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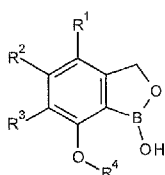
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(54) Title: USE OF BENZOXABOROLE AS FUNGICIDES



(57) Abstract: A method for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack by treating plants or plant propagation material and/or harvested food crops a fungicidally effective amount of a compound of formula (I) wherein the substituents (I) are as defined in claim 1 as well as compounds according to formula (IA) and (IB) with the same structure as the compounds of formula (I) wherein the substituents are as defined in claim 15 and 16.



USE OF BENZOXABOROLE AS FUNGICIDES

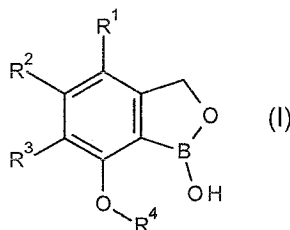
The present invention relates to the method for protecting useful plants or plant propagation material, more specifically to a method use of benzoxaboroles and salts thereof as biocides in agriculture or horticulture for controlling or preventing infestation of plants or plant propagation material, harvested food crops by phytopathogenic microorganisms, preferably fungi.

The incidence of serious fungal infections, either systemic or topical, continues to increase for plants, animals, and humans. Many fungi are common in the environment and not harmful to plants or mammals. However, some fungi can produce disease in plants, humans and/or animals.

Fungicides are compounds, of natural or synthetic origin, which act to protect plants against damage caused by fungi, including oomycetes. Current methods of agriculture rely heavily on the use of fungicides. In fact, some crops cannot be grown usefully without the use of fungicides. Using fungicides allows a grower to increase the yield of the crop and consequently, increase the value of the crop. Numerous fungicidal agents have been developed. However, the treatment of fungal infestations and infections continues to be a major problem. Furthermore, fungicide and antifungal drug resistance has become a serious problem, rendering these agents ineffective for some agricultural and therapeutic uses. On the other hand the negative influence of fungicides on vigor and growth of the treated plant or plant propagation material should be marginal or in the best case not exist, thus the fungicides should show a good crop tolerance. As such, a need exists for the development of new fungicidal and antifungal compounds and inventive uses of known compounds.

The use of benzoxaboroles and salts thereof as biocides especially fungicides for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack are known from e.g. WO2015121442.

According to the present invention there is provided a method for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack by treating plants or plant propagation material and/or harvested food crops with an effective amount of a benzoxaboroles of general formula (I)



wherein

R¹ is H;

R² is -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R⁵, C₁-C₄haloalkyl;

R³ is H;

R⁴ is H, C₁-C₄alkyl, C₁-C₄haloalkyl, phenyl, phenyl substituted by one to three R⁶;

R⁵ is independently selected from cyano and hydroxyl;

R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;

or a salt or a N-oxide thereof.

The present invention accordingly further relates to a method for controlling or preventing of infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack, preferably susceptible to fungicidal attack, by treating plants or plant propagation material and/or harvested food crops with an effective amount of benzoxaborole derivatives according to formula (I).

The present invention accordingly further relates to the use of benzoxaborole derivatives according to formula (I) for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack, preferably susceptible to fungicidal attack.

The present invention accordingly further relates to the use of benzoxaborole derivatives according to formula (I) and salts thereof for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops by treating plants or plant propagation material and/or harvested food crops with an effective amount of a benzoxaborole of general formula (I).

Accordingly the present invention also relates to a method of protecting plant propagation material and organs that grow at a later point in time against damage by phytopathogenic diseases, which method comprises applying to said propagation material a fungicidally effective amount of a compound of formula I.

In yet a further aspect of the invention, the invention provides plant propagation material treated with a plant propagation material protecting composition comprising a compound of formula (I).

A preferred embodiment of the invention relates to a method of controlling or preventing damage by phytopathogenic diseases in a growing plant or growing plant tissue said method comprising: applying onto the plant propagation material, before planting or sowing thereof a fungicidally effective amount of a compound of formula (I).

A method of controlling or preventing fungal diseases in a growing plant or growing plant tissue said method comprising: applying onto the plant propagation material before planting or sowing thereof a fungicidally effective amount of a compound of formula (I).

In a preferred embodiment the plant propagation material is a seed or a tuber. In a further preferred embodiment the plant propagation material is a seed. In a further preferred embodiment the plant propagation material is a tuber. Preferably the seeds and tubers (stem tubers and root tubers) according to this application are alive. Preferably the seeds and tubers according to this application are able to germinate.

In a further aspect of the invention, the invention provides a method of controlling or preventing damage by phytopathogenic diseases in a growing plant said method comprising applying onto the seed, before planting or sowing thereof a compound of formula (I).

In a further aspect of the invention, the invention provides a method of protecting plant propagation material and organs that grow at a later point in time against damage by phytopathogenic diseases, which method comprises applying to said propagation material a fungicidally effective amount of a compound of formula (I).

In a further aspect of the invention, the invention provides a plant propagation material comprising compound a compound of formula (I). Preferably the plant propagation material comprising a fungicidal effective amount of a compound of formula (I).

5 In a further aspect of the invention, the invention provides a coated plant propagation material coated with a compound of formula (I).

In a further aspect of the invention, the invention provides a coated plant propagation material coated with coating comprising a compound of formula (I) as defined in claim 1.

10 In a further aspect of the invention, the invention provides a plant propagation material comprising an outer coating characterized that the outer coating comprises a compound according to formula (I), preferably a seed comprising an outer coating characterized that the outer coating comprises a compound according to formula (I).

In a further aspect of the invention, the invention relates to the use of a compound of formula (I) in the preparation of a composition for coating a plant propagation material for the prevention or control of plant pathogenic fungi.

15 In a further aspect of the invention, the invention relates to a method of controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack by providing in a first step a agrochemical compositions according to the present invention comprising a compound of formula (I) and in a second step applying said composition to the plants or the locus thereof.

20 The compounds of formula (I) are applied by treating plant propagation material with a fungicidally effective amount of a compound of formula I. Preferably, compounds of formula (I) are applied by adhering compounds of formula (I) to plant propagation material in a fungicidally effective amount.

A preferred application method is seed treatment.

25 As used herein, the term "halogen" refers to fluorine, chlorine, bromine or iodine.

As used herein, the term "cyano" means a -CN group.

As used herein, the term "hydroxyl" or "hydroxy" stands for a -OH group.

30 As used herein, the term "C₁-C₄alkyl" refers to a straight or branched hydrocarbon chain radical consisting solely of carbon and hydrogen atoms, containing no unsaturation, having from one to six carbon atoms, and which is attached to the rest of the molecule by a single bond. Examples of C₁-C₄alkyl include, but are not limited to, methyl, ethyl, n-propyl, n-butyl, and the isomers thereof, for example, iso-propyl, iso-butyl, sec-butyl or tert-butyl.

35 As used herein, the term "C₁-C₄haloalkyl" refers to a straight or branched hydrocarbon chain radical consisting solely of carbon, hydrogen and halogen atoms, containing no unsaturation, having from one to four carbon atoms, and which is attached to the rest of the molecule by a single bond. Examples of C₁-C₄haloalkyl include, but are not limited to, CH₂Cl, CHCl₂, CCl₃, CH₂F, CHF₂, CF₃, CF₃CH₂, CH₃CF₂, CF₃CF₂ or CCl₃CCl₂.

Also enantiomers may occur as a result of the presence of a possible asymmetric carbon atom. Furthermore also atropisomers may occur as a result of restricted rotation about a single bond.

40 Formula I is intended to include all those possible isomeric forms, enantiomers, diastereomers and

atropisomers, and mixtures thereof. The present invention includes all those possible isomeric forms and mixtures thereof for a compound of formula (I).

The following list provides definitions, including preferred definitions, for substituents R², R⁴, R⁵ and R⁶ with reference to compounds of formula I. For any one of these substituents, any of the definitions given below may be combined with any definition of any other substituent given below or elsewhere in this document.

Preferably R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵, C₁-C₂haloalkyl; more preferably methyl or ethyl.

Preferably R⁴ is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl, phenyl substituted by one to three R⁶; more preferably methyl, ethyl or phenyl; most preferably methyl or ethyl.

Preferably R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵, C₁-C₂haloalkyl; and R⁴ is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl, phenyl substituted by one to three R⁶.

More preferably R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵, C₁-C₂haloalkyl; and R⁴ is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl.

Even more preferably R² is methyl or ethyl; and R⁴ is methyl or ethyl.

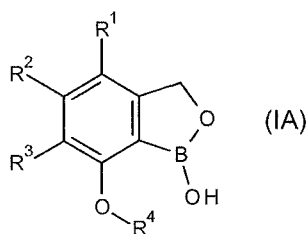
In one embodiment R² is ethyl and R⁴ is ethyl.

In a further embodiment R² is methyl; and R⁴ is ethyl.

In a further embodiment R² is ethyl; and R⁴ is methyl.

In a further embodiment R² is methyl and R⁴ is methyl.

In an embodiment A this invention further relates to a compound of formula (IA)



wherein

R¹ is H;

R² is -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R⁵, C₁-C₄haloalkyl;

R³ is H;

R⁴ is H, C₁-C₄alkyl, C₁-C₄haloalkyl, phenyl, phenyl substituted by one to three R⁶;

R⁵ is independently selected from cyano and hydroxyl;

R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;

with the proviso that not both R² and R⁴ are methyl;

or a salt or an N-oxide thereof.

Preferably in the embodiment (A) R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵, C₁-C₂haloalkyl; more preferably methyl or ethyl.

Preferably in the embodiment (A) R^4 is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl, phenyl substituted by one to three R^6 ; more preferably methyl, ethyl or phenyl; most preferably methyl or ethyl.

Preferably in the embodiment (A) R^2 is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R^5 , C₁-C₂haloalkyl; and H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl, phenyl substituted by one to three R^6 .

5 More preferably in the embodiment (A) R^2 is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R^5 , C₁-C₂haloalkyl; and R^4 is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl.

Even more preferably in the embodiment (A) R^2 is methyl or ethyl; and R^4 is methyl or ethyl.

In a further embodiment (A) R^2 is ethyl; and R^4 is ethyl.

In a further embodiment (A) R^2 is methyl; and R^4 is ethyl.

10 In a further embodiment (A) R^2 is ethyl and R^4 is methyl.

A preferred embodiment A this invention relates to a compound of formula (IA), wherein

R^1 is H;

R^2 is -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R^5 , C₁-C₄haloalkyl;

15 R^3 is H;

R^4 is phenyl, phenyl substituted by one to three R^6 ;

R^5 is independently selected from cyano and hydroxyl;

R^6 is independently selected from cyano, hydroxyl, halogen and nitro;

or a salt or an N-oxide thereof.

20

A more preferred embodiment A this invention relates to a compound of formula (IA) wherein

R^1 is H;

R^2 is C₁-C₄-alkyl, C₁-C₄haloalkyl;

R^3 is H;

25 R^4 is phenyl, phenyl substituted by one to three R^6 ;

R^6 is independently selected from cyano, hydroxyl, halogen and nitro;

or a salt or an N-oxide thereof.

In a most preferred embodiment A this invention further relates to a compound of formula (IB),

30 wherein

R^1 is H;

R^2 is methyl;

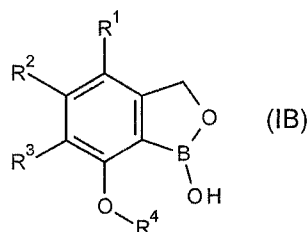
R^3 is H;

R^4 is phenyl, phenyl substituted by one to three R^6 ;

35 R^6 is independently halogen;

or a salt or an N-oxide thereof.

In an embodiment B this invention further relates to a compound of formula (IB)



wherein

R¹ is H;

R² is halogen, -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R⁵, C₁-C₄haloalkyl;

5 R³ is H;

R⁴ is phenyl, phenyl substituted by one to three R⁶;

R⁵ is independently selected from cyano and hydroxyl;

R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;

or a salt or an N-oxide thereof.

10

In a preferred embodiment B this invention further relates to a compound of formula (IB), wherein

R¹ is H;

R² is halogen, C₁-C₄-alkyl, C₁-C₄haloalkyl;

R³ is H;

15 R⁴ is phenyl, phenyl substituted by one to three R⁶;

R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;

or a salt or an N-oxide thereof.

In a more preferred embodiment B this invention further relates to a compound of formula (IB),

20 wherein

R¹ is H;

R² is halogen, C₁-C₄-alkyl;

R³ is H;

R⁴ is phenyl, phenyl substituted by one to three R⁶;

25 R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;

or a salt or an N-oxide thereof.

In an even more preferred embodiment B this invention further relates to a compound of formula (IB),

wherein

30 R¹ is H;

R² is halogen, C₁-C₄-alkyl;

R³ is H;

R⁴ is phenyl, phenyl substituted by one to three R⁶;

R⁶ is independently halogen;

35 or a salt or an N-oxide thereof.

In a most preferred embodiment B this invention further relates to a compound of formula (IB), wherein

R¹ is H;

5 R² is Cl, F, methyl;

R³ is H;

R⁴ is phenyl, phenyl substituted by one to three R⁶;

R⁶ is independently halogen;

or a salt or an N-oxide thereof.

10

In each of the embodiments A or the embodiments B preferably R⁴ is phenyl, 4-chlorophenyl, 3,5-bis-(trifluoromethyl)-phenyl, 3-chloro-5-trifluoromethyl-phenyl, 3-bromo-5-trifluoromethyl-phenyl, 3,5-dibromo-phenyl, 3,5-dichloro-phenyl, 3,4-dichloro-phenyl, 3-trifluoromethyl-phenyl, 4-bromo-3,5-dichlorophenyl, 3,5-dichloro-4-fluoro-phenyl or 3,4,5-trichloro-phenyl; more preferably R⁴ is phenyl, 4-chlorophenyl, 3-chloro-5-trifluoromethyl-phenyl, 3,5-dichloro-phenyl, 3,5-bis-(trifluoromethyl)-phenyl, 3,5-dichloro-4-fluoro-phenyl, or 3,4,5-trichloro-phenyl and even more preferably R⁴ is phenyl, 4-chlorophenyl.

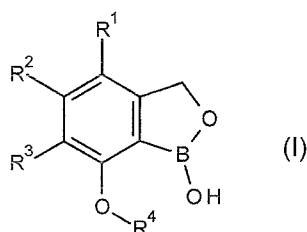
15

The compounds of formula (IA) and (IB) can be used in the same way as the compounds according to the formula (I). Thus the uses and the methods wherein the compounds of formula (IA) and (IB) are used are the same uses and methods as described the uses and methods wherein the compounds according to the formula (I) are used.

20

Compounds of formula (I), (IA) and (IB) may be prepared using commercially available starting materials or known intermediates using synthetic methods known in the art or described herein, as shown in the following schemes 0 to 3.

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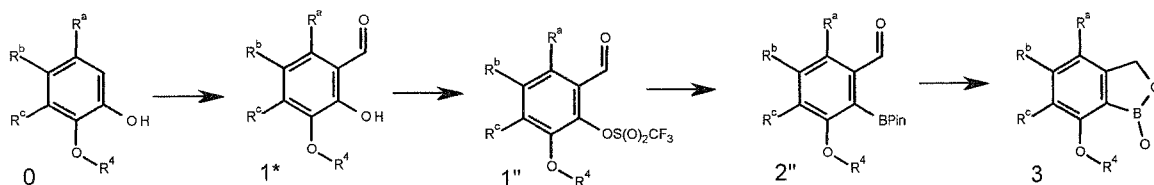
(I)

The following general chemistry schemes 0 to 3 were used as indicated in generating the examples and can be applied, using the knowledge of one of skill in the art, to other appropriate compounds to obtain additional analogues

30

In all compounds shown in the schemes below R¹, R², R³ and R⁴ are as defined above. The compound of formula 0, formula 1 and of formula 1' may be obtained commercially or using synthetic methods known in the art.

35

**Scheme-0**

Compound 0 is converted into compound 1* by treating compound 0 in a first step with
 5 hexamethylenetetramine in the presence of an organic acid, preferably in the presence of acetic acid or 2,2,2-trifluoroacetic acid and in a second step to treat the carbonylated compound of formula 1* with triflic anhydride in the presence of an organic base, preferably in the presence of pyridin.

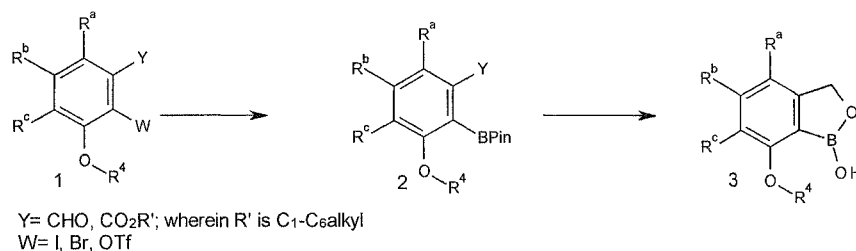
Compound 1* is converted to compound 2'' by the treatment with bis(pinacolato)diboron in
 10 presence of transition metal catalyst and appropriate ligand as necessary and base in suitable solvent at a temperature ranging from ambient temperature to the boiling point of the solvent used.

Suitable transition metal catalyst can be [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride, tetrakis(triphenylphosphine)palladium(0), Palladium(II) acetate, Palladium(II) acetylacetonate, Bis(triphenylphosphine)palladium(II) dichloride and may be used in quantities
 ranging from 1 to 5 mol%. Suitable ligands include tricyclohexylphosphine and triphenylphosphine.

15 Suitable bases include potassium acetate, potassium carbonate, and sodium carbonate and may be used in quantities ranging from 1 to 5 equivalents. Suitable solvent includes 1,4-dioxane, N,N-dimethylformamide, dimethylsulfoxide, tetrahydrofuran and toluene.

Reduction of the carbonyl compound 2'' using a suitable reducing agent followed by stirring of
 resulting mass under acidic conditions, like 6N HCl give compound 3.

20 Suitable reducing agents include hydrides like sodium borohydride, lithium aluminium hydride, borane complexes such as borane-THF complex. The reducing agents are used in quantities ranging from 1 equivalent to 5 equivalents and suitable solvents includes tetrahydrofuran, 1,4-dioxane and alcohols such as methanol, ethanol, isopropanol. The reaction temperature ranges from 0°C to boiling point of the solvent.

**Scheme-1**

Compound 1 is converted to compound 2 by the treatment with bis(pinacolato)diboron in
 presence of transition metal catalyst and appropriate ligand as necessary and base in suitable solvent
 at a temperature ranging from ambient temperature to the boiling point of the solvent used.

30 Suitable transition metal catalyst can be [1,1'-Bis(diphenylphosphino)ferrocene] palladium (II) dichloride, tetrakis(triphenylphosphine)palladium(0), Palladium (II) acetate, Palladium (II)

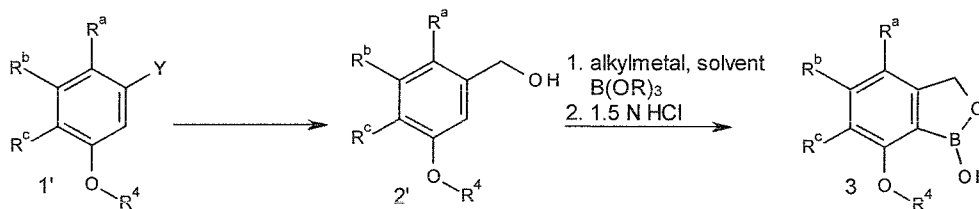
acetylacetonate, Bis(triphenylphosphine)palladium(II) dichloride and may be used in quantities ranging from 1 to 5 mol%. Suitable ligands include tricyclohexylphosphine and triphenylphosphine. Suitable bases include potassium acetate, potassium carbonate, and sodium carbonate and may be used in quantities ranging from 1 to 5 equivalents. Suitable solvent includes 1,4-dioxane, N,N-

5 dimethylformamide, dimethylsulfoxide, tetrahydrofuran and toluene.

Reduction of the carbonyl compound 2 using a suitable reducing agent followed by stirring of resulting mass under acidic conditions, like 6N HCl give compound 3.

Suitable reducing agents include hydrides like sodium borohydride, lithium aluminium hydride, borane complexes such as borane-THF complex. The reducing agents are used in quantities ranging

10 from 1 equivalent to 5 equivalents and suitable solvents includes tetrahydrofuran, 1,4-dioxane and alcohols such as methanol, ethanol, isopropanol. The reaction temperature ranges from 0°C to boiling point of the solvent.



Y = CHO, CO₂R'; wherein R' is C₁-C₆alkyl

Scheme-2

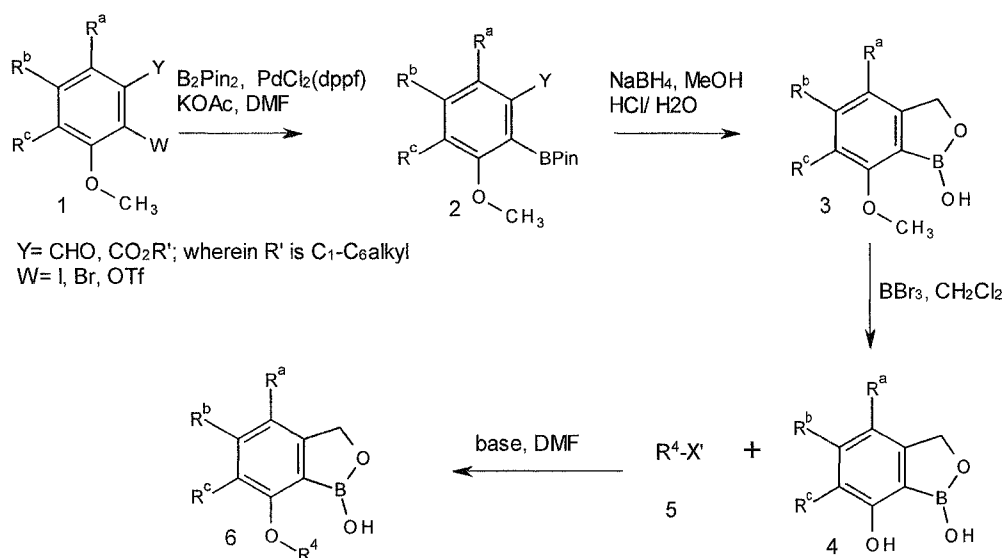
The compound 1' is converted to compound 2' using suitable reducing agents in appropriate solvents at temperatures ranging from ambient temperature to the boiling point of the solvent. Suitable reducing agents include hydrides like sodium borohydride, lithium aluminium hydride, borane complexes such as borane-THF complex. The reducing agents are used in quantities ranging from 1

20 equivalent to 5 equivalents and suitable solvents includes tetrahydrofuran, 1,4-dioxane and alcohols such as methanol, ethanol, isopropanol.

Compound 2' is converted to compound 3 by treatment with an alkyl metal to generate the anion at temperature, ranging from -78°C to ambient temperature in suitable solvent and subsequent addition of suitable alkyl boroate, followed by stirring of the reaction mass under acidic conditions like

25 aqueous HCl. For related examples, see: Shin-ichiro Mohri et al, J. Org. Chem., 1997, 62 (21), pp 7072-7073.

Suitable alkyl metal reagents include n-butyllithium, sec-butyllithium and tert-butyllithium. Suitable solvents can be tetrahydrofuran, diethylether, cyclohexane, 1,2-dimethoxyethane or a combination thereof.



Scheme-3

Compound 4 can be converted to compound 6 by treatment with compounds of formula 5, wherein X' is a halogen, preferably Cl, Br, I or -OSO₂OMe in the presence of a suitable base in a suitable solvent at a temperature ranging from 0°C to the boiling point of the solvent.

Suitable base includes K₂CO₃, Cs₂CO₃, or NaH and the suitable solvent may be dimethylformamide or tetrahydrofuran.

The compounds of formula (IA) as well as the compounds of formula (I) of this invention are useful as plant disease control agents. The present invention therefore further comprises a method for controlling plant diseases caused by fungal plant pathogens comprising applying to the plant or portion thereof to be protected, or to the plant seed to be protected, an effective amount of a compound of the invention or a fungicidal composition containing said compound. Further to this the compounds of formula (IA) may be used and applied like the compounds of formula (I) as described below.

Compounds of formula (I) and fungicidal compositions containing them may be used to control plant diseases caused by a broad spectrum of fungal plant pathogens in the Basidiomycete, Ascomycete, Oomycete and/or Deuteromycete, Blasocladiomycete, Chytridiomycete, Glomeromycete and/or Mucoromycete classes.

They are effective in controlling a broad spectrum of plant diseases, such as foliar, seed- and soilborne pathogens of ornamental, turf, vegetable, field, cereal, and fruit crops.

These pathogens may include:

Oomycetes, including Phytophthora diseases such as those caused by *Phytophthora capsici*, *Phytophthora infestans*, *Phytophthora sojae*, *Phytophthora fragariae*, *Phytophthora nicotianae*, *Phytophthora cinnamomi*, *Phytophthora citricola*, *Phytophthora citrophthora* and *Phytophthora erythroseptica*; Pythium diseases such as those caused by *Pythium aphanidermatum*, *Pythium arrhenomanes*, *Pythium graminicola*, *Pythium irregulare*, *Pythium sylvaticum* and *Pythium ultimum*; diseases caused by Peronosporales such as *Peronospora destructor*, *Peronospora parasitica*,

Plasmopara viticola, *Plasmopara halstedii*, *Pseudoperonospora cubensis*, *Albugo candida*, *Sclerophthora macrospora* and *Bremia lactucae*; and others such as *Aphanomyces cochlioides*, *Labyrinthula zosterae*, *Peronosclerospora sorghi* and *Sclerospora graminicola*.

- Ascomycetes, including blotch, spot, blast or blight diseases and/or rots for example those
- 5 caused by Pleosporales such as *Stemphylium solani*, *Stagonospora tainanensis*, *Spilocaea oleaginea*, *Setosphaeria turcica*, *Pyrenochaeta lycopersici*, *Pleospora herbarum*, *Phoma destructiva*, *Phaeosphaeria herpotrichoides*, *Phaeocryptocus gaeumannii*, *Ophiosphaerella graminicola*, *Ophiobolus graminis*, *Leptosphaeria maculans*, *Hendersonia creberrima*, *Helminthosporium tritici-repentis*, *Setosphaeria turcica*, *Drechslera glycines*, *Didymella bryoniae*, *Cycloconium*
- 10 *oleagineum*, *Corynespora cassicola*, *Cochliobolus sativus*, *Bipolaris cactivora*, *Venturia inaequalis*, *Pyrenophora teres*, *Pyrenophora tritici-repentis*, *Alternaria alternata*, *Alternaria brassicicola*, *Alternaria solani* and *Alternaria tomatophila*, Capnodiales such as *Septoria tritici*, *Septoria nodorum*, *Septoria glycines*, *Cercospora arachidicola*, *Cercospora sojae*, *Cercospora zeae-maydis*, *Cercospora capsellae* and *Cercospora herpotrichoides*, *Cladosporium carpophilum*, *Cladosporium effusum*,
- 15 *Passalora fulva*, *Cladosporium oxysporum*, *Dothistroma septosporum*, *Isariopsis clavispora*, *Mycosphaerella fijiensis*, *Mycosphaerella graminicola*, *Mycovellosiella koepekei*, *Phaeoisariopsis bataticola*, *Pseudocercospora vitis*, *Pseudocercospora herpotrichoides*, *Ramularia beticola*, *Ramularia collo-cygni*, Magnaporthales such as *Gaeumannomyces graminis*, *Magnaporthe grisea*, *Pyricularia oryzae*, Diaporthales such as *Anisogramma anomala*, *Apiognomonina errabunda*,
- 20 *Cytospora platani*, *Diaporthe phaseolorum*, *Discula destructiva*, *Gnomonia fructicola*, *Greeneria uvicola*, *Melanconium juglandinum*, *Phomopsis viticola*, *Sirococcus clavignenti-juglandacearum*, *Tubakia dryina*, *Dicarpella* spp., *Valsa ceratosperma*, and others such as *Actinothyrium graminis*, *Ascochyta pisi*, *Aspergillus flavus*, *Aspergillus fumigatus*, *Aspergillus nidulans*, *Asperisporium caricae*, *Blumeriella jaapii*, *Candida* spp., *Capnodium ramosum*, *Cephaloascus* spp., *Cephalosporium*
- 25 *gramineum*, *Ceratocystis paradoxa*, *Chaetomium* spp., *Hymenoscyphus pseudoalbidus*, *Coccidioides* spp., *Cylindrosporium padi*, *Diplocarpon malae*, *Drepanopeziza campestris*, *Elsinoe ampelina*, *Epicoccum nigrum*, *Epidermophyton* spp., *Eutypa lata*, *Geotrichum candidum*, *Gibellina cerealis*, *Gloeocercospora sorghi*, *Gloeodes pomigena*, *Gloeosporium perennans*, *Gloeotinia temulenta*, *Griphosphaeria corticola*, *Kabatiella lini*, *Leptographium microsporum*, *Leptosphaerulina crassiasca*,
- 30 *Lophodermium seditiosum*, *Marssonina graminicola*, *Microdochium nivale*, *Monilinia fructicola*, *Monographella albescens*, *Monosporascus cannonballus*, *Naemacyclus* spp., *Ophiostoma novo-ulmi*, *Paracoccidioides brasiliensis*, *Penicillium expansum*, *Pestalotia rhododendri*, *Petriellidium* spp., *Pezizula* spp., *Phialophora gregata*, *Phyllachora pomigena*, *Phymatotrichum omnivora*, *Physalospora abdita*, *Plectosporium tabacinum*, *Polyscytalum pustulans*, *Pseudopeziza medicaginis*, *Pyrenopeziza*
- 35 *brassicae*, *Ramulispora sorghi*, *Rhabdocline pseudotsugae*, *Rhynchosporium secalis*, *Sacrocladium oryzae*, *Scedosporium* spp., *Schizothyrium pomi*, *Sclerotinia sclerotiorum*, *Sclerotinia minor*, *Sclerotium* spp., *Typhula ishikariensis*, *Seimatosporium mariae*, *Lepteutypa cupressi*, *Septocytia ruborum*, *Sphaceloma perseae*, *Sporonema phacidiioides*, *Stigmata palmivora*, *Tapesia yallundae*, *Taphrina bullata*, *Thielaviopsis basicola*, *Trichoseptoria fructigena*, *Zygophiala jamaicensis*; powdery
- 40 mildew diseases for example those caused by Erysiphales such as *Blumeria graminis*, *Erysiphe*

polygoni, *Uncinula necator*, *Sphaerotheca fuliginea*, *Podosphaera leucotricha*, *Podosphaera macularis*, *Golovinomyces cichoracearum*, *Leveillula taurica*, *Microsphaera diffusa*, *Oidiopsis gossypii*, *Phyllactinia guttata* and *Oidium arachidis*; molds for example those caused by Botryosphaeriales such as *Dothiorella aromatica*, *Diplodia seriata*, *Guignardia bidwellii*, *Botrytis cinerea*, *Botryotinia allii*,
 5 *Botryotinia fabae*, *Fusicoccum amygdali*, *Lasiodiplodia theobromae*, *Macrophoma theicola*, *Macrophomina phaseolina*, *Phyllosticta cucurbitacearum*; anthracnoses for example those caused by Glomerelales such as *Colletotrichum gloeosporioides*, *Colletotrichum lagenarium*, *Colletotrichum gossypii*, *Glomerella cingulata*, and *Colletotrichum graminicola*; and wilts or blights for example those caused by Hypocreales such as *Acremonium strictum*, *Claviceps purpurea*, *Fusarium culmorum*,
 10 *Fusarium graminearum*, *Fusarium virguliforme*, *Fusarium oxysporum*, *Fusarium subglutinans*, *Fusarium oxysporum* f.sp. *cubense*, *Gerlachia nivale*, *Gibberella fujikuroi*, *Gibberella zeae*, *Gliocladium* spp., *Myrothecium verrucaria*, *Nectria ramulariae*, *Trichoderma viride*, *Trichothecium roseum*, and *Verticillium theobromae*.

Basidiomycetes, including smuts for example those caused by Ustilaginales such as
 15 *Ustilaginoidea virens*, *Ustilago nuda*, *Ustilago tritici*, *Ustilago zeae*, rusts for example those caused by Pucciniales such as *Cerotelium fici*, *Chrysomyxa arctostaphyli*, *Coleosporium ipomoeae*, *Hemileia vastatrix*, *Puccinia arachidis*, *Puccinia cacabata*, *Puccinia graminis*, *Puccinia recondita*, *Puccinia sorghi*, *Puccinia hordei*, *Puccinia striiformis* f.sp. *Hordei*, *Puccinia striiformis* f.sp. *Secalis*, *Pucciniastrum coryli*, or Uredinales such as *Cronartium ribicola*, *Gymnosporangium juniperi-*
 20 *virginianae*, *Melampsora medusae*, *Phakopsora pachyrhizi*, *Phragmidium mucronatum*, *Physopella ampeloidis*, *Tranzschelia discolor* and *Uromyces viciae-fabae*; and other rots and diseases such as those caused by *Cryptococcus* spp., *Exobasidium vexans*, *Marasmiellus inoderma*, *Mycena* spp., *Sphacelotheca reiliana*, *Typhula ishikariensis*, *Urocystis agropyri*, *Itersonilia perplexans*, *Corticium invisum*, *Laetisaria fuciformis*, *Waitea circinata*, *Rhizoctonia solani*, *Thanetophorus cucurmeris*,
 25 *Entyloma dahliae*, *Entylomella microspora*, *Neovossia molinae* and *Tilletia caries*.

Blastocladiomycetes, such as *Physoderma maydis*.

Mucoromycetes, such as *Choanephora cucurbitarum*.; *Mucor* spp.; *Rhizopus arrhizus*,

As well as diseases caused by other species and genera closely related to those listed above.

In addition to their fungicidal activity, the compounds and compositions comprising them may
 30 also have activity against bacteria such as *Erwinia amylovora*, *Erwinia caratovora*, *Xanthomonas campestris*, *Pseudomonas syringae*, *Strptomyces scabies* and other related species as well as certain protozoa.

The present invention envisages application of the compounds of the invention to plant propagation material prior to, during, or after planting, or any combination of these.

35 Although active ingredients can be applied to plant propagation material in any physiological state, a common approach is to use seeds in a sufficiently durable state to incur no damage during the treatment process. Typically, seed would have been harvested from the field; removed from the plant; and separated from any cob, stalk, outer husk, and surrounding pulp or other non-seed plant material. Seed would preferably also be biologically stable to the extent that treatment would not cause biological

damage to the seed. It is believed that treatment can be applied to seed at any time between seed harvest and sowing of seed including during the sowing process.

Methods for applying or treating active ingredients on to plant propagation material or to the locus of planting are known in the art and include dressing, coating, pelleting and soaking as well as nursery tray application, in furrow application, soil drenching, soil injection, drip irrigation, application through sprinklers or central pivot, or incorporation into soil (broad cast or in band). Alternatively or in addition active ingredients may be applied on a suitable substrate sown together with the plant propagation material.

Rates of application for these compounds can be influenced by many factors of the environment and should be determined under actual use conditions. Foliage can normally be protected when treated at a rate of from less than about 1 g/ha to about 5,000 g/ha of active ingredient. Seed and seedlings can normally be protected when seed is treated at a rate of from about 0.1 to about 10g per kilogram of seed.

Crops of useful plants in which the composition according to the invention can be used include perennial and annual crops, such as berry plants for example blackberries, blueberries, cranberries, raspberries and strawberries; cereals for example barley, maize (corn), millet, oats, rice, rye, sorghum, triticale and wheat; fibre plants for example cotton, flax, hemp, jute and sisal; field crops for example sugar and fodder beet, coffee, hops, mustard, oilseed rape (canola), poppy, sugar cane, sunflower, tea and tobacco; fruit trees for example apple, apricot, avocado, banana, cherry, citrus, nectarine, peach, pear and plum; grasses for example Bermuda grass, bluegrass, bentgrass, centipede grass, fescue, ryegrass, St. Augustine grass and Zoysia grass; herbs such as basil, borage, chives, coriander, lavender, lovage, mint, oregano, parsley, rosemary, sage and thyme; legumes for example beans, lentils, peas and soya beans; nuts for example almond, cashew, ground nut, hazelnut, peanut, pecan, pistachio and walnut; palms for example oil palm; ornamentals for example flowers, shrubs and trees; other trees, for example cacao, coconut, olive and rubber; vegetables for example asparagus, aubergine, broccoli, cabbage, carrot, cucumber, garlic, lettuce, marrow, melon, okra, onion, pepper, potato, pumpkin, rhubarb, spinach and tomato; and vines for example grapes.

Crops are to be understood as being those which are naturally occurring, obtained by conventional methods of breeding, or obtained by genetic engineering. They include crops which contain so-called output traits (e.g. improved storage stability, higher nutritional value and improved flavour).

Crops are to be understood as also including those crops which have been rendered tolerant to herbicides like bromoxynil or classes of herbicides such as ALS-, EPSPS-, GS-, HPPD- and PPO-inhibitors. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding is Clearfield® summer canola. Examples of crops that have been rendered tolerant to herbicides by genetic engineering methods include e.g. glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady®, Herculex I® and LibertyLink®.

Crops are also to be understood as being those which naturally are or have been rendered resistant to harmful insects. This includes plants transformed by the use of recombinant DNA

techniques, for example, to be capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria. Examples of toxins which can be expressed include δ -endotoxins, vegetative insecticidal proteins (Vip), insecticidal proteins of bacteria colonising nematodes, and toxins produced by scorpions, arachnids, wasps and fungi.

5 An example of a crop that has been modified to express the *Bacillus thuringiensis* toxin is the Bt maize KnockOut® (Syngenta Seeds). An example of a crop comprising more than one gene that codes for insecticidal resistance and thus expresses more than one toxin is VipCot® (Syngenta Seeds). Crops or seed material thereof can also be resistant to multiple types of pests (so-called stacked transgenic events when created by genetic modification). For example, a plant can have the
10 ability to express an insecticidal protein while at the same time being herbicide tolerant, for example Herculex I® (Dow AgroSciences, Pioneer Hi-Bred International).

The compounds according to the invention can be used as pesticidal agents in unmodified form, but they are generally formulated into compositions in various ways using formulation adjuvants, such as carriers, solvents and surface-active substances. The formulations can be in various physical
15 forms, e.g. in the form of dusting powders, gels, wettable powders, water-dispersible granules, water-dispersible tablets, effervescent pellets, emulsifiable concentrates, microemulsifiable concentrates, oil-in-water emulsions, oil-flowables, aqueous dispersions, oily dispersions, suspo-emulsions, capsule suspensions, emulsifiable granules, soluble liquids, water-soluble concentrates (with water or a water-miscible organic solvent as carrier), impregnated polymer films or in other forms known e.g. from the
20 Manual on Development and Use of FAO and WHO Specifications for Pesticides, United Nations, First Edition, Second Revision (2010). Such formulations can either be used directly or diluted prior to use. The dilutions can be made, for example, with water, liquid fertilisers, micronutrients, biological organisms, oil or solvents.

The formulations can be prepared e.g. by mixing the active ingredient with the formulation
25 adjuvants in order to obtain compositions in the form of finely divided solids, granules, solutions, dispersions or emulsions. The active ingredients can also be formulated with other adjuvants, such as finely divided solids, mineral oils, oils of vegetable or animal origin, modified oils of vegetable or animal origin, organic solvents, water, surface-active substances or combinations thereof.

The active ingredients can also be contained in very fine microcapsules. Microcapsules contain
30 the active ingredients in a porous carrier. This enables the active ingredients to be released into the environment in controlled amounts (e.g. slow-release). Microcapsules usually have a diameter of from 0.1 to 500 microns. They contain active ingredients in an amount of about from 25 to 95 % by weight of the capsule weight. The active ingredients can be in the form of a monolithic solid, in the form of fine particles in solid or liquid dispersion or in the form of a suitable solution. The encapsulating
35 membranes can comprise, for example, natural or synthetic rubbers, cellulose, styrene/butadiene copolymers, polyacrylonitrile, polyacrylate, polyesters, polyamides, polyureas, polyurethane or chemically modified polymers and starch xanthates or other polymers that are known to the person skilled in the art. Alternatively, very fine microcapsules can be formed in which the active ingredient is contained in the form of finely divided particles in a solid matrix of base substance, but the
40 microcapsules are not themselves encapsulated.

The formulation adjuvants that are suitable for the preparation of the compositions according to the invention are known *per se*. As liquid carriers there may be used: water, toluene, xylene, petroleum ether, vegetable oils, acetone, methyl ethyl ketone, cyclohexanone, acid anhydrides, acetonitrile, acetophenone, amyl acetate, 2-butanone, butylene carbonate, chlorobenzene, cyclohexane, cyclohexanol, alkyl esters of acetic acid, diacetone alcohol, 1,2-dichloropropane, diethanolamine, p-diethylbenzene, diethylene glycol, diethylene glycol abietate, diethylene glycol butyl ether, diethylene glycol ethyl ether, diethylene glycol methyl ether, *N,N*-dimethylformamide, dimethyl sulfoxide, 1,4-dioxane, dipropylene glycol, dipropylene glycol methyl ether, dipropylene glycol dibenzoate, diproxitol, alkylpyrrolidone, ethyl acetate, 2-ethylhexanol, ethylene carbonate, 1,1,1-trichloroethane, 2-heptanone, alpha-pinene, d-limonene, ethyl lactate, ethylene glycol, ethylene glycol butyl ether, ethylene glycol methyl ether, gamma-butyrolactone, glycerol, glycerol acetate, glycerol diacetate, glycerol triacetate, hexadecane, hexylene glycol, isoamyl acetate, isobornyl acetate, isooctane, isophorone, isopropylbenzene, isopropyl myristate, lactic acid, laurylamine, mesityl oxide, methoxypropanol, methyl isoamyl ketone, methyl isobutyl ketone, methyl laurate, methyl octanoate, methyl oleate, methylene chloride, m-xylene, *n*-hexane, *n*-octylamine, octadecanoic acid, octylamine acetate, oleic acid, oleylamine, o-xylene, phenol, polyethylene glycol, propionic acid, propyl lactate, propylene carbonate, propylene glycol, propylene glycol methyl ether, p-xylene, toluene, triethyl phosphate, triethylene glycol, xylenesulfonic acid, paraffin, mineral oil, trichloroethylene, perchloroethylene, ethyl acetate, amyl acetate, butyl acetate, propylene glycol methyl ether, diethylene glycol methyl ether, methanol, ethanol, isopropanol, and alcohols of higher molecular weight, such as amyl alcohol, tetrahydrofurfuryl alcohol, hexanol, octanol, ethylene glycol, propylene glycol, glycerol, *N*-methyl-2-pyrrolidone and the like.

Suitable solid carriers are, for example, talc, titanium dioxide, pyrophyllite clay, silica, attapulgite clay, kieselguhr, limestone, calcium carbonate, bentonite, calcium montmorillonite, cottonseed husks, wheat flour, soybean flour, pumice, wood flour, ground walnut shells, lignin and similar substances.

A large number of surface-active substances can advantageously be used in both solid and liquid formulations, especially in those formulations which can be diluted with a carrier prior to use. Surface-active substances may be anionic, cationic, non-ionic or polymeric and they can be used as emulsifiers, wetting agents or suspending agents or for other purposes. Typical surface-active substances include, for example, salts of alkyl sulfates, such as diethanolammonium lauryl sulfate; salts of alkylarylsulfonates, such as calcium dodecylbenzenesulfonate; alkylphenol/alkylene oxide addition products, such as nonylphenol ethoxylate; alcohol/alkylene oxide addition products, such as tridecylalcohol ethoxylate; soaps, such as sodium stearate; salts of alkyl naphthalenesulfonates, such as sodium dibutyl naphthalenesulfonate; dialkyl esters of sulfosuccinate salts, such as sodium di(2-ethylhexyl)sulfosuccinate; sorbitol esters, such as sorbitol oleate; quaternary amines, such as lauryltrimethylammonium chloride, polyethylene glycol esters of fatty acids, such as polyethylene glycol stearate; block copolymers of ethylene oxide and propylene oxide; and salts of mono- and dialkylphosphate esters; and also further substances described e.g. in McCutcheon's Detergents and Emulsifiers Annual, MC Publishing Corp., Ridgewood New Jersey (1981).

Further adjuvants that can be used in pesticidal formulations include crystallisation inhibitors, viscosity modifiers, suspending agents, dyes, anti-oxidants, foaming agents, light absorbers, mixing auxiliaries, antifoams, complexing agents, neutralising or pH-modifying substances and buffers, corrosion inhibitors, fragrances, wetting agents, take-up enhancers, micronutrients, plasticisers, glidants, lubricants, dispersants, thickeners, antifreezes, microbicides, and liquid and solid fertilisers.

The compositions according to the invention can include an additive comprising an oil of vegetable or animal origin, a mineral oil, alkyl esters of such oils or mixtures of such oils and oil derivatives. The amount of oil additive in the composition according to the invention is generally from 0.01 to 10 %, based on the mixture to be applied. For example, the oil additive can be added to a spray tank in the desired concentration after a spray mixture has been prepared. Preferred oil additives comprise mineral oils or an oil of vegetable origin, for example rapeseed oil, olive oil or sunflower oil, emulsified vegetable oil, alkyl esters of oils of vegetable origin, for example the methyl derivatives, or an oil of animal origin, such as fish oil or beef tallow. Preferred oil additives comprise alkyl esters of C₈-C₂₂ fatty acids, especially the methyl derivatives of C₁₂-C₁₈ fatty acids, for example the methyl esters of lauric acid, palmitic acid and oleic acid (methyl laurate, methyl palmitate and methyl oleate, respectively). Many oil derivatives are known from the Compendium of Herbicide Adjuvants, 10th Edition, Southern Illinois University, 2010.

The inventive compositions generally comprise from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of compounds of the present invention and from 1 to 99.9 % by weight of a formulation adjuvant which preferably includes from 0 to 25 % by weight of a surface-active substance. Whereas commercial products may preferably be formulated as concentrates, the end user will normally employ dilute formulations.

The rates of application vary within wide limits and depend on the nature of the soil, the method of application, the crop plant, the pest to be controlled, the prevailing climatic conditions, and other factors governed by the method of application, the time of application and the target crop. As a general guideline compounds may be applied at a rate of from 1 to 2000 l/ha, especially from 10 to 1000 l/ha.

Preferred formulations can have the following compositions (weight %):

Emulsifiable concentrates:

active ingredient:	1 to 95 %, preferably 60 to 90 %
surface-active agent:	1 to 30 %, preferably 5 to 20 %
liquid carrier:	1 to 80 %, preferably 1 to 35 %

Dusts:

active ingredient:	0.1 to 10 %, preferably 0.1 to 5 %
solid carrier:	99.9 to 90 %, preferably 99.9 to 99 %

Suspension concentrates:

active ingredient:	5 to 75 %, preferably 10 to 50 %
water:	94 to 24 %, preferably 88 to 30 %
surface-active agent:	1 to 40 %, preferably 2 to 30 %

Wettable powders:

active ingredient: 0.5 to 90 %, preferably 1 to 80 %

surface-active agent: 0.5 to 20 %, preferably 1 to 15 %

solid carrier: 5 to 95 %, preferably 15 to 90 %

5 Granules:

active ingredient: 0.1 to 30 %, preferably 0.1 to 15 %

solid carrier: 99.5 to 70 %, preferably 97 to 85 %

The following Examples further illustrate, but do not limit, the invention.

10

<u>Wettable powders</u>	a)	b)	c)
active ingredients	25 %	50 %	75 %
sodium lignosulfonate	5 %	5 %	-
sodium lauryl sulfate	3 %	-	5 %
sodium diisobutyl naphthalenesulfonate	-	6 %	10 %
phenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	2 %	-
highly dispersed silicic acid	5 %	10 %	10 %
Kaolin	62 %	27 %	-

The combination is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders that can be diluted with water to give suspensions of the desired concentration.

<u>Powders for dry seed treatment</u>	a)	b)	c)
active ingredients	25 %	50 %	75 %
light mineral oil	5 %	5 %	5 %
highly dispersed silicic acid	5 %	5 %	-
Kaolin	65 %	40 %	-
Talcum	-	-	20 %

15

The combination is thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording powders that can be used directly for seed treatment.

<u>Emulsifiable concentrate</u>	
active ingredients	10 %
octylphenol polyethylene glycol ether (4-5 mol of ethylene oxide)	3 %
calcium dodecylbenzenesulfonate	3 %
castor oil polyglycol ether (35 mol of ethylene oxide)	4 %
Cyclohexanone	30 %

xylene mixture	50 %
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Emulsions of any required dilution, which can be used in plant protection, can be obtained from this concentrate by dilution with water.

<u>Dusts</u>	a)	b)	c)
Active ingredients	5 %	6 %	4 %
Talcum	95 %	-	-
Kaolin	-	94 %	-
mineral filler	-	-	96 %

Ready-for-use dusts are obtained by mixing the combination with the carrier and grinding the mixture in a suitable mill. Such powders can also be used for dry dressings for seed.

<u>Extruder granules</u>	
Active ingredients	15 %
sodium lignosulfonate	2 %
carboxymethylcellulose	1 %
Kaolin	82 %

The combination is mixed and ground with the adjuvants, and the mixture is moistened with water. The mixture is extruded and then dried in a stream of air.

<u>Coated granules</u>	
Active ingredients	8 %
polyethylene glycol (mol. wt. 200)	3 %
Kaolin	89 %

The finely ground combination is uniformly applied, in a mixer, to the kaolin moistened with polyethylene glycol. Non-dusty coated granules are obtained in this manner.

Suspension concentrate

active ingredients	40 %
propylene glycol	10 %
nonylphenol polyethylene glycol ether (15 mol of ethylene oxide)	6 %
Sodium lignosulfonate	10 %
carboxymethylcellulose	1 %
silicone oil (in the form of a 75 % emulsion in water)	1 %
Water	32 %

The finely ground combination is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water. Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

Flowable concentrate for seed treatment

active ingredients	40 %
propylene glycol	5 %
copolymer butanol PO/EO	2 %
Tristyrenephenol with 10-20 moles EO	2 %
1,2-benzisothiazolin-3-one (in the form of a 20% solution in water)	0.5 %
monoazo-pigment calcium salt	5 %
Silicone oil (in the form of a 75 % emulsion in water)	0.2 %
Water	45.3 %

The finely ground combination is intimately mixed with the adjuvants, giving a suspension concentrate from which suspensions of any desired dilution can be obtained by dilution with water.

- 5 Using such dilutions, living plants as well as plant propagation material can be treated and protected against infestation by microorganisms, by spraying, pouring or immersion.

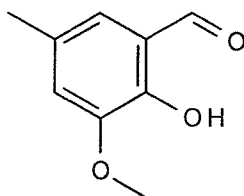
Slow Release Capsule Suspension

- 10 28 parts of the combination are mixed with 2 parts of an aromatic solvent and 7 parts of toluene diisocyanate/polymethylene-polyphenylisocyanate-mixture (8:1). This mixture is emulsified in a mixture of 1.2 parts of polyvinylalcohol, 0.05 parts of a defoamer and 51.6 parts of water until the desired particle size is achieved. To this emulsion a mixture of 2.8 parts 1,6-diaminohexane in 5.3 parts of water is added. The mixture is agitated until the polymerization reaction is completed. The obtained capsule suspension is stabilized by adding 0.25 parts of a thickener and 3 parts of a
- 15 dispersing agent. The capsule suspension formulation contains 28% of the active ingredients. The medium capsule diameter is 8-15 microns. The resulting formulation is applied to seeds as an aqueous suspension in an apparatus suitable for that purpose.

- The Examples which follow serve to illustrate the invention. The compounds of the invention can be distinguished from known compounds by virtue of greater efficacy at low application rates,
- 20 which can be verified by the person skilled in the art using the experimental procedures outlined in the Examples, using lower application rates if necessary, for example 60 ppm, 20 ppm, 6 ppm, 2 ppm or 0.6 ppm.

Example 1: Preparation of 1-hydroxy-7-methoxy-5-methyl-3H-2,1-benzoxaborole

- 25 Synthesis of 2-hydroxy-3-methoxy-5-methyl-benzaldehyde



2,2,2-trifluoroacetic acid (60 ml, 6 mL/g) was added slowly at 0-10°C to hexamethylenetetramine (20 g, 2 equiv., 144.7555 mmol) taken in a 3-neck reaction flask (The addition was observed to be exothermal) under nitrogen atmosphere. The resulting mixture was allowed to stir for 15-20 minutes.

5 2-methoxy-4-methyl-phenol (10 g, 72.3778 mmol) was then added slowly to the reaction mixture and after complete addition, reaction mixture was heated to 80°C for 3 hours.

Reaction mixture was cooled to ambient temperature and 50% H₂SO₄ (10 ml) was added dropwise and the mixture stirred for one hour. The reaction mixture was then extracted with ethyl acetate (3X 100 ml). Combined organic layers were washed with water (4 X 50 ml), dried over sodium sulphate

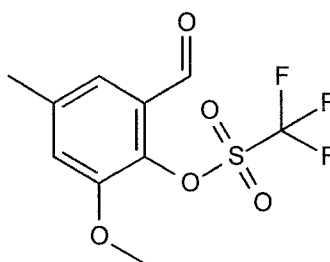
10 and concentrated to give the crude product.

The crude was subject to flash chromatography over silicagel (110g prepacked column) with cyclohexane/ethylacetate 99.5:0.5 to 20:80 as eluent to obtain 2-hydroxy-3-methoxy-5-methyl-benzaldehyde (2.8 g, 17 mmol, 23% Yield) as a yellow solid.

¹H NMR (400 MHz, chloroform-*d*) δ ppm 2.35 (s, 3 H) 3.91 (s, 3 H) 6.95 (d, J=9.43 Hz, 2 H) 9.86 (s, 1 H) 10.91 (s, 1 H). LCMS : rt 1.29 min 166.8 (M+H) (LCMS Method-A)

15

Synthesis (2-formyl-6-methoxy-4-methyl-phenyl) trifluoromethanesulfonate

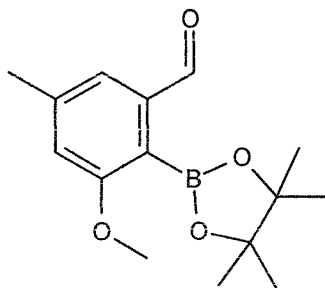


To a stirred solution of 2-hydroxy-3-methoxy-5-methyl-benzaldehyde (24.0 g, 144 mmol) and pyridine
20 (47 mL, 3.000 equiv., 433 mmol) in dichloromethane (240 mL) was added triflic anhydride (37.2 mL, 1.5 equiv., 217 mmol) at 0°C. The resulting mixture was stirred at ambient temperature for 3 hrs. Reaction mixture was then diluted with dichloromethane (50 ml) and the organic layer was separated from the aqueous layer. Combined organic layers were washed with water (3 X 50 mL) followed by brine (50 mL), dried over anhydrous Na₂SO₄, filtered and evaporated completely to afford the product
25 (2-formyl-6-methoxy-4-methyl-phenyl) trifluoromethane sulfonate (36 g, 120.71 mmol, 83.6% Yield) as a grey solid.

¹H NMR (400 MHz, chloroform-*d*) δ ppm 2.44 (s, 3 H) 3.95 (s, 3 H) 7.11 (s, 1 H) 7.33 (s, 1 H) 10.22 (s, 1 H)

30

Synthesis of 3-methoxy-5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde

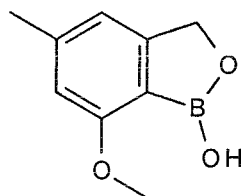


To a stirred solution of (2-formyl-6-methoxy-4-methyl-phenyl) trifluoromethanesulfonate (36 g, 120.71 mmol) in toluene (360 mL, 10 mL/g, 100 mass%), (degassed with Nitrogen for 10 mins) was added BIS(PINACOLATO)DIBORANE (64.5 g, 2.0 equiv., 241.42 mmol), potassium acetate (35.5 g, 3 equiv., 362.12 mmol) and [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) chloride complex with dichloromethane (1:1) (4.9 g, 0.05 equiv., 6.0354 mmol). The reaction mixture was stirred at 110°C for 12 hr.

The reaction mixture was cooled to ambient temperature and poured in water (50 ml). The aqueous layer was extracted with EtOAc (3X 30 ml). Combined organic layers were washed with water (2 x 250 mL) followed by brine (250 mL) and dried over Na₂SO₄, filtered and evaporated completely to give crude mass. The crude compound was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to afford 3-methoxy-5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (27 g, 97.79 mmol, 81.01% Yield) as white solid.

¹H NMR (400 MHz, chloroform-*d*) δ ppm 1.43 - 1.46 (m, 12 H) 2.42 (s, 3 H) 3.82 (s, 3 H) 6.90 (s, 1 H) 7.22 (s, 1H) 9.91 (s, 1 H)

Synthesis of 1-hydroxy-7-methoxy-5-methyl-3H-2,1-benzoxaborole (Compound-1)



To a stirred solution of 3-methoxy-5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzaldehyde (10 g, 36.22 mmol) in methanol (100 mL, 10 mL/g), was added sodium borohydride in portions (2.79 g, 2 equiv., 72.44 mmol) over a period of 15 mins at 0-5°C . Reaction mass was then stirred at ambient temperature. When TLC confirmed the completion of the reaction, the reaction mixture was poured in water: Acetone (1: 1) mixture (40 ml) and organic solvent was evaporated off under vacuum. The aqueous layer was acidified with 6N HCl and stirred at ambient temperature overnight. The desired compound precipitated and the solid mass was filtered, washed with cyclohexane and dried under high vacuum to 1-hydroxy-7-methoxy-5-methyl-3H-2,1-benzoxaborole (4.5 g, 25 mmol, 70% Yield) as a white solid.

¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 2.33 (s, 3 H) 3.78 (s, 3 H) 4.87 (s, 2 H) 6.65 (s, 1 H) 6.75 (s, 1 H) 8.66 (s, 1 H)

LC-MS: rt 1.24 min 178.8.(M+H) (LCMS Method A)

The compounds listed in Table I were prepared in an analogous manner from the suitably substituted intermediates which may be obtained commercially or using synthetic methods known in the art.

5 In Table 1 and throughout the description that follows, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; MS stands for mass spectrum; "%" is percent by weight, unless corresponding concentrations are indicated in other units. The following abbreviations are used throughout this description:

m.p. = melting point

b.p.= boiling point.

S = singlet

br = broad

d = doublet

dd = doublet of doublets

t = triplet

q = quartet

m = multiplet

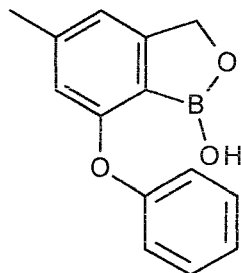
ppm = parts per million

10 **Table-1**

S. N o.	Compound No.	¹ H NMR	RT (min)	[M+H] (measure d)	Method	m.p (°C)
1	Compound 4	¹ H NMR (400 MHz, DMSO-d ₆) δ ppm 2.29 (s, 3 H) 4.97 (s, 2 H) 6.52 (s, 1 H) 6.96 - 7.02 (m, 3 H) 7.12 (t, J=7.21 Hz, 1 H) 7.38 (t, J=7.76 Hz, 2 H) 8.78 (s, 1 H)	1.58	240.8	Method A	87-89
2	Compound 5		1.733	261.8	Method A	96-98
3	Compound 6	¹ H NMR (400 MHz, DMSO-d ₆) δ ppm 5.00 (s, 2 H) 6.76 (s, 1 H) 7.06 (d, J=7.58 Hz, 2 H) 7.31 (s, 1 H) 7.44 (d, J=6.49 Hz, 2 H) 9.04 (s, 1 H)	1.613	294.7	Method A	142-144

Synthesis of 1-hydroxy-5-methyl-7-phenoxy-3H-2,1-benzoxaborole (Compound-4)

The compound was prepared in an analogous manner.



- 5 ¹H NMR (400 MHz, DMSO-*d*₆) δ ppm 2.29 (s, 3 H) 4.97 (s, 2 H) 6.52 (s, 1 H) 6.96 - 7.02 (m, 3 H) 7.12 (t, *J*=7.21 Hz, 1 H) 7.38 (t, *J*=7.76 Hz, 2 H) 8.78 (s, 1 H)
LC-MS: rt 1.58 min 240.8 (M+H) (LCMS Method-A)

LCMS Method A:**Instrumentation** :-

- 10 Mass Spectrometer : 6410 Triple quadrupole Mass Spectrometer from Agilent Technologies
HPLC : Agilent 1200 Series HPLC

Optimized Mass Parameter :-

- 15 Ionisation method : Electrospray (ESI)
Polarity : positive and Negative Polarity Switch
Scan Type : MS2 Scan
Capillary (kV) : 4.00
Fragmentor (V) : 100.00
20 Gas Temperature (°C) : 350
Gas Flow (L/min) : 11
Nebulizer Gas (psi) : 45
Mass range : 110 to 1000 Da
DAD Wavelength range (nm) : 210 to 400

25

Optimized Chromatographic parameter :-

Gradient conditions

(Solvent A: Water, 0.1% formic acid and Solvent B: Acetonitrile, 0.1% formic acid)

- | | Time (minutes) | A (%) | B (%) | Flow rate (ml/min) |
|----|----------------|-------|-------|--------------------|
| 30 | 0 | 90 | 10 | 1.8 |

0.9	0	100	1.8
1.8	0	100	1.8
2.2	90	10	1.8
2.5	90	10	1.8

5Type of column: KINETEX EVO C18; **Column length:** 50 mm; **Internal diameter of column:** 4.6 mm; **Particle Size:** 2.6 μ ; **Temperature:** 40°C.

Biological Activity

10 Botryotinia fuckeliana (Botrytis cinerea) / liquid culture (Gray mould)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (Vogels broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 3-4 days after application.

15 The compound 1, 4 and 5 gave at least 80% control of Botryotinia fuckeliana at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

Glomerella lagenarium (Colletotrichum lagenarium) / liquid culture (Anthracnose)

20 Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is measured photometrically 3-4 days after application.

The compound 1, 4, 5 and 6 gave at least 80% control of Glomerella lagenarium at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

25 Fusarium culmorum / liquid culture (Head blight)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 3-4 days after application.

30 The compound 1, 4, 5 and 6 gave at least 80% control of Fusarium culmorum at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

Fusarium culmorum / wheat / spikelet preventative (Head blight)

35 Wheat spikelets cv. Monsun are placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The spikelets are inoculated with a spore suspension of the fungus 1 day after application. The inoculated spikelets are incubated at 20 °C and 60% rh under a light regime of 72 h semi darkness followed by 12 h light / 12 h darkness in a climate chamber and the activity of a compound is assessed as percent disease control compared to

untreated when an appropriate level of disease damage appears on untreated check spikelets (6 - 8 days after application).

The compound 4 gave at least 80% control of *Fusarium culmorum* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development:

5 *Gaeumannomyces graminis* / liquid culture (Take-all of cereals)

Mycelial fragments of the fungus from cryogenic storage were directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 4-5 days after application.

10 The compounds 1, 4, 5 and 6 gave at least 80% control of *Gaeumannomyces graminis* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

Phaeosphaeria nodorum (*Septoria nodorum*) / wheat / leaf disc preventative (Glume blotch)

15 Wheat leaf segments cv. Kanzler are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 2 days after application. The inoculated test leaf disks are incubated at 20 °C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf disks (5 - 7 days after application).

20 The compounds 5 and 6 gave at least 80% control of *Phaeosphaeria nodorum* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development:

Monographella nivalis (*Microdochium nivale*) / liquid culture (foot rot cereals)

25 Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 4-5 days after application.

The compound 1, 4, 5 and 6 gave at least 80% control of *Monographella nivalis* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

30 *Mycosphaerella arachidis* (*Cercospora arachidicola*) / liquid culture (early leaf spot)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 4-5 days after application.

35 The compound 1, 4, 5 and 6 gave at least 80% control of *Mycosphaerella arachidis* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

Puccinia recondita f. sp. *tritici* / wheat / leaf disc preventative (Brown rust)

Wheat leaf segments cv. Kanzler are placed on agar in multiwell plates (24-well format) and sprayed with the formulated test compound diluted in water. The leaf disks are inoculated with a spore suspension of the fungus 1 day after application. The inoculated leaf segments are incubated at 19 °C and 75% rh under a light regime of 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (7 - 9 days after application).
The compound 4, 5 and 6 gave at least 80% control of *Puccinia recondita* f. sp. *tritici* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development:

Magnaporthe grisea (Pyricularia oryzae) / rice / leaf disc preventative (Rice Blast)

Rice leaf segments cv. Ballila are placed on agar in a multiwell plate (24-well format) and sprayed with the formulated test compound diluted in water. The leaf segments are inoculated with a spore suspension of the fungus 2 days after application. The inoculated leaf segments are incubated at 22 °C and 80% rh under a light regime of 24 h darkness followed by 12 h light / 12 h darkness in a climate cabinet and the activity of a compound is assessed as percent disease control compared to untreated when an appropriate level of disease damage appears in untreated check leaf segments (5 - 7 days after application).

The compound 4 and 5 gave at least 80% control of *Magnaporthe grisea* at 200 ppm when compared to untreated control under the same conditions, which showed extensive disease development:

Pythium ultimum / liquid culture (seedling damping off)

Mycelia fragments and oospores of a newly grown liquid culture of the fungus are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal mycelia/spore mixture is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 2-3 days after application.

The compound 1, 4, 5 and 6 gave at least 80% control of *Pythium ultimum* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

Thanatephorus cucumeris (Rhizoctonia solani) / liquid culture (foot rot, damping-off)

Mycelia fragments of a newly grown liquid culture of the fungus are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of the test compounds into a microtiter plate (96-well format), the nutrient broth containing the fungal material is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 3-4 days after application.

The compound 4, 5 and 6 gave at least 80% control of *Thanatephorus cucumeris* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development:

Sclerotinia sclerotiorum / liquid culture (cottony rot)

Mycelia fragments of a newly grown liquid culture of the fungus are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate

(96-well format) the nutrient broth containing the fungal material is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 3-4 days after application.

The compound 1, 4 and 5 gave at least 80% control of *Sclerotinia sclerotiorum* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

Mycosphaerella graminicola (Septoria tritici) / liquid culture (Septoria blotch)

Conidia of the fungus from cryogenic storage are directly mixed into nutrient broth (PDB potato dextrose broth). After placing a (DMSO) solution of test compound into a microtiter plate (96-well format), the nutrient broth containing the fungal spores is added. The test plates are incubated at 24 °C and the inhibition of growth is determined photometrically 4-5 days after application.

The compound 1, 4, 5 and 6 gave at least 80% control of *Mycosphaerella graminicola* at 20 ppm when compared to untreated control under the same conditions, which showed extensive disease development.

Fusarium graminearum (Giberella zeae) / seed treatment on corn

A defined amount of mycelium of *F. graminearum* is blended with soil and trays are filled with the inoculated soil. The formulated test compound is applied to corn seeds. The treated corn seeds are then sown into the inoculated soil. Until germination the test is stored at 10° C and a rel. humidity of 80% in the dark. After germination the test is transferred to 13° C and a rel. humidity of 70% with a photoperiod of 14h. The evaluation is done by counting the emerged plants.

The compound 1 showed 93% disease control of *Fusarium graminearum* at 20g/100kg compared to an untreated control under the same conditions, which showed extensive disease development.

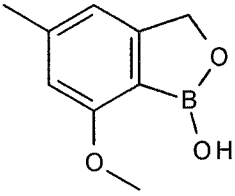
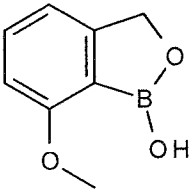
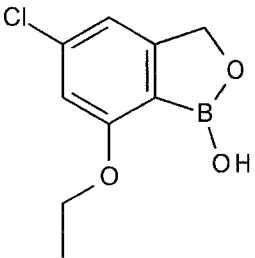
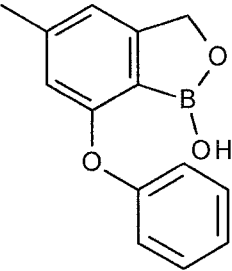
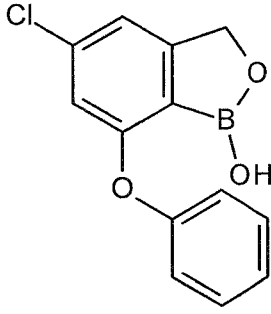
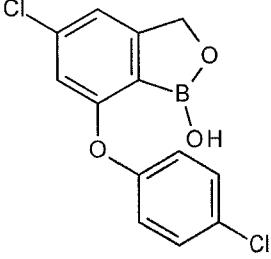
Crop Tolerance

Formulated test compounds are applied to barley seeds cv. Merian. The treated seeds are then sown into soil. The test is stored at 11° C and a rel. humidity of 70% for 17 days. The number of germinated seeds has been counted three times (10, 13 and 17 days after sowing). Shoots were harvested 17 days after sowing (DAS), dried and the dry weight was determined with a balance.

Compound 1 (according to the invention) showed superior crop tolerance to the compounds 2 and 3 (not according to the invention) indicated by higher germination rates and a higher shoot dry weight (see table below).

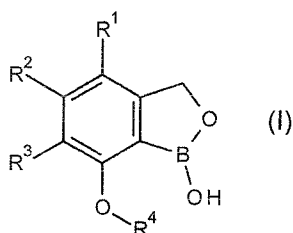
Compound	Rate in g / 100kg seed	Germination 10DAS in %	Germination 13DAS in %	Germination 17DAS in %	Shoot dry weight in g
Compound 1	20	85	96	96	1.40
Compound 2	20	0	78	91	0.94
Compound 3	20	13	59	87	0.93

The following table shows the structure of compound 1, compound 2 compound 3 and compound 4:

Compound 1 (according to the invention)	
Compound 2 (not according to the invention)	
Compound 3 (not according to the invention)	
Compound 4 (according to the invention)	
Compound 5 (according to the invention)	
Compound 6 (according to the invention)	

Claims:

1. A method for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack by treating plants or plant propagation material and/or harvested food crops with an effective amount of a benzoxaboroles of general formula (I)



wherein

R² is -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R⁵, C₁-C₄haloalkyl;

R³ is H;

R⁴ is H, C₁-C₄alkyl, C₁-C₄haloalkyl, phenyl, phenyl substituted by one to three R⁶;

R⁵ is independently selected from cyano and hydroxyl;

R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;

or a salt or a N-oxide thereof.

2. The method according to claim 1 wherein R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵.

3. The method according to claim 1 or claim 2, wherein

R⁴ is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl, phenyl substituted by one to three R⁶.

4. The method according to any one of claims 1 to 3, wherein

R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵, C₁-C₂haloalkyl; and

R⁴ is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl, phenyl substituted by one to three R⁶.

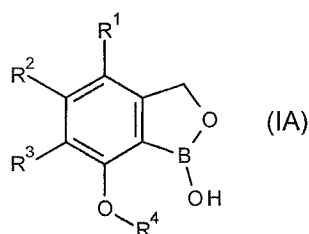
5. The method according to claims 4, wherein

R² is methyl or ethyl and

R⁴ is methyl or ethyl.

6. A compound of formula (IA)

- 30 -



wherein

R¹ is H;

R² is -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R⁵, C₁-C₄haloalkyl;

5 R³ is H;

R⁴ is H, C₁-C₄alkyl, C₁-C₄haloalkyl, phenyl, phenyl substituted by one to three R⁶;

R⁵ is independently selected from cyano and hydroxyl;

R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;

with the proviso that not both R² and R⁴ are methyl;

10 or a salt or an N-oxide thereof.

7. The compound according to 6, wherein R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵, C₁-C₂haloalkyl.

15 8. The compound according to claims 6 or 7, wherein R⁴ is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl, phenyl substituted by one to three R⁶.

9. The compound according to any of the claims 6 to 8, wherein

R² is C₁-C₂-alkyl, C₁-C₂-alkyl substituted by one to three R⁵, C₁-C₂haloalkyl; and

20 R⁴ is H, C₁-C₂alkyl, C₁-C₂haloalkyl, phenyl.

10. The compound according to any of the claims 6 to 9, wherein

R² is methyl or ethyl; and

R⁴ is methyl or ethyl.

25

11. An agrochemical composition comprising a fungicidally effective amount of a compound of formula (IA) according to any one of claims 6 to 10.

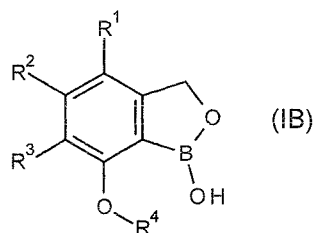
12. The composition according to claim 11, further comprising at least one additional active
30 ingredient and/or an agrochemically acceptable diluent or carrier.

13. A method for controlling or preventing infestation of plants or plant propagation material and/or harvested food crops susceptible to microbial attack by treating plants or plant propagation material and/or harvested food crops a fungicidally effective amount of a compound of formula (I) according to

any of claims 6 to 10, or a composition according to the claims 12 or 13, is applied to the plants, to parts thereof or the locus thereof.

14. Use of a compound of formula (I) according to any one of claims 6 to 10 or a composition
5 according to the claims 12 or claim 13, as a fungicide.

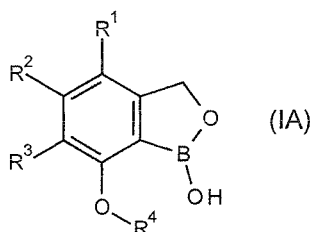
15. A compound of formula (IB)



wherein

- 10 R¹ is H;
 R² is halogen, -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R⁵, C₁-C₄haloalkyl;
 R³ is H;
 R⁴ is phenyl, phenyl substituted by one to three R⁶;
 R⁵ is independently selected from cyano and hydroxyl;
 15 R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;
 or a salt or an N-oxide thereof.

16. A compound of formula (IA)



- 20 wherein
 R¹ is H;
 R² is -CN, C₁-C₄-alkyl, C₁-C₄-alkyl substituted by one to three R⁵, C₁-C₄haloalkyl;
 R³ is H;
 R⁴ is H, C₁-C₄alkyl, C₁-C₄haloalkyl, phenyl, phenyl substituted by one to three R⁶;
 25 R⁵ is independently selected from cyano and hydroxyl;
 R⁶ is independently selected from cyano, hydroxyl, halogen and nitro;
 with the proviso that not both R² and R⁴ are methyl;
 or a salt or an N-oxide thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2017/064455

A. CLASSIFICATION OF SUBJECT MATTER
INV. A01N55/08 A01P3/00 A01P1/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2015/121442 A1 (SYNGENTA PARTICIPATIONS AG [CH]) 20 August 2015 (2015-08-20) cited in the application Cpds 103-105; claims 1-10. ----- -/--	1-16



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

25 July 2017

Date of mailing of the international search report

04/08/2017

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Bueno Torres, Pilar

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/064455

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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