition of 50 parts by weight of dispersants and wetting agents and prepared as water-dispersible or water-soluble granules by means of technical appliances (e. g. extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active substance. The composition has an active substance content of 50% by weight.

vii) Water-dispersible powders and water-soluble powders (WP, SP, SS, WS)

75 parts by weight of a compound I according to the invention are ground in a rotor-stator mill with addition of 25 parts by weight of dispersants, wetting agents and silica gel. Dilution with water gives a stable dispersion or solution of the active substance. The active substance content of the composition is 75% by weight.

viii) Gel (GF)

In an agitated ball mill, 20 parts by weight of a compound I according to the invention are comminuted with addition of 10 parts by weight of dispersants, 1 part by weight of a gelling agent wetters and 70 parts by weight of water or of an organic solvent to give a fine suspension of the active substance. Dilution with water gives a stable suspension of the active substance, whereby a composition with 20% (w/w) of active substance is obtained.

2. Composition types to be applied undiluted

ix)Dustable powders (DP, DS)

5 parts by weight of a compound I according to the invention are ground finely and mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dustable composition having an active substance content of 5% by weight.

x) Granules (GR, FG, GG, MG)

0.5 parts by weight of a compound I according to the invention is ground finely and associated with 99.5 parts by weight of carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted having an active substance content of 0.5% by weight.

xi)ULV solutions (UL)

10 parts by weight of a compound I according to the invention are dissolved in 90 parts by weight of an organic solvent, e. g. xylene. This gives a composition to be applied undiluted having an active substance content of 10% by weight.

The agrochemical compositions generally comprise between 0.01 and 95%, preferably be-

tween 0.1 and 90%, most preferably between 0.5 and 90%, by weight of active substance. The active substances are employed in a purity of from 90% to 100%, preferably from 95% to 100% (according to NMR spectrum).

Water-soluble concentrates (LS), flowable concentrates (FS), powders for dry treatment (DS), water-dispersible powders for slurry treatment (WS), water-soluble powders (SS), emulsions (ES) emulsifiable concentrates (EC) and gels (GF) are usually employed for the purposes of treatment of plant propagation materials, particularly seeds. These compositions can be applied to plant propagation materials, particularly seeds, diluted or undiluted. The compositions in question give, after two-to-tenfold dilution, active substance concentrations of from 0.01 to 60% by weight, preferably from 0.1 to 40% by weight, in the ready-to-use preparations. Application can be carried out before or during sowing. Methods for applying or treating agrochemical compounds and compositions thereof, respectively, on to plant propagation material, especially seeds, are known in the art, and include dressing, coating, pelleting, dusting, soaking and in-furrow application methods of the propagation material. In a preferred embodiment, the compounds or the compositions thereof, respectively, are applied on to the plant propagation material by a method such that germination is not induced, e. g. by seed dressing, pelleting, coating and dusting.

In a preferred embodiment, a suspension-type (FS) composition is used for seed treatment. Typcially, a FS composition may comprise 1-800 g/l of active substance, 1-200 g/l Surfactant, 0 to 200 g/l antifreezing agent, 0 to 400 g/l of binder, 0 to 200 g/l of a pigment and up to 1 liter of a solvent, preferably water.

The active substances can be used as such or in the form of their compositions, e. g. in the form of directly sprayable solutions, powders, suspensions, dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading, brushing, immersing or pouring. The application forms depend entirely on the intended purposes; it is intended to ensure in each case the finest possible distribution of the active substances according to the invention.

Aqueous application forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance, wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active substance concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.001 to 1% by weight of active substance.

The active substances may also be used successfully in the ultra-low-volume process (ULV), it being possible to apply compositions comprising over 95% by weight of active substance, or even to apply the active substance without additives.

When employed in plant protection, the amounts of active substances applied are, depending on the kind of effect desired, from 0.001 to 2 kg per ha, preferably from 0.005 to 2 kg per ha, more preferably from 0.05 to 0.9 kg per ha, in particular from 0.1 to 0.75 kg per ha.

In treatment of plant propagation materials such as seeds, e. g. by dusting, coating or

drenching seed, amounts of active substance of from 0.1 to 1000 g, preferably from 1 to 1000 g, more preferably from 1 to 100 g and most preferably from 5 to 100 g, per 100 kilogram of plant propagation material (preferably seed) are generally required.

When used in the protection of materials or stored products, the amount of active substance applied depends on the kind of application area and on the desired effect. Amounts customarily applied in the protection of materials are, e. g., 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active substance per cubic meter of treated material.

Various types of oils, wetters, adjuvants, herbicides, bactericides, other fungicides and/or pesticides may be added to the active substances or the compositions comprising them, if appropriate not until immediately prior to use (tank mix). These agents can be admixed with the compositions according to the invention in a weight ratio of 1:100 to 100:1, preferably 1:10 to 10:1.

Adjuvants which can be used are in particular organic modified polysiloxanes such as Break Thru S 240®; alcohol alkoxylates such as Atplus 245®, Atplus MBA 1303®, Plurafac LF 300® and Lutensol ON 30®; EO/PO block polymers, e. g. Pluronic RPE 2035® and Genapol B®; alcohol ethoxylates such as Lutensol XP 80®; and dioctyl sulfosuccinate sodium such as Leophen RA®.

The compositions according to the invention can, in the use form as fungicides, also be present together with other active substances, e. g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers, as pre-mix or, if appropriate, not until immeadiately prior to use (tank mix).

Mixing the compounds I or the compositions comprising them in the use form as fungicides with other fungicides results in many cases in an expansion of the fungicidal spectrum of activity being obtained or in a prevention of fungicide resistance development. Furthermore, in many cases, synergistic effects are obtained.

The following list of active substances, in conjunction with which the compounds according to the invention can be used, is intended to illustrate the possible combinations but does not limit them:

A) Respiration inhibitors

- Inhibitors of complex III at Q_o site (e.g. strobilurins): azoxystrobin, coumethoxystrobin, coumoxystrobin, dimoxystrobin, enestroburin, fenaminstrobin, fenoxystrobin/flufenoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, trifloxystrobin, 2-[2-(2,5-dimethyl-phenoxymethyl)-phenyl]-3-methoxy-acrylic acid methyl ester and 2-(2-(3-(2,6-dichlorophenyl)-1-methyl-allylideneaminooxymethyl)-phenyl)-2-methoxyimino-N-methyl-acetamide, pyribencarb, triclopyricarb/chlorodincarb, famoxadone, fenamidone;
- inhibitors of complex III at Q_i site: cyazofamid, amisulbrom, [(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate;

- inhibitors of complex II (e. g. carboxamides): benodanil, bixafen, boscalid, carboxin, fenfuram, fluopyram, flutolanil, fluxapyroxad, furametpyr, isopyrazam, mepronil, oxycarboxin, penflufen, penthiopyrad, sedaxane, tecloftalam, thifluzamide, N-(4'-trifluoromethylthiobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(2-(1,3,3-trimethyl-butyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-[9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide;
- other respiration inhibitors (e.g. complex I, uncouplers): diflumetorim, (5,8-difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine; nitrophenyl derivates: binapacryl, dinobuton, dinocap, fluazinam; ferimzone; organometal compounds: fentin salts, such as fentin-acetate, fentin chloride or fentin hydroxide; ametoctradin; and silthiofam;

B) Sterol biosynthesis inhibitors (SBI fungicides)

- C14 demethylase inhibitors (DMI fungicides): triazoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclobutanil, oxpoconazole, paclobutrazole, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole; imidazoles: imazalil, pefurazoate, prochloraz, triflumizol; pyrimidines, pyridines and piperazines: fenarimol, nuarimol, pyrifenox, triforine;
- Delta14-reductase inhibitors: aldimorph, dodemorph, dodemorph-acetate, fenpropimorph, tridemorph, fenpropidin, piperalin, spiroxamine;
- Inhibitors of 3-keto reductase: fenhexamid;

C) Nucleic acid synthesis inhibitors

- phenylamides or acyl amino acid fungicides: benalaxyl, benalaxyl-M, kiralaxyl, metalaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl;
- others: hymexazole, octhilinone, oxolinic acid, bupirimate, 5-fluorocytosine, 5-fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine, 5-fluoro-2-(4-fluorophenylmethoxy)pyrimidin-4-amine;

D) Inhibitors of cell division and cytoskeleton

- tubulin inhibitors, such as benzimidazoles, thiophanates: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl; triazolopyrimidines: 5-chloro-7-(4-methyl-piperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine
- other cell division inhibitors: diethofencarb, ethaboxam, pencycuron, fluopicolide, zoxamide, metrafenone, pyriofenone;

E) Inhibitors of amino acid and protein synthesis

- methionine synthesis inhibitors (anilino-pyrimidines): cyprodinil, mepanipyrim, pyrimethanil;
- protein synthesis inhibitors: blasticidin-S, kasugamycin, kasugamycin hydrochloride-hydrate, mildiomycin, streptomycin, oxytetracyclin, polyoxine, validamycin A;

F) Signal transduction inhibitors

- MAP / histidine kinase inhibitors: fluoroimid, iprodione, procymidone, vinclozolin, fenpiclonil, fludioxonil;
- G protein inhibitors: quinoxyfen;

G) Lipid and membrane synthesis inhibitors

- Phospholipid biosynthesis inhibitors: edifenphos, iprobenfos, pyrazophos, isoprothiolane;
- lipid peroxidation: dicloran, quintozene, tecnazene, tolclofos-methyl, biphenyl, chloroneb, etridiazole;
- phospholipid biosynthesis and cell wall deposition: dimethomorph, flumorph, mandipropamid, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and N-(1-(1-(4-cyano-phenyl)-ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester;
- compounds affecting cell membrane permeability and fatty acides: propamocarb, propamocarb-hydrochlorid

H) Inhibitors with Multi Site Action

- inorganic active substances: Bordeaux mixture, copper acetate, copper hydroxide, copper oxychloride, basic copper sulfate, sulfur;
- thio- and dithiocarbamates: ferbam, mancozeb, maneb, metam, metiram, propineb, thiram, zineb, ziram;
- organochlorine compounds (e.g. phthalimides, sulfamides, chloronitriles): anilazine, chlorothalonil, captafol, captan, folpet, dichlofluanid, dichlorophen, flusulfamide, hexachlorobenzene, pentachlorphenole and its salts, phthalide, tolylfluanid, N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-methyl-benzenesulfonamide;
- guanidines and others: guanidine, dodine, dodine free base, guazatine, guazatine-acetate, iminoctadine, iminoctadine-triacetate, iminoctadine-tris(albesilate), dithianon;

I) Cell wall synthesis inhibitors

- inhibitors of glucan synthesis: validamycin, polyoxin B; melanin synthesis inhibitors: pyroquilon, tricyclazole, carpropamid, dicyclomet, fenoxanil;

J) Plant defence inducers

- acibenzolar-S-methyl, probenazole, isotianil, tiadinil, prohexadione-calcium; phosphonates: fosetyl, fosetyl-aluminum, phosphorous acid and its salts;

K) Unknown mode of action

- bronopol, chinomethionat, cyflufenamid, cymoxanil, dazomet, debacarb, diclomezine, difenzoquat, difenzoquat-methylsulfate, diphenylamin, fenpyrazamine, flumetover, flusulfamide, flutianil, methasulfocarb, nitrapyrin, nitrothal-isopropyl, oxin-copper, proquinazid, tebufloquin, tecloftalam, triazoxide, 2-butoxy-6-iodo-3-propylchromen-4-one, N-(cyclopropylmethoxyimino-(6-difluoro-methoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide, N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(4-(4-fluoro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(2-methyl-5-trifluoromethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, N'-(5-difluoromethyl-2-methyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, 2-{1-[2-(5-methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(1,2,3,4-tetrahydro-naphthalen-1-yl)-amide, 2-{1-[2-(5-methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(R)-1,2,3,4-tetrahydro-naphthalen-1-yl-amide, 1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone, methoxy-acetic acid 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester, *N*-Methyl-2-{1-[(5-methyl-3-trifluoromethyl-1H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-*N*-[(1R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-

thiazolecarboxamide, 3-[5-(4-methylphenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine, 3-[5-(4-chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (pyrisoxazole), N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzoimidazole,

2-(4-chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-ynyloxy-acetamide;

L) Antifungal biocontrol agents, plant bioactivators: *Ampelomyces quisqualis* (e.g. AQ 10® from Intrachem Bio GmbH & Co. KG, Germany), *Aspergillus flavus* (e.g. AFLAGUARD® from Syngenta, CH), *Aureobasidium pullulans* (e.g. BOTECTOR® from bio-ferm GmbH, Germany), *Bacillus pumilus* (e.g. NRRL Accession No. B-30087 in SONATA® and BALLAD® Plus from AgraQuest Inc., USA), *Bacillus subtilis* (e.g. isolate NRRL-Nr. B-21661 in RHAPSODY®, SERENADE® MAX and SERENADE® ASO from AgraQuest Inc., USA), *Bacillus subtilis* var. *amyloliquefaciens* FZB24 (e.g. TAEGRO® from Novozyme Biologicals, Inc., USA), *Candida oleophila* I-82 (e.g. ASPIRE® from Ecogen Inc., USA), *Candida saitoana* (e.g. BIOCURE® (in mixture with lysozyme) and BIOCOAT® from Micro Flo Company, USA (BASF SE) and Arysta), Chitosan (e.g. ARMOUR-ZEN from BotriZen Ltd., NZ), *Clonostachys rosea* f. *catenulata,* also named *Gliocladium catenulatum* (e.g. isolate J1446: PRESTOP® from Verdera, Finland), *Coniothyrium minitans* (e.g. CONTANS® from Prophyta, Germany), *Cryphonectria parasitica* (e.g. *Endothia parasitica* from CNICM, France), *Cryptococcus albidus* (e.g. YIELD PLUS® from Anchor Bio-Technologies, South Africa), *Fusarium oxysporum* (e.g. BIOFOX® from S.I.A.P.A., Italy, FUSACLEAN® from Natural Plant Protection, France), *Metschnikowia fructicola* (e.g. SHEMER® from Agrogreen, Israel), *Microdochium dimerum* (e.g. ANTIBOT® from Agrauxine, France), *Phlebiopsis gigantea* (e.g. ROTSOP® from Verdera, Finland), *Pseudozyma flocculosa* (e.g. SPORODEX® from Plant Products Co. Ltd., Canada), *Pythium oligandrum* DV74 (e.g. POLYVERSUM® from Remeslo SSRO, Biopreparaty, Czech Rep.), *Reynoutria sachlinensis* (e.g. REGALIA® from Marrone BioInnovations, USA), *Talaromyces flavus* V117b (e.g. PROTUS® from Prophyta, Germany), *Trichoderma asperellum* SKT-1 (e.g. ECO-HOPE® from Kumiai Chemical Industry Co., Ltd., Japan), *T. atroviride* LC52 (e.g. SENTINEL® from Agrimm Technologies Ltd, NZ), *T. harzianum* T-22 (e.g. PLANTSHIELD® der Firma BioWorks Inc., USA), *T. harzianum* TH 35 (e.g. ROOT PRO® from Mycontrol Ltd., Israel), *T. harzianum* T-39 (e.g. TRICHODEX® and TRICHODERMA 2000® from Mycontrol Ltd., Israel and Makhteshim Ltd., Israel), *T. harzianum* and *T. viride* (e.g. TRICHOPEL from Agrimm Technologies Ltd, NZ), *T. harzianum* ICC012 and *T. viride* ICC080 (e.g. REMEDIER® WP from Isagro Ricerca, Italy), *T. polysporum* and *T. harzianum* (e.g. BINAB® from BINAB Bio-Innovation AB, Sweden), *T. stromaticum* (e.g. TRICOVAB® from C.E.P.L.A.C., Brazil), *T. virens* GL-21 (e.g. SOILGARD® from Certis LLC, USA), *T. viride* (e.g. TRIECO® from Ecosense Labs. (India) Pvt. Ltd., Indien, BIO-CURE® F from T. Stanes & Co. Ltd., Indien), *T. viride* TV1 (e.g. T. viride TV1 from Agribiotec srl, Italy), *Ulocladium oudemansii* HRU3 (e.g. BOTRY-ZEN® from Botry-Zen Ltd, NZ);

M) Growth regulators

abscisic acid, amidochlor, ancymidol, 6-benzylaminopurine, brassinolide, butralin, chlormequat (chlormequat chloride), choline chloride, cyclanilide, daminozide, dikegulac, dimethipin, 2,6-dimethylpuridine, ethephon, flumetralin, flurprimidol, fluthiacet, forchlorfenuron, gibberellic acid,

inabenfide, indole-3-acetic acid , maleic hydrazide, mefluidide, mepiquat (mepiquat chloride), naphthaleneacetic acid, N-6-benzyladenine, paclobutrazol, prohexadione (prohexadione-calcium), prohydrojasmon, thidiazuron, triapenthenol, tributyl phosphorotrithioate, 2,3,5-tri-iodobenzoic acid , trinexapac-ethyl and uniconazole;

N) Herbicides

- acetamides: acetochlor, alachlor, butachlor, dimethachlor, dimethenamid, flufenacet, mefenacet, metolachlor, metazachlor, napropamide, naproanilide, pethoxamid, pretilachlor, propachlor, thenylchlor;
- amino acid derivatives: bilanafos, glyphosate, glufosinate, sulfosate;
- aryloxyphenoxypropionates: clodinafop, cyhalofop-butyl, fenoxaprop, fluazifop, haloxyfop, metamifop, propaquizafop, quizalofop, quizalofop-P-tefuryl;
- Bipyridyls: diquat, paraquat;
- (thio)carbamates: asulam, butylate, carbetamide, desmedipham, dimepiperate, eptam (EPTC), esprocarb, molinate, orbencarb, phenmedipham, prosulfocarb, pyributicarb, thiobencarb, triallate;
- cyclohexanediones: butroxydim, clethodim, cycloxydim, profoxydim, sethoxydim, tepraloxydim, tralkoxydim;
- dinitroanilines: benfluralin, ethalfluralin, oryzalin, pendimethalin, prodiamine, trifluralin;
- diphenyl ethers: acifluorfen, aclonifen, bifenox, diclofop, ethoxyfen, fomesafen, lactofen, oxyfluorfen;
- hydroxybenzonitriles: bomoxynil, dichlobenil, ioxynil;
- imidazolinones: imazamethabenz, imazamox, imazapic, imazapyr, imazaquin, imazethapyr;
- phenoxy acetic acids: clomeprop, 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4-DB, dichlorprop, MCPA, MCPA-thioethyl, MCPB, Mecoprop;
- pyrazines: chloridazon, flufenpyr-ethyl, fluthiacet, norflurazon, pyridate;
- pyridines: aminopyralid, clopyralid, diflufenican, dithiopyr, fluridone, fluroxypyr, picloram, picolinafen, thiazopyr;
- sulfonyl ureas: amidosulfuron, azimsulfuron, bensulfuron, chlorimuron-ethyl, chlorsulfuron, cinosulfuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, iodosulfuron, mesosulfuron, metazosulfuron, metsulfuron-methyl, nicosulfuron, oxasulfuron, primisulfuron, prosulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron, thifensulfuron, triasulfuron, tribenuron, trifloxysulfuron, triflusulfuron, tritosulfuron, 1-((2-chloro-6-propyl-imidazo[1,2-b]pyridazin-3-yl)sulfonyl)-3-(4,6-dimethoxy-pyrimidin-2-yl)urea;
- triazines: ametryn, atrazine, cyanazine, dimethametryn, ethiozin, hexazinone, metamitron, metribuzin, prometryn, simazine, terbuthylazine, terbutryn, triaziflam;
- ureas: chlorotoluron, daimuron, diuron, fluometuron, isoproturon, linuron, methabenzthiazuron,tebuthiuron;
- other acetolactate synthase inhibitors: bispyribac-sodium, cloransulam-methyl, diclosulam, florasulam, flucarbazone, flumetsulam, metosulam, ortho-sulfamuron, penoxsulam, propoxycarbazone, pyribambenz-propyl, pyribenzoxim, pyriftalid, pyriminobac-methyl, pyrimisulfan, pyrithiobac, pyroxasulfone, pyroxsulam;
- others: amicarbazone, aminotriazole, anilofos, beflubutamid, benazolin, bencarba-

zone,benfluresate, benzofenap, bentazone, benzobicyclon, bicyclopyrone, bromacil, bromobutide, butafenacil, butamifos, cafenstrole, carfentrazone, cinidon-ethyl, chlorthal, cinmethylin, clomazone, cumyluron, cyprosulfamide, dicamba, difenzoquat, diflufenzopyr, *Drechslera monoceras*, endothal, ethofumesate, etobenzanid, fenoxasulfone, fentrazamide, flumiclorac-pentyl, flumioxazin, flupoxam, flurochloridone, flurtamone, indanofan, isoxaben, isoxaflutole, lenacil, propanil, propyzamide, quinclorac, quinmerac, mesotrione, methyl arsonic acid, naptalam, oxadiargyl, oxadiazon, oxaziclomefone, pentoxazone, pinoxaden, pyraclonil, pyraflufen-ethyl, pyrasulfotole, pyrazoxyfen, pyrazolynate, quinoclamine, saflufenacil, sulcotrione, sulfentrazone, terbacil, tefuryltrione, tembotrione, thiencarbazone, topramezone, (3-[2-chloro-4-fluoro-5-(3-methyl-2,6-dioxo-4-trifluoromethyl-3,6-dihydro-2H-pyrimidin-1-yl)-phenoxy]-pyridin-2-yloxy)-acetic acid ethyl ester, 6-amino-5-chloro-2-cyclopropyl-pyrimidine-4-carboxylic acid methyl ester, 6-chloro-3-(2-cyclopropyl-6-methyl-phenoxy)-pyridazin-4-ol, 4-amino-3-chloro-6-(4-chloro-phenyl)-5-fluoro-pyridine-2-carboxylic acid, 4-amino-3-chloro-6-(4-chloro-2-fluoro-3-methoxy-phenyl)-pyridine-2-carboxylic acid methyl ester, and 4-amino-3-chloro-6-(4-chloro-3-dimethylamino-2-fluoro-phenyl)-pyridine-2-carboxylic acid methyl ester.

O) Insecticides

- organo(thio)phosphates: acephate, azamethiphos, azinphos-methyl, chlorpyrifos, chlorpyrifos-methyl, chlorfenvinphos, diazinon, dichlorvos, dicrotophos, dimethoate, disulfoton, ethion, fenitrothion, fenthion, isoxathion, malathion, methamidophos, methidathion, methyl-parathion, mevinphos, monocrotophos, oxydemeton-methyl, paraoxon, parathion, phenthoate, phosalone, phosmet, phosphamidon, phorate, phoxim, pirimiphos-methyl, profenofos, prothiofos, sulprophos, tetrachlorvinphos, terbufos, triazophos, trichlorfon;
- carbamates: alanycarb, aldicarb, bendiocarb, benfuracarb, carbaryl, carbofuran, carbosulfan, fenoxycarb, furathiocarb, methiocarb, methomyl, oxamyl, pirimicarb, propoxur, thiodicarb, triazamate;
- pyrethroids: allethrin, bifenthrin, cyfluthrin, cyhalothrin, cyphenothrin, cypermethrin, alpha-cypermethrin, beta-cypermethrin, zeta-cypermethrin, deltamethrin, esfenvalerate, etofenprox, fenpropathrin, fenvalerate, imiprothrin, lambda-cyhalothrin, permethrin, prallethrin, pyrethrin I and II, resmethrin, silafluofen, tau-fluvalinate, tefluthrin, tetramethrin, tralomethrin, transfluthrin, profluthrin, dimefluthrin;
- insect growth regulators: a) chitin synthesis inhibitors: benzoylureas: chlorfluazuron, cyramazin, diflubenzuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, teflubenzuron, triflumuron; buprofezin, diofenolan, hexythiazox, etoxazole, clofentazine; b) ecdysone antagonists: halofenozide, methoxyfenozide, tebufenozide, azadirachtin; c) juvenoids: pyriproxyfen, methoprene, fenoxycarb; d) lipid biosynthesis inhibitors: spirodiclofen, spiromesifen, spirotetramat;
- nicotinic receptor agonists/antagonists compounds: clothianidin, dinotefuran, imidacloprid, thiamethoxam, nitenpyram, acetamiprid, thiacloprid, 1-(2-chloro-thiazol-5-ylmethyl)-2-nitrimino-3,5-dimethyl-[1,3,5]triazinane;
- GABA antagonist compounds: endosulfan, ethiprole, fipronil, vaniliprole, pyrafluprole, pyriprole, 5-amino-1-(2,6-dichloro-4-methyl-phenyl)-4-sulfinamoyl-1H-pyrazole-3-carbothioic acid amide;

- macrocyclic lactone insecticides: abamectin, emamectin, milbemectin, lepimectin, spinosad, spinetoram;
- mitochondrial electron transport inhibitor (METI) I acaricides: fenazaquin, pyridaben, tebufenpyrad, tolfenpyrad, flufenerim;
- METI II and III compounds: acequinocyl, fluacyprim, hydramethylnon;
- Uncouplers: chlorfenapyr;
- oxidative phosphorylation inhibitors: cyhexatin, diafenthiuron, fenbutatin oxide, propargite;
- moulting disruptor compounds: cryomazine;
- mixed function oxidase inhibitors: piperonyl butoxide;
- sodium channel blockers: indoxacarb, metaflumizone;
- others: benclothiaz, bifenazate, cartap, flonicamid, pyridalyl, pymetrozine, sulfur, thiocyclam, flubendiamide, chlorantraniliprole, cyazypyr (HGW86), cyenopyrafen, flupyrazofos, cyflumetofen, amidoflumet, imicyafos, bistrifluron, and pyrifluquinazon.

The present invention furthermore relates to agrochemical compositions comprising a mixture of at least one compound I (component 1) and at least one further active substance useful for plant protection, e. g. selected from the groups A) to O) (component 2), in particular one further fungicide, e. g. one or more fungicide from the groups A) to F), as described above, and if desired one suitable solvent or solid carrier. Those mixtures are of particular interest, since many of them at the same application rate show higher efficiencies against harmful fungi. Furthermore, combating harmful fungi with a mixture of compounds I and at least one fungicide from groups A) to L), as described above, is more efficient than combating those fungi with individual compounds I or individual fungicides from groups A) to L). By applying compounds I together with at least one active substance from groups A) to O) a synergistic effect can be obtained, i.e. more then simple addition of the individual effects is obtained (synergistic mixtures).

According to this invention, applying the compounds I together with at least one further active substance is to be understood to denote, that at least one compound of formula I and at least one further active substance occur simultaneously at the site of action (i.e. the harmful fungi to be controlled or their habitats such as infected plants, plant propagation materials, particularly seeds, surfaces, materials or the soil as well as plants, plant propagation materials, particularly seeds, soil, surfaces, materials or rooms to be protected from fungal attack) in a fungicidally effective amount. This can be obtained by applying the compounds I and at least one further active substance simultaneously, either jointly (e. g. as tank-mix) or sperately, or in succession, wherein the time interval between the individual applications is selected to ensure that the active substance applied first still occurs at the site of action in a sufficient amount at the time of application of the further active substance(s). The order of application is not essential for working of the present invention.

In binary mixtures, i.e. compositions according to the invention comprising one compound I (component 1) and one further active substance (component 2), e. g. one active substance from groups A) to O), the weight ratio of component 1 and component 2 generally depends from the properties of the active substances used, usually it is in the range of from 1:100 to 100:1, regularly in the range of from 1:50 to 50:1, preferably in the range of from 1:20 to 20:1, more preferably in the range of from 1:10 to 10:1 and in particular in the range of from 1:3 to 3:1.

In ternary mixtures, i.e. compositions according to the invention comprising one compound I (component 1) and a first further active substance (component 2) and a second further active substance (component 3), e. g. two active substances from groups A) to O), the weight ratio of component 1 and component 2 depends from the properties of the active substances used, preferably it is in the range of from 1:50 to 50:1 and particularly in the range of from 1:10 to 10:1, and the weight ratio of component 1 and component 3 preferably is in the range of from 1:50 to 50:1 and particularly in the range of from 1:10 to 10:1.

The components can be used individually or already partially or completely mixed with one another to prepare the composition according to the invention. It is also possible for them to be packaged and used further as combination composition such as a kit of parts.

In one embodiment of the invention, the kits may include one or more, including all, components that may be used to prepare a subject agrochemical composition. E. g., kits may include one or more fungicide component(s) and/or an adjuvant component and/or a insecticide component and/or a growth regulator component and/or a herbicde. One or more of the components may already be combined together or pre-formulated. In those embodiments where more than two components are provided in a kit, the components may already be combined together and as such are packaged in a single container such as a vial, bottle, can, pouch, bag or canister. In other embodiments, two or more components of a kit may be packaged separately, i. e., not pre-formulated. As such, kits may include one or more separate containers such as vials, cans, bottles, pouches, bags or canisters, each container containing a separate component for an agrochemical composition. In both forms, a component of the kit may be applied separately from or together with the further components or as a component of a combination composition according to the invention for preparing the composition according to the invention.

The user applies the composition according to the invention usually from a predosage device, a knapsack sprayer, a spray tank or a spray plane. Here, the agrochemical composition is made up with water and/or buffer to the desired application concentration, it being possible, if appropriate, to add further auxiliaries, and the ready-to-use spray liquor or the agrochemical composition according to the invention is thus obtained. Usually, 50 to 500 liters of the ready-to-use spray liquor are applied per hectare of agricultural useful area, preferably 100 to 400 liters.

According to one embodiment, individual components of the composition according to the invention such as parts of a kit or parts of a binary or ternary mixture may be mixed by the user himself in a spray tank and further auxiliaries may be added, if appropriate (tank mix).

In a further embodiment, either individual components of the composition according to the invention or partially premixed components, e. g. components comprising compounds I and/or active substances from the groups A) to O), may be mixed by the user in a spray tank and further auxiliaries and additives may be added, if appropriate (tank mix).

In a further embodiment, either individual components of the composition according to the invention or partially premixed components, e. g. components comprising compounds I and/or active substances from the groups A) to O), can be applied jointly (e. .g. after tankmix) or consecutively.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group A) (component 2) and particularly selected from azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, orysastrobin, picoxystrobin, pyra-

clostrobin, trifloxystrobin; famoxadone, fenamidone; bixafen, boscalid, fluopyram, fluxapyroxad, isopyrazam, penflufen, penthiopyrad, sedaxane; ametoctradin, cyazofamid, fluazinam, fentin salts, such as fentin acetate.

Preference is given to mixtures comprising a compound of formula I (component 1) and at least one active substance selected from group B) (component 2) and particularly selected from cyproconazole, difenoconazole, epoxiconazole, fluquinconazole, flusilazole, flutriafol, metconazole, myclobutanil, penconazole, propiconazole, prothioconazole, triadimefon, triadimenol, tebuconazole, tetraconazole, triticonazole, prochloraz, fenarimol, triforine; dodemorph, fenpropimorph, tridemorph, fenpropidin, spiroxamine; fenhexamid.

Preference is given to mixtures comprising a compound of formula I (component 1) and at least one active substance selected from group C) (component 2) and particularly selected from metalaxyl, (metalaxyl-M) mefenoxam, ofurace.

Preference is given to mixtures comprising a compound of formula I (component 1) and at least one active substance selected from group D) (component 2) and particularly selected from benomyl, carbendazim, thiophanate-methyl, ethaboxam, fluopicolide, zoxamide, metrafenone, pyriofenone.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group E) (component 2) and particularly selected from cyprodinil, mepanipyrim, pyrimethanil.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group F) (component 2) and particularly selected from iprodione, fludioxonil, vinclozolin, quinoxyfen.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group G) (component 2) and particularly selected from dimethomorph, flumorph, iprovalicarb, benthiavalicarb, mandipropamid, propamocarb.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group H) (component 2) and particularly selected from copper acetate, copper hydroxide, copper oxychloride, copper sulfate, sulfur, mancozeb, metiram, propineb, thiram, captafol, folpet, chlorothalonil, dichlofluanid, dithianon.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group I) (component 2) and particularly selected from carpropamid and fenoxanil.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group J) (component 2) and particularly selected from acibenzolar-S-methyl, probenazole, tiadinil, fosetyl, fosetyl-aluminium, H_3PO_3 and salts thereof.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group K) (component 2) and particularly selected from cymoxanil, proquinazid and *N*-methyl-2-{1-[(5-methyl-3-trifluoromethyl-1H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-*N*-[(1R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide.

Preference is also given to mixtures comprising a compound I (component 1) and at least one active substance selected from group L) (component 2) and particularly selected from *Bacillus subtilis* strain NRRL No. B-21661, *Bacillus pumilus* strain NRRL No. B-30087 and *Ulocladium oudemansii* .

Accordingly, the present invention furthermore relates to compositions comprising one compound I (component 1) and one further active substance (component 2), which further active substance is selected from the column "Component 2" of the lines B-1 to B-360 of Table B.

A further embodiment relates to the compositions B-1 to B-360 listed in Table B, where a row of Table B corresponds in each case to a fungicidal composition comprising one of the in the present specification individualized compounds of formula I (component 1) and the respective further active substance from groups A) to O) (component 2) stated in the row in question. Preferably, the compositions described comprise the active substances in synergistically effective amounts.

Table B: Composition comprising one indiviualized compound I and one further active substance from groups A) to O)

Mixture	Component 1	Component 2
B-1	one individualized compound I	Azoxystrobin
B-2	one individualized compound I	Coumethoxystrobin
B-3	one individualized compound I	Coumoxystrobin
B-4	one individualized compound I	Dimoxystrobin
B-5	one individualized compound I	Enestroburin
B-6	one individualized compound I	Fenaminstrobin
B-7	one individualized compound I	Fenoxystrobin/Flufenoxystrobin
B-8	one individualized compound I	Fluoxastrobin
B-9	one individualized compound I	Kresoxim-methyl
B-10	one individualized compound I	Metominostrobin
B-11	one individualized compound I	Orysastrobin
B-12	one individualized compound I	Picoxystrobin
B-13	one individualized compound I	Pyraclostrobin
B-14	one individualized compound I	Pyrametostrobin
B-15	one individualized compound I	Pyraoxystrobin
B-16	one individualized compound I	Pyribencarb
B-17	one individualized compound I	Trifloxystrobin
B-18	one individualized compound I	Triclopyricarb/Chlorodincarb
B-19	one individualized compound I	2-[2-(2,5-dimethyl-phenoxymethyl)-phenyl]-3-methoxy-acrylic acid methyl ester
B-20	one individualized compound I	2-(2-(3-(2,6-dichlorophenyl)-1-methyl-allylideneaminooxymethyl)-phenyl)-2-methoxyimino-N-methyl-acetamide
B-21	one individualized compound I	Benalaxyl
B-22	one individualized compound I	Benalaxyl-M
B-23	one individualized compound I	Benodanil
B-24	one individualized compound I	Bixafen
B-25	one individualized compound I	Boscalid
B-26	one individualized compound I	Carboxin

Mixture	Component 1	Component 2
B-27	one individualized compound I	Fenfuram
B-28	one individualized compound I	Fenhexamid
B-29	one individualized compound I	Flutolanil
B-30	one individualized compound I	Fluxapyroxad
B-31	one individualized compound I	Furametpyr
B-32	one individualized compound I	Isopyrazam
B-33	one individualized compound I	Isotianil
B-34	one individualized compound I	Kiralaxyl
B-35	one individualized compound I	Mepronil
B-36	one individualized compound I	Metalaxyl
B-37	one individualized compound I	Metalaxyl-M
B-38	one individualized compound I	Ofurace
B-39	one individualized compound I	Oxadixyl
B-40	one individualized compound I	Oxycarboxin
B-41	one individualized compound I	Penflufen
B-42	one individualized compound I	Penthiopyrad
B-43	one individualized compound I	Sedaxane
B-44	one individualized compound I	Tecloftalam
B-45	one individualized compound I	Thifluzamide
B-46	one individualized compound I	Tiadinil
B-47	one individualized compound I	2-Amino-4-methyl-thiazole-5-carboxylic acid anilide
B-48	one individualized compound I	N-(4'-trifluoromethylthiobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide
B-49	one individualized compound I	N-(2-(1,3,3-trimethyl-butyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide
B-50	one individualized compound I	N-[9-(dichloromethylene)-1,2,3,4-tetra-hydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyr-azole-4-carboxamide
B-51	one individualized compound I	Dimethomorph
B-52	one individualized compound I	Flumorph
B-53	one individualized compound I	Pyrimorph
B-54	one individualized compound I	Flumetover
B-55	one individualized compound I	Fluopicolide
B-56	one individualized compound I	Fluopyram
B-57	one individualized compound I	Zoxamide
B-58	one individualized compound I	Carpropamid
B-59	one individualized compound I	Diclocymet

Mixture	Component 1	Component 2
B-60	one individualized compound I	Mandipropamid
B-61	one individualized compound I	Oxytetracyclin
B-62	one individualized compound I	Silthiofam
B-63	one individualized compound I	N-(6-methoxy-pyridin-3-yl) cyclopropanecarboxylic acid amide
B-64	one individualized compound I	Azaconazole
B-65	one individualized compound I	Bitertanol
B-66	one individualized compound I	Bromuconazole
B-67	one individualized compound I	Cyproconazole
B-68	one individualized compound I	Difenoconazole
B-69	one individualized compound I	Diniconazole
B-70	one individualized compound I	Diniconazole-M
B-71	one individualized compound I	Epoxiconazole
B-72	one individualized compound I	Fenbuconazole
B-73	one individualized compound I	Fluquinconazole
B-74	one individualized compound I	Flusilazole
B-75	one individualized compound I	Flutriafol
B-76	one individualized compound I	Hexaconazol
B-77	one individualized compound I	Imibenconazole
B-78	one individualized compound I	Ipconazole
B-79	one individualized compound I	Metconazole
B-80	one individualized compound I	Myclobutanil
B-81	one individualized compound I	Oxpoconazol
B-82	one individualized compound I	Paclobutrazol
B-83	one individualized compound I	Penconazole
B-84	one individualized compound I	Propiconazole
B-85	one individualized compound I	Prothioconazole
B-86	one individualized compound I	Simeconazole
B-87	one individualized compound I	Tebuconazole
B-88	one individualized compound I	Tetraconazole
B-89	one individualized compound I	Triadimefon
B-90	one individualized compound I	Triadimenol
B-91	one individualized compound I	Triticonazole
B-92	one individualized compound I	Uniconazole
B-93	one individualized compound I	Cyazofamid
B-94	one individualized compound I	Imazalil
B-95	one individualized compound I	Imazalil-sulfate
B-96	one individualized compound I	Pefurazoate
B-97	one individualized compound I	Prochloraz
B-98	one individualized compound I	Triflumizole
B-99	one individualized compound I	Benomyl

Mixture	Component 1	Component 2
B-100	one individualized compound I	Carbendazim
B-101	one individualized compound I	Fuberidazole
B-102	one individualized compound I	Thiabendazole
B-103	one individualized compound I	Ethaboxam
B-104	one individualized compound I	Etridiazole
B-105	one individualized compound I	Hymexazole
B-106	one individualized compound I	2-(4-Chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-ynyloxy-acetamide
B-107	one individualized compound I	Fluazinam
B-108	one individualized compound I	Pyrifenox
B-109	one individualized compound I	3-[5-(4-Chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (Pyrisoxazole)
B-110	one individualized compound I	3-[5-(4-Methyl-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine
B-111	one individualized compound I	Bupirimate
B-112	one individualized compound I	Cyprodinil
B-113	one individualized compound I	5-Fluorocytosine
B-114	one individualized compound I	5-Fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine
B-115	one individualized compound I	5-Fluoro-2-(4-fluorophenylmethoxy)-pyrimidin-4-amine
B-116	one individualized compound I	Diflumetorim
B-117	one individualized compound I	(5,8-Difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine
B-118	one individualized compound I	Fenarimol
B-119	one individualized compound I	Ferimzone
B-120	one individualized compound I	Mepanipyrim
B-121	one individualized compound I	Nitrapyrin
B-122	one individualized compound I	Nuarimol
B-123	one individualized compound I	Pyrimethanil
B-124	one individualized compound I	Triforine
B-125	one individualized compound I	Fenpiclonil
B-126	one individualized compound I	Fludioxonil
B-127	one individualized compound I	Aldimorph
B-128	one individualized compound I	Dodemorph
B-129	one individualized compound I	Dodemorph-acetate
B-130	one individualized compound I	Fenpropimorph
B-131	one individualized compound I	Tridemorph
B-132	one individualized compound I	Fenpropidin

Mixture	Component 1	Component 2
B-133	one individualized compound I	Fluoroimid
B-134	one individualized compound I	Iprodione
B-135	one individualized compound I	Procymidone
B-136	one individualized compound I	Vinclozolin
B-137	one individualized compound I	Famoxadone
B-138	one individualized compound I	Fenamidone
B-139	one individualized compound I	Flutianil
B-140	one individualized compound I	Octhilinone
B-141	one individualized compound I	Probenazole
B-142	one individualized compound I	Fenpyrazamine
B-143	one individualized compound I	Acibenzolar-S-methyl
B-144	one individualized compound I	Ametoctradin
B-145	one individualized compound I	Amisulbrom
B-146	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutyryloxymethoxy-4-methoxypyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-[1,5]dioxonan-7-yl] 2-methylpropanoate
B-147	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate
B-148	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate
B-149	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate
B-150	one individualized compound I	[(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate
B-151	one individualized compound I	Anilazin
B-152	one individualized compound I	Blasticidin-S
B-153	one individualized compound I	Captafol
B-154	one individualized compound I	Captan
B-155	one individualized compound I	Chinomethionat
B-156	one individualized compound I	Dazomet
B-157	one individualized compound I	Debacarb
B-158	one individualized compound I	Diclomezine

Mixture	Component 1	Component 2
B-159	one individualized compound I	Difenzoquat,
B-160	one individualized compound I	Difenzoquat-methylsulfate
B-161	one individualized compound I	Fenoxanil
B-162	one individualized compound I	Folpet
B-163	one individualized compound I	Oxolinsäure
B-164	one individualized compound I	Piperalin
B-165	one individualized compound I	Proquinazid
B-166	one individualized compound I	Pyroquilon
B-167	one individualized compound I	Quinoxyfen
B-168	one individualized compound I	Triazoxid
B-169	one individualized compound I	Tricyclazole
B-170	one individualized compound I	2-Butoxy-6-iodo-3-propyl-chromen-4-one
B-171	one individualized compound I	5-Chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzoimidazole
B-172	one individualized compound I	5-Chloro-7-(4-methyl-piperidin-1-yl)-6-(2,4,6-trifluoro-phenyl)-[1,2,4]triazolo[1,5-a]pyrimidine
B-173	one individualized compound I	Ferbam
B-174	one individualized compound I	Mancozeb
B-175	one individualized compound I	Maneb
B-176	one individualized compound I	Metam
B-177	one individualized compound I	Methasulphocarb
B-178	one individualized compound I	Metiram
B-179	one individualized compound I	Propineb
B-180	one individualized compound I	Thiram
B-181	one individualized compound I	Zineb
B-182	one individualized compound I	Ziram
B-183	one individualized compound I	Diethofencarb
B-184	one individualized compound I	Benthiavalicarb
B-185	one individualized compound I	Iprovalicarb
B-186	one individualized compound I	Propamocarb
B-187	one individualized compound I	Propamocarb hydrochlorid
B-188	one individualized compound I	Valifenalate
B-189	one individualized compound I	N-(1-(1-(4-cyanophenyl)ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester
B-190	one individualized compound I	Dodine
B-191	one individualized compound I	Dodine free base
B-192	one individualized compound I	Guazatine
B-193	one individualized compound I	Guazatine-acetate

Mixture	Component 1	Component 2
B-194	one individualized compound I	Iminoctadine
B-195	one individualized compound I	Iminoctadine-triacetate
B-196	one individualized compound I	Iminoctadine-tris(albesilate)
B-197	one individualized compound I	Kasugamycin
B-198	one individualized compound I	Kasugamycin-hydrochloride-hydrate
B-199	one individualized compound I	Polyoxine
B-200	one individualized compound I	Streptomycin
B-201	one individualized compound I	Validamycin A
B-202	one individualized compound I	Binapacryl
B-203	one individualized compound I	Dicloran
B-204	one individualized compound I	Dinobuton
B-205	one individualized compound I	Dinocap
B-206	one individualized compound I	Nitrothal-isopropyl
B-207	one individualized compound I	Tecnazen
B-208	one individualized compound I	Fentin salts
B-209	one individualized compound I	Dithianon
B-210	one individualized compound I	Isoprothiolane
B-211	one individualized compound I	Edifenphos
B-212	one individualized compound I	Fosetyl, Fosetyl-aluminium
B-213	one individualized compound I	Iprobenfos
B-214	one individualized compound I	Phosphorous acid (H_3PO_3) and derivatives
B-215	one individualized compound I	Pyrazophos
B-216	one individualized compound I	Tolclofos-methyl
B-217	one individualized compound I	Chlorothalonil
B-218	one individualized compound I	Dichlofluanid
B-219	one individualized compound I	Dichlorophen
B-220	one individualized compound I	Flusulfamide
B-221	one individualized compound I	Hexachlorbenzene
B-222	one individualized compound I	Pencycuron
B-223	one individualized compound I	Pentachlorophenol and salts
B-224	one individualized compound I	Phthalide
B-225	one individualized compound I	Quintozene
B-226	one individualized compound I	Thiophanate Methyl
B-227	one individualized compound I	Tolylfluanid
B-228	one individualized compound I	N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-methyl-benzenesulfonamide
B-229	one individualized compound I	Bordeaux mixture
B-230	one individualized compound I	Copper acetate
B-231	one individualized compound I	Copper hydroxide
B-232	one individualized compound I	Copper oxychloride

Mixture	Component 1	Component 2
B-233	one individualized compound I	basic Copper sulfate
B-234	one individualized compound I	Sulfur
B-235	one individualized compound I	Biphenyl
B-236	one individualized compound I	Bronopol
B-237	one individualized compound I	Cyflufenamid
B-238	one individualized compound I	Cymoxanil
B-239	one individualized compound I	Diphenylamin
B-240	one individualized compound I	Metrafenone
B-241	one individualized compound I	Pyriofenone
B-242	one individualized compound I	Mildiomycin
B-243	one individualized compound I	Oxin-copper
B-244	one individualized compound I	Prohexadione calcium
B-245	one individualized compound I	Spiroxamine
B-246	one individualized compound I	Tebufloquin
B-247	one individualized compound I	Tolylfluanid
B-248	one individualized compound I	N-(Cyclopropylmethoxyimino-(6-difluoromethoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide
B-249	one individualized compound I	N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine
B-250	one individualized compound I	N'-(4-(4-fluoro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine
B-251	one individualized compound I	N'-(2-methyl-5-trifluoromethyl-4-(3-tri-methylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine
B-252	one individualized compound I	N'-(5-difluoromethyl-2-methyl-4-(3-tri-methylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine
B-253	one individualized compound I	2-{1-[2-(5-Methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(1,2,3,4-tetrahydro-naphthalen-1-yl)-amide
B-254	one individualized compound I	2-{1-[2-(5-Methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(R)-1,2,3,4-tetrahydro-naphthalen-1-yl-amide

Mixture	Component 1	Component 2
B-255	one individualized compound I	1-[4-[4-[5-(2,6-difluorophenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone
B-256	one individualized compound I	Methoxy-acetic acid 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester
B-257	one individualized compound I	*N*-Methyl-2-{1-[(5-methyl-3-trifluoromethyl-1H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-*N*-[(1R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide
B-258	one individualized compound I	*Bacillus subtilis* NRRL No. B-21661
B-259	one individualized compound I	*Bacillus pumilus* NRRL No. B-30087
B-260	one individualized compound I	*Ulocladium oudemansii*
B-261	one individualized compound I	Carbaryl
B-262	one individualized compound I	Carbofuran
B-263	one individualized compound I	Carbosulfan
B-264	one individualized compound I	Methomylthiodicarb
B-265	one individualized compound I	Bifenthrin
B-266	one individualized compound I	Cyfluthrin
B-267	one individualized compound I	Cypermethrin
B-268	one individualized compound I	alpha-Cypermethrin
B-269	one individualized compound I	zeta-Cypermethrin
B-270	one individualized compound I	Deltamethrin
B-271	one individualized compound I	Esfenvalerate
B-272	one individualized compound I	Lambda-cyhalothrin
B-273	one individualized compound I	Permethrin
B-274	one individualized compound I	Tefluthrin
B-275	one individualized compound I	Diflubenzuron
B-276	one individualized compound I	Flufenoxuron
B-277	one individualized compound I	Lufenuron
B-278	one individualized compound I	Teflubenzuron
B-279	one individualized compound I	Spirotetramate
B-280	one individualized compound I	Clothianidin
B-281	one individualized compound I	Dinotefuran
B-282	one individualized compound I	Imidacloprid
B-283	one individualized compound I	Thiamethoxam
B-284	one individualized compound I	Acetamiprid
B-285	one individualized compound I	Thiacloprid
B-286	one individualized compound I	Endosulfan
B-287	one individualized compound I	Fipronil
B-288	one individualized compound I	Abamectin

Mixture	Component 1	Component 2
B-289	one individualized compound I	Emamectin
B-290	one individualized compound I	Spinosad
B-291	one individualized compound I	Spinetoram
B-292	one individualized compound I	Hydramethylnon
B-293	one individualized compound I	Chlorfenapyr
B-294	one individualized compound I	Fenbutatin oxide
B-295	one individualized compound I	Indoxacarb
B-296	one individualized compound I	Metaflumizone
B-297	one individualized compound I	Flonicamid
B-298	one individualized compound I	Lubendiamide
B-299	one individualized compound I	Chlorantraniliprole
B-300	one individualized compound I	Cyazypyr (HGW86)
B-301	one individualized compound I	Cyflumetofen
B-302	one individualized compound I	Acetochlor
B-303	one individualized compound I	Dimethenamid
B-304	one individualized compound I	metolachlor
B-305	one individualized compound I	Metazachlor
B-306	one individualized compound I	Glyphosate
B-307	one individualized compound I	Glufosinate
B-308	one individualized compound I	Sulfosate
B-309	one individualized compound I	Clodinafop
B-310	one individualized compound I	Fenoxaprop
B-311	one individualized compound I	Fluazifop
B-312	one individualized compound I	Haloxyfop
B-313	one individualized compound I	Paraquat
B-314	one individualized compound I	Phenmedipham
B-315	one individualized compound I	Clethodim
B-316	one individualized compound I	Cycloxydim
B-317	one individualized compound I	Profoxydim
B-318	one individualized compound I	Sethoxydim
B-319	one individualized compound I	Tepraloxydim
B-320	one individualized compound I	Pendimethalin
B-321	one individualized compound I	Prodiamine
B-322	one individualized compound I	Trifluralin
B-323	one individualized compound I	Acifluorfen
B-324	one individualized compound I	Bromoxynil
B-325	one individualized compound I	Imazamethabenz
B-326	one individualized compound I	Imazamox
B-327	one individualized compound I	Imazapic
B-328	one individualized compound I	Imazapyr
B-329	one individualized compound I	Imazaquin

Mixture	Component 1	Component 2
B-330	one individualized compound I	Imazethapyr
B-331	one individualized compound I	2,4-Dichlorophenoxyacetic acid (2,4-D)
B-332	one individualized compound I	Chloridazon
B-333	one individualized compound I	Clopyralid
B-334	one individualized compound I	Fluroxypyr
B-335	one individualized compound I	Picloram
B-336	one individualized compound I	Picolinafen
B-337	one individualized compound I	Bensulfuron
B-338	one individualized compound I	Chlorimuron-ethyl
B-339	one individualized compound I	Cyclosulfamuron
B-340	one individualized compound I	Iodosulfuron
B-341	one individualized compound I	Mesosulfuron
B-342	one individualized compound I	Metsulfuron-methyl
B-343	one individualized compound I	Nicosulfuron
B-344	one individualized compound I	Rimsulfuron
B-345	one individualized compound I	Triflusulfuron
B-346	one individualized compound I	Atrazine
B-347	one individualized compound I	Hexazinone
B-348	one individualized compound I	Diuron
B-349	one individualized compound I	Florasulam
B-350	one individualized compound I	Pyroxasulfone
B-351	one individualized compound I	Bentazone
B-352	one individualized compound I	Cinidon-ethyl
B-353	one individualized compound I	Cinmethylin
B-354	one individualized compound I	Dicamba
B-355	one individualized compound I	Diflufenzopyr
B-356	one individualized compound I	Quinclorac
B-357	one individualized compound I	Quinmerac
B-358	one individualized compound I	Mesotrione
B-359	one individualized compound I	Saflufenacil
B-360	one individualized compound I	Topramezone

The active substances referred to as component 2, their preparation and their activity against harmful fungi is known (cf.: http://www.alanwood.net/pesticides/); these substances are commercially available. The compounds described by IUPAC nomenclature, their preparation and their fungicidal activity are also known (cf. Can. J. Plant Sci. 48(6), 587-94, 1968; EP-A 141 317; EP-A 152 031; EP-A 226 917; EP-A 243 970; EP-A 256 503; EP-A 428 941; EP-A 532 022; EP-A 1 028 125; EP-A 1 035 122; EP-A 1 201 648; EP-A 1 122 244, JP 2002316902; DE 19650197; DE 10021412; DE 102005009458; US 3,296,272; US 3,325,503; WO 98/46608; WO 99/14187; WO 99/24413; WO 99/27783; WO 00/29404; WO 00/46148; WO 00/65913; WO 01/54501; WO 01/56358; WO 02/22583; WO 02/40431;

WO 03/10149; WO 03/11853; WO 03/14103; WO 03/16286; WO 03/53145; WO 03/61388; WO 03/66609; WO 03/74491; WO 04/49804; WO 04/83193; WO 05/120234; WO 05/123689; WO 05/123690; WO 05/63721; WO 05/87772; WO 05/87773; WO 06/15866; WO 06/87325; WO 06/87343; WO 07/82098; WO 07/90624, WO 11/028657).

The mixtures of active substances can be prepared as compositions comprising besides the active ingridients at least one inert ingredient by usual means, e. g. by the means given for the compositions of compounds I.

Concerning usual ingredients of such compositions reference is made to the explanations given for the compositions containing compounds I.

The mixtures of active substances according to the present invention are suitable as fungicides, as are the compounds of formula I. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, especially from the classes of the Ascomycetes, Basidiomycetes, Deuteromycetes and Peronosporomycetes (syn. Oomycetes). In addition, it is refered to the explanations regarding the fungicidal activity of the compounds and the compositions containing compounds I, respectively.

I. Examples of the action against harmful fungi

The fungicidal action of the compounds I was demonstrated by the following experiments:

A) Greenhouse tests

The spray solutions were prepared in several steps:

The stock solution were prepared: a mixture of acetone and/or dimethylsulfoxide and the wetting agent/emulsifier Wettol, which is based on ethoxylated alkylphenoles, in a relation (volume) solvent-emulsifier of 99 to 1 was added to 25 mg of the compound to give a total of 5 ml. Water was then added to total volume of 100 ml.

This stock solution was diluted with the described solvent-emulsifier-water mixture to the given concentration.

Use example 1. Preventative control of leaf blotch on wheat caused by Septoria tritici

Leaves of pot-grown wheat seedling were sprayed to run-off with an aqueous suspension of the active compound or their mixture, prepared as described. The plants were allowed to air-dry. At the following day the plants were inoculated with an aqueous spore suspension of Septoria tritici. Then the trial plants were immediately transferred to a humid chamber at 18-22°C and a relative humidity close to 100%. After 4 days the plants were transferred to a chamber with 18-22°C and a relative humidity close to 70 %. After 4 weeks the extent of fungal attack on the leaves was visually assessed as % diseased leaf area. All plants did not show any symptoms of phytotoxicity.

In this test, the sample which has been treated with 500 ppm of the active substance I.1 showed up at most 15% growth of the pathogen, whereas the untreated plants were 70% infected.

Use example 2. Preventative control of brown rust on wheat caused by Puccinia recondita

The first two developed leaves of pot-grown wheat seedling were sprayed to run-off with an

aqueous suspension, containing the concentration of active ingredient or their mixture as described below. The next day the plants were inoculated with spores of Puccinia recondita. To ensure the success the artificial inoculation, the plants were transferred to a humid chamber without light and a relative humidity of 95 to 99% and 20 to 24°C for 24 h. Then the trial plants were cultivated for 6 days in a greenhouse chamber at 20-24°C and a relative humidity between 65 and 70%. The extent of fungal attack on the leaves was visually assessed as % diseased leaf area. All plants did not show any symptoms of phytotoxicity.
In this test, the sample which has been treated with 500 ppm of the active substance I.1 showed up at most 15% growth of the pathogen, whereas the untreated plants were 80% infected.

Use example 3. Preventative fungicidal control of *Botrytis cinerea* on leaves of green pepper

Young seedlings of green pepper were grown in pots to the 4 to 5 leaf stage. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The next day the plants were inoculated with a aqueous biomalt solution containig the spore suspension of *Botrytis cinerea.* Then the plants were immediately transferred to a humid chamber. After 5 days at 22 to 24 °C and a relative humidity close to 100 % the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the sample which has been treated with 500 ppm of the active substance from the Table 1, R-12 showed up at most 5% growth of the pathogen, whereas the untreated plants were 100% infected.

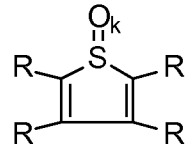
Use example 4. Control of late blight on tomatoes caused by *Phytophthora infestans*

Young seedlings of tomato plants were grown in pots. These plants were sprayed to run-off with an aqueous suspension, containing the concentration of active ingredient or their mixture mentioned in the table below. The next day, the treated plants were inoculated with an aqueous suspension of sporangia of *Phytophthora infestans*. After inoculation, the trial plants were immediately transferred to a humid chamber. After 6 days at 18 to 24 °C and a relative humidity close to 100 % the extent of fungal attack on the leaves was visually assessed as % diseased leaf area.

In this test, the sample which has been treated with 500 ppm of the active substance from the Table 1, R-12 showed up at most 0 % growth of the pathogen, whereas the untreated plants were 90% infected.

Claims

1. Use of compounds of formula I



I,

wherein:

k indicates the number of the oxygen atoms bound to the sulfur atom of the thiophene moiety and k is 0, 1 or 2;

R is CN, -(C=X)-R^C or -CH=N-O-R^E;

X is O or S;

R^C is hydrogen, C_1-C_4-alkyl, C_2-C_4-alkenyl, C_2-C_4-alkynyl, -O-R^E or NR^AR^B;

R^A,R^B independently of one another are hydrogen or C_1-C_4-alkyl;

R^E is hydrogen or C_1-C_4-alkyl;

provided that all four R substituents are identical;

and the agriculturally acceptable salts thereof;

for combating phytopathogenic harmful fungi.

2. The use of compounds of formula I according to claim 1, wherein R is CN.

3. The use of compounds of formula I according to claim 1 or 2, wherein k is 0.

4. A method for combating harmful fungi, comprising:
treating the fungi or the materials, plants, the soil or seeds to be protected against fungal attack with an effective amount of at least one compound of formula I as defined in any of the claims 1 to 3, or a composition comprising such compound.

5. Seed coated with at least one compound of formula I as defined in any of the claims 1 to 3 in an amount of from 0.1 g to 10 kg per 100 kg of seed.

6. Agrochemical compositions, wherein said composition comprise an auxiliary and at least one compound of formula I, as defined in any of the claims 1 to 3, an N-oxide or an agriculturally acceptable salt thereof and at least one further fungicidally active compound selected from the classes A) to L):

A) Respiration inhibitors
- Inhibitors of complex III at Qo site (e.g. strobilurins): azoxystrobin, coumethoxystrobin, coumoxystrobin, dimoxystrobin, enestroburin, fenaminstrobin, fenoxystrobin/flufenoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin, pyrametostrobin, pyraoxystrobin, trifloxystrobin, 2-[2-(2,5-dimethyl-phenoxymethyl)-phenyl]-3-methoxy-acrylic acid methyl ester and 2-(2-(3-(2,6-dichlorophenyl)-1-methyl-allylideneaminooxymethyl)-phenyl)-2-methoxyimino-N-methyl-acetamide, pyribencarb, triclopyricarb/chlorodincarb, famoxadone, fenamidone;
- inhibitors of complex III at Qi site: cyazofamid, amisulbrom, [(3S,6S,7R,8R)-8-benzyl-3-[(3-acetoxy-4-methoxy-pyridine-2-carbonyl)-amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(acetoxymethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[(3-isobutoxycarbonyloxy-4-methoxy-pyridine-2-carbonyl)amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate, [(3S,6S,7R,8R)-8-benzyl-3-[[3-(1,3-benzodioxol-5-ylmethoxy)-4-methoxy-pyridine-2-carbonyl]amino]-6-methyl-4,9-dioxo-1,5-dioxonan-7-yl] 2-methylpropanoate;
- inhibitors of complex II (e. g. carboxamides): benodanil, bixafen, boscalid, carboxin, fenfuram, fluopyram, flutolanil, fluxapyroxad, furametpyr, isopyrazam, mepronil, oxycarboxin, penflufen, penthiopyrad, sedaxane, tecloftalam, thifluzamide, N-(4'-trifluoromethylthiobiphenyl-2-yl)-3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxamide, N-(2-(1,3,3-trimethyl-butyl)-phenyl)-1,3-dimethyl-5-fluoro-1H-pyrazole-4-carboxamide, N-[9-(dichloromethylene)-1,2,3,4-tetrahydro-1,4-methanonaphthalen-5-yl]-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide;
- other respiration inhibitors (e.g. complex I, uncouplers): diflumetorim, (5,8-difluoroquinazolin-4-yl)-{2-[2-fluoro-4-(4-trifluoromethylpyridin-2-yloxy)-phenyl]-ethyl}-amine; nitrophenyl derivates: binapacryl, dinobuton, dinocap, fluazinam; ferimzone; organometal compounds: fentin salts, such as fentin-acetate, fentin chloride or fentin hydroxide; ametoctradin; and silthiofam;

B) Sterol biosynthesis inhibitors (SBI fungicides)
- C14 demethylase inhibitors (DMI fungicides): triazoles: azaconazole, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, diniconazole-M, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imibenconazole, ipconazole, metconazole, myclo-

butanil, oxpoconazole, paclobutrazole, penconazole, propiconazole, prothioconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triticonazole, uniconazole; imidazoles: imazalil, pefurazoate, prochloraz, triflumizol; pyrimidines, pyridines and piperazines: fenarimol, nuarimol, pyrifenox, triforine;

- Delta14-reductase inhibitors: aldimorph, dodemorph, dodemorph-acetate, fenpropimorph, tridemorph, fenpropidin, piperalin, spiroxamine;
- Inhibitors of 3-keto reductase: fenhexamid;

C) Nucleic acid synthesis inhibitors

- phenylamides or acyl amino acid fungicides: benalaxyl, benalaxyl-M, kiralaxyl, metalaxyl, metalaxyl-M (mefenoxam), ofurace, oxadixyl;
- others: hymexazole, octhilinone, oxolinic acid, bupirimate, 5-fluorocytosine, 5-fluoro-2-(p-tolylmethoxy)pyrimidin-4-amine, 5-fluoro-2-(4-fluorophenylmethoxy)pyrimidin-4-amine;

D) Inhibitors of cell division and cytoskeleton

- tubulin inhibitors, such as benzimidazoles, thiophanates: benomyl, carbendazim, fuberidazole, thiabendazole, thiophanate-methyl; triazolopyrimidines: 5-chloro-7-(4-methylpiperidin-1-yl)-6-(2,4,6-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine
- other cell division inhibitors: diethofencarb, ethaboxam, pencycuron, fluopicolide, zoxamide, metrafenone, pyriofenone;

E) Inhibitors of amino acid and protein synthesis

- methionine synthesis inhibitors (anilino-pyrimidines): cyprodinil, mepanipyrim, pyrimethanil;
- protein synthesis inhibitors: blasticidin-S, kasugamycin, kasugamycin hydrochloride-hydrate, mildiomycin, streptomycin, oxytetracyclin, polyoxine, validamycin A;

F) Signal transduction inhibitors

- MAP / histidine kinase inhibitors: fluoroimid, iprodione, procymidone, vinclozolin, fenpiclonil, fludioxonil;
- G protein inhibitors: quinoxyfen;

G) Lipid and membrane synthesis inhibitors

- Phospholipid biosynthesis inhibitors: edifenphos, iprobenfos, pyrazophos, isoprothiolane;
- lipid peroxidation: dicloran, quintozene, tecnazene, tolclofos-methyl, biphenyl, chloroneb, etridiazole;
- phospholipid biosynthesis and cell wall deposition: dimethomorph, flumorph, mandipropamid, pyrimorph, benthiavalicarb, iprovalicarb, valifenalate and N-(1-(1-(4-cyano-phenyl)ethanesulfonyl)-but-2-yl) carbamic acid-(4-fluorophenyl) ester;
- compounds affecting cell membrane permeability and fatty acides: propamocarb, propamocarb-hydrochlorid

H) Inhibitors with Multi Site Action

- inorganic active substances: Bordeaux mixture, copper acetate, copper hydroxide, copper oxychloride, basic copper sulfate, sulfur;
- thio- and dithiocarbamates: ferbam, mancozeb, maneb, metam, metiram, propineb, thiram, zineb, ziram;
- organochlorine compounds (e.g. phthalimides, sulfamides, chloronitriles): anilazine, chlorothalonil, captafol, captan, folpet, dichlofluanid, dichlorophen, flusulfamide, hexachlorobenzene, pentachlorphenole and its salts, phthalide, tolylfluanid, N-(4-chloro-2-nitro-phenyl)-N-ethyl-4-methyl-benzenesulfonamide;
- guanidines and others: guanidine, dodine, dodine free base, guazatine, guazatine-acetate, iminoctadine, iminoctadine-triacetate, iminoctadine-tris(albesilate), dithianon;

l) Cell wall synthesis inhibitors

- inhibitors of glucan synthesis: validamycin, polyoxin B; melanin synthesis inhibitors: pyroquilon, tricyclazole, carpropamid, dicyclomet, fenoxanil;

J) Plant defence inducers

- acibenzolar-S-methyl, probenazole, isotianil, tiadinil, prohexadione-calcium; phosphonates: fosetyl, fosetyl-aluminum, phosphorous acid and its salts;

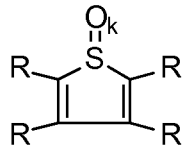
K) Unknown mode of action

- bronopol, chinomethionat, cyflufenamid, cymoxanil, dazomet, debacarb, diclomezine, difenzoquat, difenzoquat-methylsulfate, diphenylamin, fenpyrazamine, flumetover, flusulfamide, flutianil, methasulfocarb, nitrapyrin, nitrothal-isopropyl, oxin-copper, proquinazid, tebufloquin, tecloftalam, triazoxide, 2-butoxy-6-iodo-3-propylchromen-4-one, N-(cyclo-propylmethoxyimino-(6-difluoro-methoxy-2,3-difluoro-phenyl)-methyl)-2-phenyl acetamide, N'-(4-(4-chloro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(4-(4-fluoro-3-trifluoromethyl-phenoxy)-2,5-dimethyl-phenyl)-N-ethyl-N-methyl formamidine, N'-(2-methyl-5-trifluoromethyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, N'-(5-difluoromethyl-2-methyl-4-(3-trimethylsilanyl-propoxy)-phenyl)-N-ethyl-N-methyl formamidine, 2-{1-[2-(5-methyl-3-trifluoromethyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(1,2,3,4-tetrahydro-naphthalen-1-yl)-amide, 2-{1-[2-(5-methyl-3-trifluoro-methyl-pyrazole-1-yl)-acetyl]-piperidin-4-yl}-thiazole-4-carboxylic acid methyl-(R)-1,2,3,4-tetrahydro-naphthalen-1-yl-amide, 1-[4-[4-[5-(2,6-difluoro-phenyl)-4,5-dihydro-3-isoxazolyl]-2-thiazolyl]-1-piperidinyl]-2-[5-methyl-3-(trifluoromethyl)-1H-pyrazol-1-yl]ethanone, methoxy-acetic acid 6-tert-butyl-8-fluoro-2,3-dimethyl-quinolin-4-yl ester, N-methyl-2-{1-[(5-methyl-3-trifluoromethyl-1H-pyrazol-1-yl)-acetyl]-piperidin-4-yl}-N-[(1R)-1,2,3,4-tetrahydronaphthalen-1-yl]-4-thiazolecarboxamide, 3-[5-(4-methylphenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine, 3-[5-(4-chloro-phenyl)-2,3-dimethyl-isoxazolidin-3-yl]-pyridine (pyrisoxazole), N-(6-methoxy-pyridin-3-yl) cyclo-

propanecarboxylic acid amide, 5-chloro-1-(4,6-dimethoxy-pyrimidin-2-yl)-2-methyl-1H-benzoimidazole, 2-(4-chloro-phenyl)-N-[4-(3,4-dimethoxy-phenyl)-isoxazol-5-yl]-2-prop-2-ynyloxy-acetamide;

L) Antifungal biocontrol agents, plant bioactivators
Ampelomyces quisqualis, Aspergillus flavus, Aureobasidium pullulans, Bacillus pumilus, Bacillus subtilis, Bacillus subtilis var. amyloliquefaciens FZB24, Candida oleophila I-82, Candida saitoana, Chitosan, Clonostachys rosea f. catenulata also named Gliocladium catenulatum, Coniothyrium minitans, Cryphonectria parasitica, Cryptococcus albidus, Fusarium oxysporum, Metschnikowia fructicola, Microdochium dimerum, Phlebiopsis gigantea, Pseudozyma flocculosa, Pythium oligandrum DV74, Reynoutria sachlinensis, Talaromyces flavus V117b, Trichoderma asperellum SKT-1, T. atroviride LC52, T. harzianum T-22, T. harzianum TH 35, T. harzianum T-39, T. harzianum and T. viride, T. harzianum ICC012 and T. viride ICC080, T. polysporum and T. harzianum, T. stromaticum, T. virens GL-21, T. viride, T. viride TV1, Ulocladium oudemansii HRU3.

7. Compounds of formula I



I,

wherein:

k indicates the number of the oxygen atoms bound to the sulfur atom of the thiophene moiety and k is 0, 1 or 2;

R is CN, -(C=X)-R^C or -CH=N-O-R^E;

X is O or S;

R^C is hydrogen, C_1-C_4-alkyl, C_2-C_4-alkenyl, C_2-C_4-alkynyl, -O-R^E or NR^AR^B;

R^A,R^B independently of one another are hydrogen or C_1-C_4-alkyl;

R^E is hydrogen or C_1-C_4-alkyl;

provided that all four R substituents are identical;

and the agriculturally acceptable salts thereof;

except for thiophene-2,3,4,5-tetracarbonitrile, thiophene-2,3,4,5-tetracarbaldehyde, thiophene-2,3,4,5-tetracarboxylic acid, thiophene-2,3,4,5-tetracarboxamide, tetramethyl thiophene-2,3,4,5-tetracarboxylate, tetraethyl thiophene-2,3,4,5-tetracarboxylate, tetra(tert.-butyl) thiophene-2,3,4,5-tetracarboxylate and thiophene-2,3,4,5-tetracarboximidic acid.

8. The compounds according to claim 7, wherein k is 0.

9. The compounds according to any of the claims 7 to 8, wherein R is -(C=O)-R^C.

10. The compounds according to claim 9, wherein R^C is -O-R^E and R^E is propyl.

11. The compounds according to claim to any of the claims 7 to 8, wherein R is -(C=O)-NR^AR^B, wherein R^A is not hydrogen.

12. The compounds according to any of the claims 7 to 8, wherein R is -CH=N-O-R^E.

13. Agrochemical compositions wherein said composition comprise an auxiliary and at least one compound of formula I, as defined in any of the claims 7 to 12, an N-oxide or an agriculturally acceptable salt thereof.

14. The compositions according to claim 13, comprising additionally a further active compound.

15. Seed coated with at least one compound of formula I as defined in any of the claims 7 to 12 in an amount of from 0.1 g to 10 kg per 100 kg of seed.