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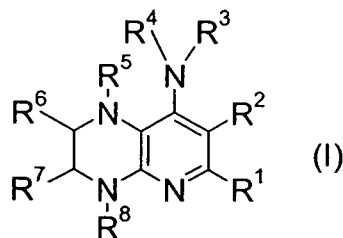
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(54) Title: TETRAHYDROPYRIDO [2, 3-B] PYRAZINE AND DIHYDROPYRIDO [2, 3-B] PYRAZINE DERIVATIVES AS PLANT FUNGICIDES



with R^5 on the adjacent nitrogen atom; or R^6 is part of an endocyclic C=C double bond together with R^7 on the adjacent carbon atom; or R^7 is part of an endocyclic C=N double bond together with R^8 on the adjacent nitrogen atom.

(57) Abstract: The present invention relates to novel tetrahydropyrido[2,3-b]pyrazine and dihydropyrido[2,3-b]pyrazine derivatives of formula I as active ingredients which have microbiocidal activity, in particular fungicidal activity: formula (I) wherein R^1 is for example halogen; R^2 is for example optionally substituted aryl or heteroaryl; R^3 and R^4 , each independently of each other, are for example hydrogen, halogen or cyano; or R^3 and R^4 together with the nitrogen atom to which they are attached form an optionally substituted heterocyclic ring; R^5 and R^8 , each independently of other, are for example hydrogen, C_1 - C_6 alkyl or C_1 - C_6 haloalkyl; R^6 and R^7 , each independently of each other, are for example hydrogen, C_1 - C_6 alkyl or C_1 - C_6 haloalkyl; or R^6 is part of an endocyclic C=N double bond together

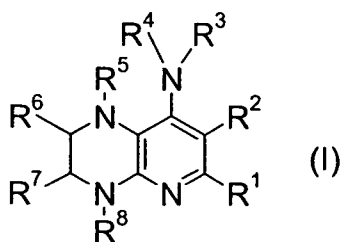
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Novel tetrahydropyrido[2,3-b]pyrazine and dihydropyrido[2,3-b]pyrazine derivatives

The present invention relates to novel tetrahydropyrido[2,3-b]pyrazine and dihydropyrido[2,3-b]pyrazine derivatives as active ingredients which have microbiocidal activity, in particular fungicidal activity. The invention also relates to preparation of these active ingredients, to novel heterocyclic derivatives used as intermediates in the preparation of these active ingredients, to preparation of these novel intermediates, to agrochemical compositions which comprise at least one of the novel active ingredients, to preparation of these compositions and to the use of the active ingredients or compositions in agriculture or horticulture for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms, preferably fungi.

The present invention provides a compound of formula I:



wherein

- 15 R^1 is halogen, C_1 - C_6 alkyl or cyano;
 R^2 is optionally substituted aryl or heteroaryl;
 R^3 and R^4 , each independently of each other, are hydrogen, halogen, cyano, C_1 - C_8 alkyl, C_3 - C_8 cycloalkyl, C_1 - C_8 haloalkyl, C_1 - C_8 haloalkyl(C_3 - C_8)cycloalkyl(C_1 - C_8)alkyl, C_1 - C_8 alkyl(C_3 - C_8)cycloalkyl(C_1 - C_8)alkyl, C_1 - C_8 alkenyl, C_1 - C_8 alkynyl, C_3 - C_8 cycloalkyl, C_3 - C_8 cycloalkyl(C_1 - C_6)alkyl, C_1 - C_6 alkoxy, C_1 - C_6 alkylthio, C_1 - C_6 alkylcarbonyl, C_1 - C_6 alkoxycarbonyl, C_1 - C_6 haloalkyl, C_1 - C_6 haloalkoxy, aryl, heteroaryl or tri(C_1 - C_4)alkylsilyl; or
 R^3 and R^4 together with the nitrogen atom to which they are attached form an optionally substituted heterocyclic ring;
 R^5 and R^8 , each independently of other, are hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl,
25 C_1 - C_6 alkylcarbonyl, C_1 - C_6 alkoxycarbonyl, C_2 - C_6 alkenyl, C_2 - C_6 haloalkenyl or C_1 - C_6 alkylsulfonyl;

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R^6 and R^7 , each independently of each other, are hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, or cyano; or

R^6 is part of an endocyclic C=N double bond together with R^5 on the adjacent nitrogen atom; or

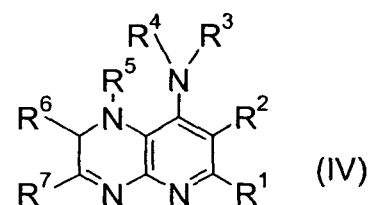
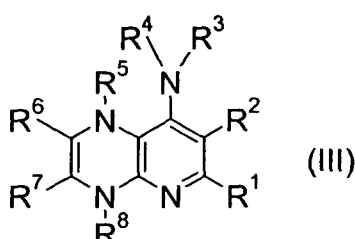
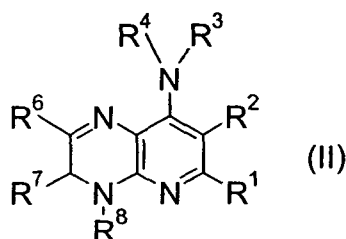
5 R^6 is part of an endocyclic C=C double bond together with R^7 on the adjacent carbon atom; or

R^7 is part of an endocyclic C=N double bond together with R^8 on the adjacent nitrogen atom.

10 In the case where R^5 is part of an endocyclic C=N double bond together with R^6 on the adjacent nitrogen atom, there can only be one double bond in the pyrazine ring thereby forming a dihydropyrido[2,3-b]pyrazine ring system. Similarly in the case where R^7 is part of an endocyclic C=N double bond together with R^8 on the adjacent nitrogen atom, there can only be one double bond in the pyrazine ring thereby forming a dihydropyrido[2,3-b]pyrazine ring system.

15

In the case where R^5 and R^6 , or R^6 and R^7 , or R^7 and R^8 form a double bond, the other possible structures embraced by the invention are 3,4-dihydropyrido[2,3-b]pyrazines (II), 1,4-dihydropyrido[2,3-b]pyrazines (III), or 1,2-dihydropyrido[2,3-b]pyrazines (IV).



20

In the above definition aryl includes aromatic hydrocarbon rings like phenyl, naphthyl, anthracenyl, phenanthrenyl and biphenyl, with phenyl being preferred.

25

Heteroaryl stands for aromatic ring systems comprising mono-, bi- or tricyclic systems wherein at least one oxygen, nitrogen or sulfur atom is present as a ring member. Examples are furyl, thienyl, pyrrolyl, imidazolyl, pyrazolyl, thiazolyl, isothiazolyl, oxazolyl, isoxazolyl, oxadiazolyl, thiadiazolyl, triazolyl, tetrazolyl, pyridyl, pyridazinyl, pyrimidinyl,

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pyrazinyl, triazinyl, tetrazinyl, indolyl, benzothiophenyl, benzofuranyl, benzimidazolyl, indazolyl, benzotriazolyl, benzothiazolyl, benzoxazolyl, quinolinyl, isoquinolinyl, phthalazinyl, quinoxalinyl, quinazolinyl, cinnolinyl and naphthyridinyl. Each heteroaryl can be linked by a carbon atom or by a nitrogen atom to the 1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazine.

5

In the above definition, R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted heterocyclic ring, preferably an optionally substituted 3 to 10 membered mono or bicyclic alkyl or alkylene ring, where one or two ring carbon atoms can be replaced by oxygen, sulphur or nitrogen. Heterocyclic rings are for example

10 pyrrolodinyl, pyrazolidinyl, piperidinyl, piperazinyl, morpholin-4-yl, 3-aza-bicyclo[3.1.0]hexyl, 3-aza-bicyclo[3.1.1]heptyl, 3-aza-bicyclo[4.1.0]heptyl or 8-aza-bicyclo[3.2.1]octyl. Examples of heterocyclic rings are described in WO 03/091254.

The above aryl, heteroaryl groups and heterocyclic rings may be optionally

15 substituted. This means that they may carry one or more identical or different substituents. Normally not more than three substituents are present at the same time. Examples of substituents of aryl, heteroaryl and heterocyclic groups are: halogen, alkyl, haloalkyl, cycloalkyl, cycloalkylalkyl, alkenyl, haloalkenyl, cycloalkenyl, alkynyl, haloalkynyl, alkyloxy, haloalkyloxy, cycloalkoxy, alkenyloxy, haloalkenyloxy, alkynyloxy, haloalkenyloxy, alkylthio,

20 haloalkylthio, cycloalkylthio, alkenylthio, alkynylthio, alkylcarbonyl, haloalkylcarbonyl, cycloalkylcarbonyl, alkenylcarbonyl, alkynylcarbonyl, alkoxyalkyl, cyano, nitro, hydroxy, mercapto, amino, alkylamino, dialkylamino. Typical examples include phenyl, 2-fluorophenyl, 2-chlorophenyl, 2-trifluoromethylphenyl, 2-methylphenyl, 2,3-difluorophenyl, 2,4-difluorophenyl, 2,5-difluorophenyl, 2,6-difluorophenyl, 2,3-dichlorophenyl, 2,4-dichlorophenyl,

25 2,5-dichlorophenyl, 2,6-dichlorophenyl, 2-chloro-3-fluorophenyl, 2-chloro-4-fluorophenyl, 2-chloro-5-fluorophenyl, 2-chloro-6-fluorophenyl, 3-chloro-2-fluorophenyl, 4-chloro-2-fluorophenyl, 5-chloro-2-fluorophenyl, 2-fluoro-3-trifluoromethylphenyl, 2-fluoro-4-trifluoromethylphenyl, 2-fluoro-5-trifluoromethylphenyl, 2-fluoro-6-trifluoromethylphenyl, 2-chloro-3-trifluoromethylphenyl, 2-chloro-4-trifluoromethylphenyl, 2-chloro-5-

30 trifluoromethylphenyl, 2-chloro-6-trifluoromethylphenyl, 4-fluoro-2-trifluoromethylphenyl, 4-chloro-2-trifluoromethylphenyl, 2-fluoro-3-methylphenyl, 2-fluoro-4-methylphenyl, 2-fluoro-5-methylphenyl, 2-fluoro-6-methylphenyl, 2-chloro-3-methylphenyl, 2-chloro-4-methylphenyl, 2-

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chloro-5-methylphenyl, 2-chloro-6-methylphenyl, 4-fluoro-2-methylphenyl, 4-chloro-2-methylphenyl, 2,3,4-trifluorophenyl, 2,3,6-trifluorophenyl, 2,4,6-trifluorophenyl, 2,3,4-trichlorophenyl, 2,3,6-trichlorophenyl, 2,4,6-trichlorophenyl, 2,6-difluoro-4-methoxyphenyl, 2,6-difluoro-4-trifluoromethoxyphenyl, 2,6-difluoro-4-trifluoromethylphenyl, 2,6-difluoro-4-cyanophenyl, 2,6-difluoro-4-methylphenyl, 2,6-dichloro-4-methoxyphenyl, 2,6-dichloro-4-trifluoromethoxyphenyl, 2,6-dichloro-4-trifluoromethylphenyl, 2,6-dichloro-4-cyanophenyl, 2,6-dichloro-4-methylphenyl, pentafluorophenyl, 3,5-difluoropyridin-2-yl, 3,5-dichloropyridin-2-yl, 3-chloro-5-fluoropyridin-2-yl, 5-chloro-3-fluoropyridin-2-yl, 3-fluoro-5-trifluoromethylpyridin-2-yl, 3-chloro-5-trifluoromethylpyridin-2-yl, 3-trifluoromethylpyridin-2-yl, 2,4-difluoropyridin-3-yl, 2,4-dichloropyridin-3-yl, 2,4,6-trifluoropyridin-3-yl, 2,4,6-trichloropyridin-3-yl, 3,5-difluoropyridin-4-yl, 3,5-dichloropyridin-4-yl, 5-chloropyrimidin-4-yl, 2,5-difluorothiophen-3-yl and 2,5-dichlorothiophen-3-yl.

In the above definition halogen is fluorine, chlorine, bromine or iodine.

The alkyl, alkenyl or alkynyl radicals may be straight-chained or branched.

Alkyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, methyl, ethyl, propyl, butyl, pentyl, hexyl and the isomers thereof, for example, isopropyl, isobutyl, sec-butyl, tert-butyl, isopentyl or tert-pentyl.

A haloalkyl group may contain one or more identical or different halogen atoms and, for example, may stand for CH_2Cl , CHCl_2 , CCl_3 , CH_2F , CHF_2 , CF_3 , CF_3CH_2 , CH_3CF_2 , CF_3CF_2 , or CCl_3CCl_2 .

Cycloalkyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl. Cycloalkyl can also be fused or annelated bicyclic ring systems, for example bicyclo[3.1.0]hexyl, bicyclo[4.1.0]heptyl, bicyclo[2.1.1]hexyl, bicyclo[3.2.1]octyl, bicyclo[2.2.2]octyl, or bicyclo[3.1.1]hept-3-yl.

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Alkenyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, ethenyl, allyl, 1-propenyl, buten-2-yl, buten-3-yl, penten-1-yl, penten-3-yl, hexen-1-yl or 4-methyl-3-pentenyl.

5 Alkynyl on its own or as part of another substituent is, depending upon the number of carbon atoms mentioned, for example, ethynyl, propyn-1-yl, propyn-2-yl, butyn-1-yl, butyn-2-yl, 1-methyl-2-butylnyl, hexyn-1-yl or 1-ethyl-2-butylnyl.

10 The presence of one or more possible asymmetric carbon atoms in a compound of formula I means that the compound may occur in optically isomeric, that means enantiomeric or diastereomeric forms. As a result of the presence of a possible aliphatic C=C double bond, geometric isomerism, that means cis-trans or (*E*)-(*Z*) isomerism may also occur. Also atropisomers may occur as a result of restricted rotation about a single bond. The present invention intends to include all those possible isomeric forms and mixtures
15 thereof for a compound of formula I.

In each case, the compounds of formula I according to the invention are in free form or in an agronomically usable salt form.

20 In a first embodiment, R¹ in the compounds of formula I according to the invention is halogen, C₁-C₆alkyl or cyano.

In a second embodiment, R² in the compounds of formula I according to the invention is an optionally substituted aryl or heteroaryl.

25

In a third embodiment, R³ and R⁴ in the compounds of formula I according to the invention, each independently of each other, are hydrogen, C₁-C₈alkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₈cycloalkyl, C₃-C₈cycloalkyl(C₁-C₆)alkyl, aryl or heteroaryl.

30

In a fourth embodiment, R³ and R⁴ in the compounds of formula I according to the invention, together with the nitrogen atom to which they are attached form an optionally

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substituted mono or bicyclic three- to ten-membered alkyl or alkylene ring, where one or two ring carbon atoms can be replaced by oxygen, sulphur or nitrogen.

5 In a fifth embodiment, R⁵ and R⁸ in the compounds of formula I according to the invention, each independently of each other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkylcarbonyl or C₁-C₆alkoxycarbonyl.

10 In a sixth embodiment, R⁶ and R⁷ in the compounds of formula I according to the invention, each independently of each other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or cyano.

15 In a seventh embodiment, R⁶ together with R⁵ on the adjacent nitrogen atom in the compounds of formula I according to the invention, are part of an endocyclic C=N double bond .

In an eighth embodiment, R⁶ together with R⁷ on the adjacent carbon atom in the compounds of formula I according to the invention, are part of an endocyclic C=C double bond.

20 In a ninth embodiment, R⁷ together with R⁸ on the adjacent nitrogen atom in the compounds of formula I according to the invention, are part of an endocyclic C=N double bond .

25 Preferred subgroups of compounds of formula I according to the invention are those wherein

R¹ is halogen or C₁-C₆alkyl;

R² is optionally substituted aryl or heteroaryl;

30 R³ and R⁴, each independently of each other, are hydrogen, C₁-C₈alkyl, C₃-C₈cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₃-C₈alkenyl, C₃-C₈cycloalkyl, C₃-C₈cycloalkyl(C₁-C₆)alkyl, aryl or heteroaryl; or

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R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted mono or bicyclic three- to ten-membered alkyl or alkylene ring, where one or two ring carbon atoms can be replaced by oxygen or nitrogen;

R⁵ and R⁸, each independently of each other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl,

5 C₁-C₆alkylcarbonyl or C₁-C₆alkoxycarbonyl;

R⁶ and R⁷, each independently of each other, are hydrogen, C₁-C₆alkyl or C₁-C₆haloalkyl; or

R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom; or

R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.

10

More preferred subgroups of compounds of formula I according to the invention are those wherein

R¹ is halogen or C₁-C₃alkyl;

R² is optionally substituted phenyl, pyridyl or pyrimidinyl;

15 R³ and R⁴, each independently of each other, are hydrogen, C₁-C₆alkyl, C₃-C₈cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₃-C₆alkenyl or C₃-C₈cycloalkyl(C₁-C₆)alkyl; or

R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted mono or bicyclic three- to ten-membered alkyl or alkylene ring, where one or two
20 ring carbon atoms can be replaced by nitrogen;

R⁵ and R⁸, each independently of each other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or C₁-C₆alkylcarbonyl;

R⁶ and R⁷, each independently of each other, are hydrogen, C₁-C₆alkyl or C₁-C₆haloalkyl; or

R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom;

25 or

R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.

Most preferred subgroups of compounds of formula I according to the invention are those wherein

30 R¹ is fluoro;

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R² is 2,4,6-trifluorophenyl, 2,6-difluoro-4-methoxyphenyl, 2,6-difluorophenyl, 2-chloro-6-fluorophenyl, 3,5-difluoropyridin-2-yl, 3-chloro-5-fluoropyridin-2-yl, 3,5-dichloropyridin-2-yl or 5-chloro-pyrimidin-4-yl;

R³ and R⁴, each independently of each other, are hydrogen, C₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl; or

R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted monocyclic three- to eight-membered alkyl ring, where one or two ring carbon atoms can be replaced by nitrogen;

R⁵ and R⁸, each independently of each other, are hydrogen, methyl or C₁-C₄alkylcarbonyl;

R⁶ and R⁷, each independently of each other, are hydrogen or methyl; or

R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom; or

R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.

Especially preferred subgroups of compounds of formula I according to the invention are those wherein

R¹ is fluoro;

R² is 2,4,6-trifluorophenyl, 2,6-difluoro-4-methoxyphenyl, 2,6-difluorophenyl, 2-chloro-6-fluorophenyl, 3,5-difluoropyridin-2-yl, 3-chloro-5-fluoropyridin-2-yl, 3,5-dichloropyridin-2-yl or 5-chloro-pyrimidin-4-yl;

R³ and R⁴, each independently of each other, are hydrogen, C₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl; or

R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted monocyclic three- to eight-membered alkyl ring, where one or two ring carbon atoms can be replaced by nitrogen;

R⁵ and R⁸, each independently of each other, are hydrogen, methyl or C₁-C₄alkylcarbonyl;

R⁶ and R⁷, each independently of each other, are hydrogen or methyl; or

R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom; or

R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.

Preferred individual compounds are:

- [6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2,2,2-trifluoro-1-methylethyl)-amine (Compound No. I.d.05),
- 5 (1-cyclopropyl-2,2,2-trifluoroethyl)-[6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. 1.d.08),
- [6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2-methyl-1-trifluoromethylpropyl)-amine (Compound No. I.d.011),
- (2,2-dimethyl-1-trifluoromethylpropyl)-[6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-
- 10 tetrahydropyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.d.014),
- (1,2-dimethylpropyl)-[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.d.018),
- [6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(1,2,2-trimethylpropyl)-amine (Compound No. I.d.021),
- 15 (1-cyclopropyl-ethyl)-[6-fluoro-7-(2,4,6-trifluoro-phenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. 1.d.022),
- (1-cyclopropylethyl)-[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.d.024),
- cyclopentyl-[6-fluoro-7-(2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-
- 20 amine (Compound No. 1.d.027),
- [7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2,2,2-trifluoro-1-methylethyl)-amine (Compound No. I.i.05),
- (1-cyclopropyl-2,2,2-trifluoroethyl)-[7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-
- tetrahydropyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.i.08),
- 25 [7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2-methyl-1-trifluoromethylpropyl)-amine (Compound No. I.i.011),
- [7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2,2-dimethyl-1-trifluoromethylpropyl)-amine (Compound No. I.i.014),
- [7-((R)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(1,2-
- 30 dimethylpropyl)-amine (Compound No. I.i.018),
- [7-((R)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(1,2,2-trimethylpropyl)-amine (Compound No. I.i.021), and

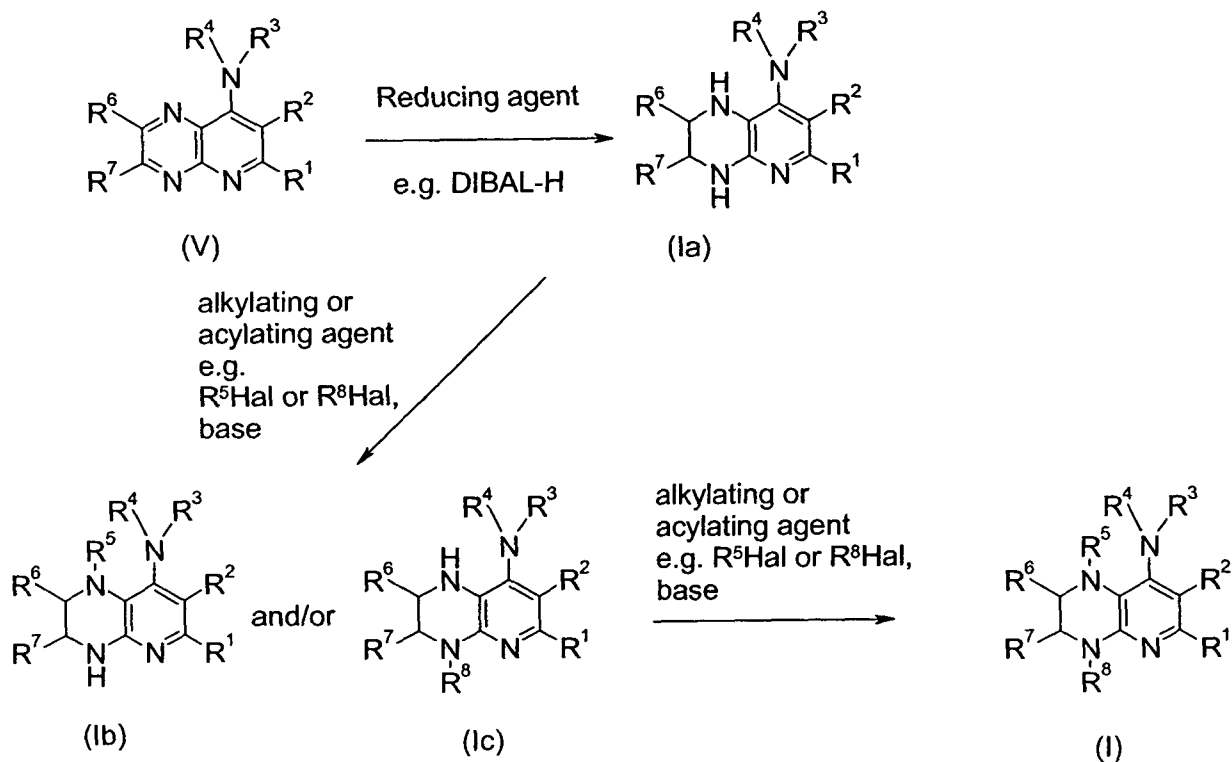
- 10 -

(1-cyclopropylethyl)-[7-((R)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.i.024).

Certain pyrido[2,3-b]pyrazine derivatives have been proposed for controlling plant-destructive fungi, for example those described in WO 2004/056825. However, the action of those preparations is not satisfactory in all aspects of agricultural needs. Surprisingly, with the compounds of formula I, new kinds of fungicides having a high level of biological activity have now been found.

Compounds of formula (Ia), which are examples of compounds of formula (I) where R^5 and R^8 are hydrogen, can be obtained by reduction of compounds of formula (V) with at least two equivalents of a reducing agent such as di-isobutylaluminium hydride (DIBAL-H), sodium borohydride or lithium aluminium hydride in a suitable organic solvent such as tetrahydrofuran (THF) or ethanol, as shown in Scheme 1. The preparation of compounds of formula (V) is already described in WO2004/056825.

Scheme 1



Compounds of formula (Ib) or (Ic), which are examples of compounds of formula (I) where one of R^5 and R^8 is hydrogen and the other is C_1 - C_6 alkyl, C_1 - C_6 haloalkyl,

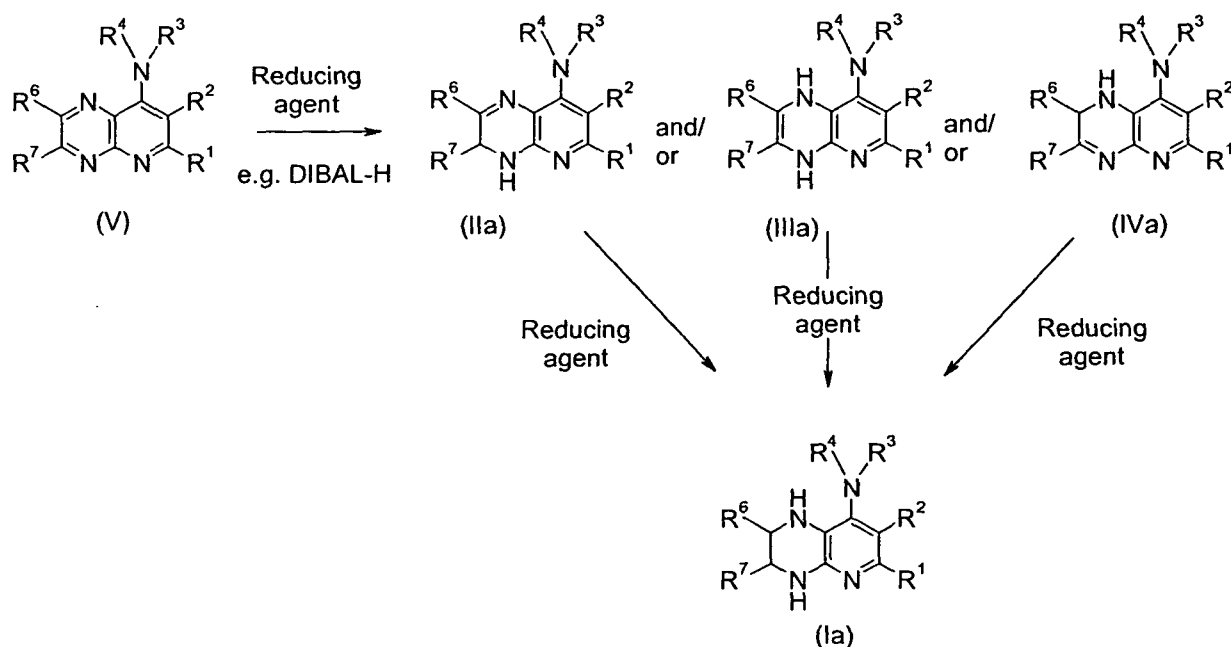
- 5 C_1 - C_6 alkylcarbonyl or C_1 - C_6 alkoxycarbonyl, can be obtained by reaction of compounds of formula (Ia) with an alkyl halide $R^5\text{Hal}$ or $R^8\text{Hal}$ where Hal is a halogen such as chlorine, bromine or iodine and R^5 and R^8 are C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, for example methyl iodide, ethyl bromide, allyl bromide, propargyl bromide or benzyl chloride, or with an acyl halide $R^5\text{Hal}$ or $R^8\text{Hal}$ where R^5 and R^8 are C_1 - C_6 alkylcarbonyl or C_1 - C_6 alkoxycarbonyl and Hal is
- 10 chlorine, for example acetyl chloride or ethyl chloroformate, in the presence of a base such as potassium carbonate, pyridine, triethylamine or di-isopropyl ethylamine in a suitable organic solvent such as THF or dichloromethane.

- Compounds of formula (I) where both of R^5 and R^8 are not hydrogen can be obtained
- 15 by further reaction of compounds (Ib) or (Ic) with an alkylating agent $R^5\text{Hal}$ or $R^8\text{Hal}$ or with

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an acylating group such as a C₁-C₆alkylcarbonyl or C₁₋₆alkoxycarbonyl chloride as described above. It should be noted that in compounds of formula (I) R⁵ and R⁸ can be different, for example R⁵ can be C₁-C₆alkyl and R⁸ can be C₁-C₆alkylcarbonyl.

Scheme 2



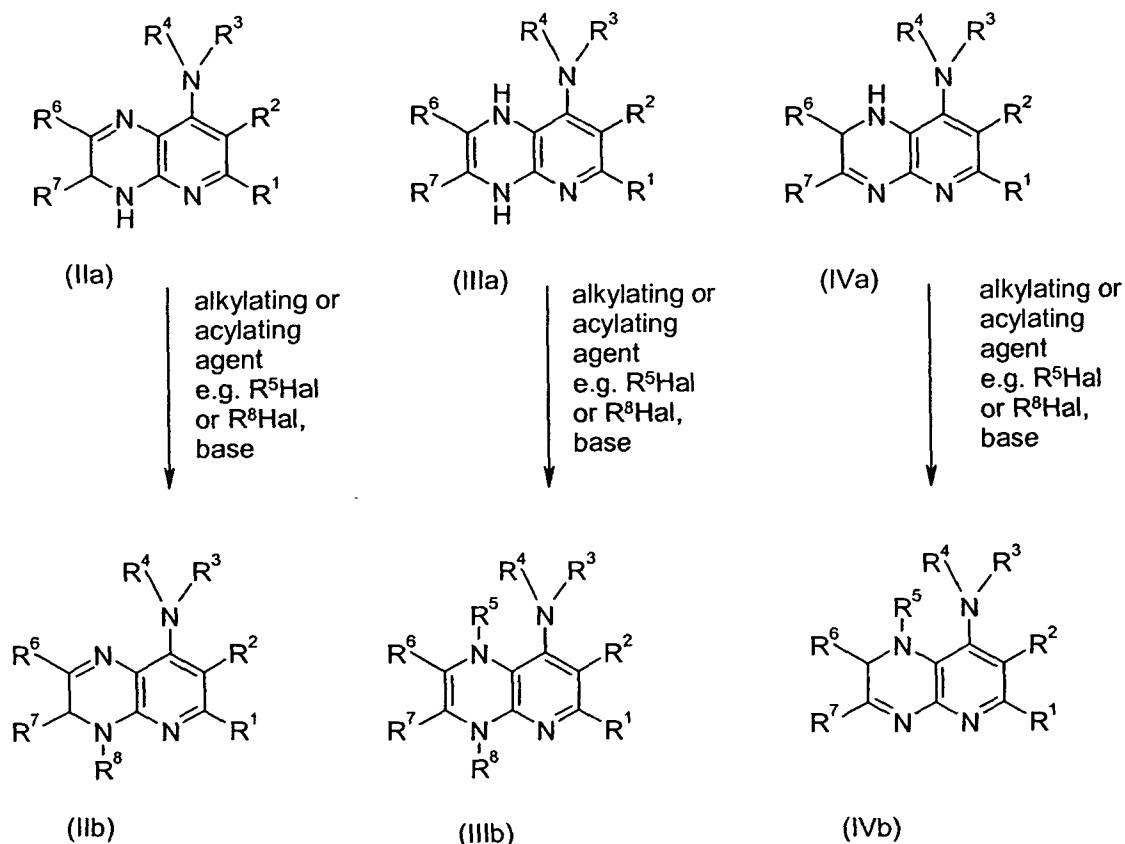
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Partially reduced compounds of formula (IIa), (IIIa) and (IVa) can be obtained alone or in mixture with one or both of the other partially reduced compounds, by reduction of compounds of formula (V) with less than two equivalents of a reducing agent such as diisobutylaluminium hydride (DIBAL-H), sodium borohydride or lithium aluminium hydride in a suitable organic solvent such as tetrahydrofuran (THF) or ethanol, as shown in Scheme 2. If compounds of formula (IIa), (IIIa) or (IVa) are produced as a mixture they can be separated and purified by chromatography or crystallisation. Further reduction of compounds of formula (IIa), (IIIa) or (IVa) with at least one equivalent of a reducing agent such as DIBAL-H as described above gives the fully reduced compound of formula (Ia).

15

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Scheme 3



As shown in Scheme 3, partially reduced compounds of formula (IIb), (IIIb) or (IVb) where R⁵ or R⁸ are C₁-C₆alkyl or C₁-C₆haloalkyl, can be obtained by reaction of compounds of formula (IIa), (IIIa), or (IVa) with an alkyl halide R⁵Hal or R⁸Hal where R⁵ and R⁸ are C₁-C₆alkyl or C₁-C₆haloalkyl and Hal is a halogen such as bromine or iodine, for example methyl iodide, ethyl bromide, allyl bromide, propargyl bromide or benzyl chloride, or with an acyl halide R⁵Hal or R⁸Hal where R⁵ and R⁸ are C₁-C₆alkylcarbonyl or C₁-C₆alkoxycarbonyl and Hal is chlorine, for example acetyl chloride or ethyl chloroformate, in the presence of a base such as potassium carbonate, pyridine, triethylamine or di-isopropylethylamine in a suitable organic solvent such as dichloromethane or THF.

Surprisingly, it has now been found that the novel compounds of formula I have, for practical purposes, a very advantageous spectrum of activities for protecting plants against diseases that are caused by fungi as well as by bacteria and viruses.

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The compounds of formula I can be used in the agricultural sector and related fields of use as active ingredients for controlling plant pests or on non-living materials for control of spoilage microorganisms or organisms potentially harmful to man. The novel compounds are distinguished by excellent activity at low rates of application, by being well tolerated by plants and by being environmentally safe. They have very useful curative, preventive and systemic properties and are used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests that occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) of different crops of useful plants, while at the same time protecting also those parts of the plants that grow later e.g. from phytopathogenic microorganisms.

It is also possible to use compounds of formula I as dressing agents for the treatment of plant propagation material, e.g., seed, such as fruits, tubers or grains, or plant cuttings (for example rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil. The propagation material can be treated with a composition comprising a compound of formula I before planting: seed, for example, can be dressed before being sown. The active ingredients according to the invention can also be applied to grains (coating), either by impregnating the seeds in a liquid formulation or by coating them with a solid formulation. The composition can also be applied to the planting site when the propagation material is being planted, for example, to the seed furrow during sowing. The invention relates also to such methods of treating plant propagation material and to the plant propagation material so treated.

Furthermore the compounds according to present invention can be used for controlling fungi in related areas, for example in the protection of technical materials, including wood and wood related technical products, in food storage, in hygiene management.

In addition, the invention could be used to protect non-living materials from fungal attack, e.g. lumber, wall boards and paint.

- 15 -

The compounds of formula I are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. *Botrytis* spp., *Alternaria* spp.) and Basidiomycetes (e.g. *Rhizoctonia* spp., *Hemileia* spp., *Puccinia* spp., *Phakopsora* spp., *Ustilago* spp., *Tilletia* spp.). Additionally, they are also effective against Ascomycetes (e.g. *Venturia* spp., *Blumeria* spp., *Podosphaera leucotricha*, *Monilinia* spp., *Fusarium* spp., *Uncinula* spp., *Mycosphaerella* spp., *Pyrenophora* spp., *Rhynchosporium secalis*, *Magnaporthe* spp., *Colletotrichum* spp., *Gaeumannomyces graminis*, *Tapesia* spp., *Ramularia* spp., *Microdochium nivale*, *Sclerotinia* spp.) and Oomycetes (e.g. *Phytophthora* spp., *Pythium* spp., *Plasmopara* spp., *Pseudoperonospora cubensis*). Outstanding activity has been observed against powdery mildews (e.g. *Uncinula necator*), rusts (e.g. *Puccinia* spp.) and leaf spots (e.g. *Septoria tritici*). Furthermore, the novel compounds of formula I are effective against phytopathogenic bacteria and viruses (e.g. against *Xanthomonas* spp, *Pseudomonas* spp, *Erwinia amylovora* as well as against the tobacco mosaic virus).

Within the scope of present invention, target crops to be protected typically comprise the following species of plants: cereal (wheat, barley, rye, oat, rice, maize, sorghum and related species); beet (sugar beet and fodder beet); pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries); leguminous plants (beans, lentils, peas, soybeans); oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts); cucumber plants (pumpkins, cucumbers, melons); fibre plants (cotton, flax, hemp, jute); citrus fruit (oranges, lemons, grapefruit, mandarins); vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, paprika); lauraceae (avocado, cinnamomum, camphor) or plants such as tobacco, nuts, coffee, eggplants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as turf and ornamentals.

The target crops in accordance with the invention include conventional as well as genetically enhanced or engineered varieties such as, for example, insect resistant (e.g. Bt. and VIP varieties) as well as disease resistant, herbicide tolerant (e.g. glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady® and LibertyLink®) and nematode tolerant varieties. By way of example,

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suitable genetically enhanced or engineered crop varieties include the Stoneville 5599BR cotton and Stoneville 4892BR cotton varieties.

5 The compounds of formula I are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions or suspensions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations e.g. in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising,
10 dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances. The compositions may also contain further adjuvants such as stabilizers, antifoams, viscosity regulators, binders or tackifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

15 Suitable carriers and adjuvants can be solid or liquid and are substances useful in formulation technology, e.g. natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilizers. Such carriers are for example described in WO 97/33890.

20 The compounds of formula I are normally used in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession with further compounds. These further compounds can be e.g. fertilizers or micronutrient donors or other preparations, which influence the growth of plants. They can also be selective herbicides as well as insecticides, fungicides, bactericides, nematocides, molluscicides or mixtures of
25 several of these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

The compounds of formula I are normally used in the form of fungicidal compositions for controlling or protecting against phytopathogenic microorganisms, comprising as active
30 ingredient at least one compound of formula I, in free form or in agrochemically usable salt form, and at least one of the above-mentioned adjuvants.

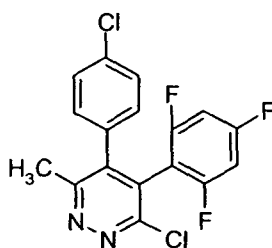
The compounds of formula I can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are:

- 5 Azoles, such as azaconazole, BAY 14120, bitertanol, bromuconazole, cyproconazole, difenoconazole, diniconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriafol, hexaconazole, imazalil, imibenconazole, ipconazole, metconazole, myclobutanil, pefurazoate, penconazole, prothioconazole, pyrifenox, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole;
- 10 Pyrimidinyl carbinols, such as ancymidol, fenarimol, nuarimol;
2-amino-pyrimidines, such as bupirimate, dimethirimol, ethirimol;
Morpholines, such as dodemorph, fenpropidine, fenpropimorph, spiroxamine, tridemorph;
Anilinopyrimidines, such as cyprodinil, mepanipyrim, pyrimethanil;
- 15 Pyrroles, such as fenpiclonil, fludioxonil;
Phenylamides, such as benalaxyl, furalaxyl, metalaxyl, R-metalaxyl, ofurace, oxadixyl;
Benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole;
- 20 Dicarboximides, such as chlozolate, dichlozoline, iprodione, myclozoline, procymidone, vinclozoline;
- Carboxamides, such as boscalid, carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, penthiopyrad, thifluzamide; guanidines, such as guazatine, dodine, iminoctadine;
- Strobilurines, such as azoxystrobin, dimoxystrobin (SSF 129), enestroburin, fluoxastrobin, kresoxim-methyl, metominostrobin, trifloxystrobin, orysastrobin, picoxystrobin,
- 25 pyraclostrobin;
- Dithiocarbamates, such as ferbam, mancozeb, maneb, metiram, propineb, thiram, zineb, ziram;
- N-halomethylthiotetrahydrophthalimides, such as captafol, captan, dichlofluanid, fluoromides, folpet, tolyfluanid;
- 30 Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper;
- Nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl;

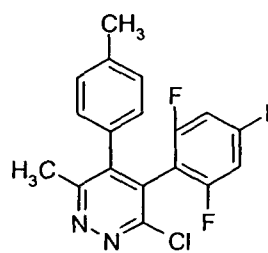
- 18 -

Organo-p-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosdiphen, pyrazophos, tolclofos-methyl;

Pyridazine-derivatives which are known and may be prepared by methods as described in WO 05/121104 and WO 06/001175, such as 3-chloro-5-(4-chloro-phenyl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine (formula P.1) and 3-chloro-6-methyl-5-p-tolyl-4-(2,4,6-trifluoro-phenyl)-pyridazine (formula P.2);

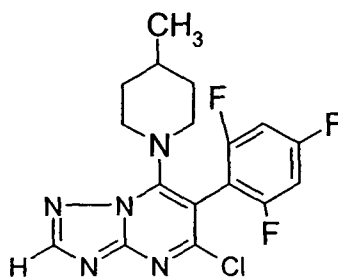


P.1



P.2

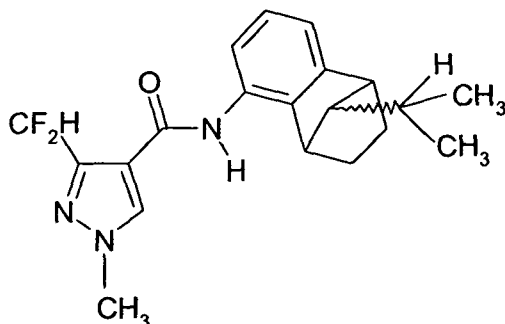
Triazolopyrimidine derivatives which are known and may be prepared by methods as described in WO98/46607, such as 5-chloro-7-(4-methyl-piperidin-1-yl)-6-(2,4,6-trifluoro-phenyl)- [1,2,4]triazolo[1,5-a]pyrimidine (formula T.1);



T.1

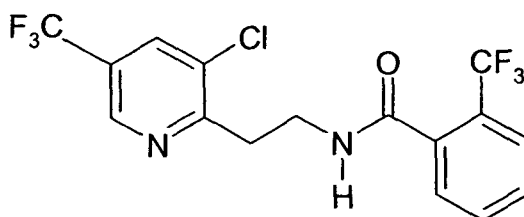
Carboxamide derivatives which are known and may be prepared by methods as described in WO04/035589 and in WO06/37632, such as 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-isopropyl-1,2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (formula U.1);

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U.1

Benzamide derivatives which are known and may be prepared by methods as
 5 described in WO 2004/016088, such as N-{-2-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]ethyl}-
 2-trifluoromethylbenzamide (formula V.1);



V.1

10 and

Various others, such as acibenzolar-S-methyl, anilazine, benthiavalicarb, blasticidin-S,
 chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclocymet,
 diclomezine, dicloran, diethofencarb, dimethomorph, SYP-LI90 (proposed name: flumorph),
 dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone,
 15 fluazinam, fluopicolide, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb,
 cyazofamid, kasugamycin, mandipropamid, methasulfocarb, metrafenone, nicobifen,
 pencycuron, phthalide, polyoxins, probenazole, propamocarb, proquinazid, pyroquilon,
 quinoxifen, quintozone, sulfur, tiadinil, triazoxide, tricyclazole, triforine, validamycin,
 zoxamide.

20 A method of controlling or preventing an infestation of crop plants, harvested food
 crops or non-living materials by phytopathogenic or spoilage microorganisms or organisms

- 20 -

potentially harmful to man, especially phytopathogenic microorganisms that are fungal organisms, which comprises the application of a compound of formula I as active ingredient to the plant, to parts of the plants or to the locus thereof, to seeds or to any part of the non-living materials.

5

Controlling or preventing means reducing the infestation of crop plants or of non-living materials by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, to such a level that an improvement is demonstrated.

10

A preferred method of controlling or preventing an infestation of crop plants by phytopathogenic microorganisms, especially fungal organisms, which comprises the application of a compound of formula I, or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compounds of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granulates can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds or tubers either with a liquid formulation of the fungicide or coating them with a solid formulation.

20

A formulation [that is, a composition containing the compound of formula I] and, if desired, a solid or liquid adjuvant or monomers for encapsulating the compound of formula I, is prepared in a known manner, typically by intimately mixing and/or grinding the compound with extenders, for example solvents, solid carriers and, optionally, surface active compounds (surfactants).

25

The agrochemical formulations will usually contain from 0.1 to 99% by weight, preferably from 0.1 to 95% by weight, of the compound of formula I, 99.9 to 1% by weight, preferably 99.8 to 5% by weight, of a solid or liquid adjuvant, and from 0 to 25% by weight, preferably from 0.1 to 25% by weight, of a surfactant.

30

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Advantageous rates of application are normally from 5g to 2kg of active ingredient (a.i.) per hectare (ha), preferably from 10g to 1kg a.i./ha, most preferably from 20g to 600g a.i./ha. When used as seed drenching agent, convenient dosages are from 10mg to 1g of active substance per kg of seeds.

5

Whereas it is preferred to formulate commercial products as concentrates, the end user will normally use dilute formulations.

10 The following non-limiting Examples illustrate the above-described invention in more detail.

Example 1: This example illustrates the preparation of (1,2-dimethylpropyl)-[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No.I.d.018)

15

Di-isobutylaluminium hydride (DIBAL-H, 1.7 ml) is added to a solution of (1,2-dimethylpropyl)-[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-pyrido[2,3-b]pyrazin-8-yl]-amine (0.21 g) in dichloromethane (2.3 ml) at -78 °C. The reaction mixture is stirred at -78 °C for 5 h. A solution of sodium potassium tartrate (20%, 10 ml) is added and the reaction mixture 20 diluted with diethyl ether and then allowed to warm to room temperature over 1 hour. The aqueous layer is extracted with diethyl ether (3 x 20 ml), and the combined organic layers dried over magnesium sulphate, filtered and concentrated *in vacuo*. The residue is purified by recrystallisation from diethyl ether-hexane) to give (1,2-dimethylpropyl)-[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound 25 No.I.d.018) as a yellow solid (0.161g), mp. 148-150 °C.

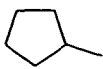
¹H NMR (CDCl₃) δ ppm: 0.69 (d, 3H), 0.72 (d, 3H), 0.83 (d, 3H), 1.55-1.47 (m, 1H), 2.45 (s, 1H), 2.90 (septet, 1H), 3.28-3.22 (m, 2H), 3.49-3.46 (m, 2H), 4.44 (d, 1H), 4.66 (s, 1H), 6.73 (m, 2H).

30 Table 1 below illustrates examples of individual compounds of formula I according to the invention.

Table 1

Compound No.	R ³	R ⁴
1	<i>i</i> -C ₃ H ₇	H
2	<i>t</i> -C ₃ H ₇	H
3	CF ₃ CH ₂	H
4	CF ₃ (CH ₃)CH	H
5	(<i>S</i>)-CF ₃ (CH ₃)CH	H
6	(<i>R</i>)-CF ₃ (CH ₃)CH	H
7	CF ₃ (<i>c</i> -C ₃ H ₇)CH	H
8	(<i>S</i>)-CF ₃ (<i>c</i> -C ₃ H ₇)CH	H
9	(<i>R</i>)-CF ₃ (<i>c</i> -C ₃ H ₇)CH	H
10	CF ₃ (<i>i</i> -C ₃ H ₇)CH	H
11	(<i>S</i>)-CF ₃ (<i>i</i> -C ₃ H ₇)CH	H
12	(<i>R</i>)-CF ₃ (<i>i</i> -C ₃ H ₇)CH	H
13	CF ₃ (<i>t</i> -C ₄ H ₉)CH	H
14	(<i>S</i>)-CF ₃ (<i>t</i> -C ₄ H ₉)CH	H
15	(<i>R</i>)-CF ₃ (<i>t</i> -C ₄ H ₉)CH	H
16	(CH ₃) ₂ CH(CH ₃)CH	H
17	(<i>S</i>)-(CH ₃) ₂ CH(CH ₃)CH	H
18	(<i>R</i>)-(CH ₃) ₂ CH(CH ₃)CH	H
19	(CH ₃) ₃ C(CH ₃)CH	H
20	(<i>S</i>)-(CH ₃) ₃ C(CH ₃)CH	H
21	(<i>R</i>)-(CH ₃) ₃ C(CH ₃)CH	H
22	CH ₃ (<i>c</i> -C ₃ H ₇)CH	H
23	(<i>S</i>)-CH ₃ (<i>c</i> -C ₃ H ₇)CH	H
24	(<i>R</i>)-CH ₃ (<i>c</i> -C ₃ H ₇)CH	H
25	-(CH ₂) ₂ CH(CH ₃)(CH ₂) ₂ -	
26	-(CH ₂) ₄ -	

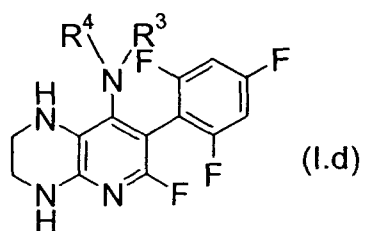
- 23 -

Compound No.	R ³	R ⁴
27		H
28		H

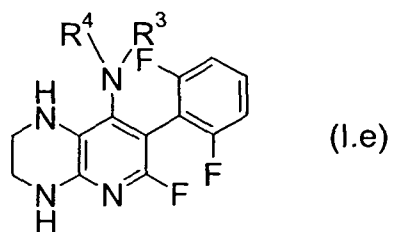
where:

5

a) 28 compounds of formula (I.d):

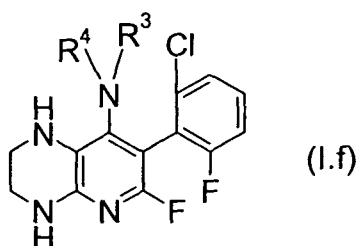
wherein R³ and R⁴ are as defined in Table 1.

10 b) 28 compounds of formula (I.e):

wherein R³ and R⁴ are as defined in Table 1.

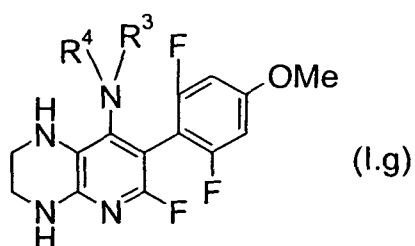
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c) 28 compounds of formula (I.f):



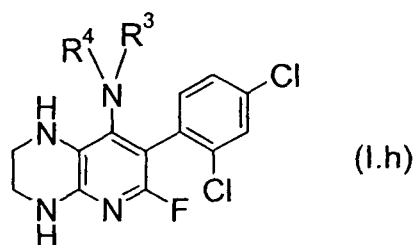
wherein R³ and R⁴ are as defined in Table 1.

5 d) 28 compounds of formula (I.g):



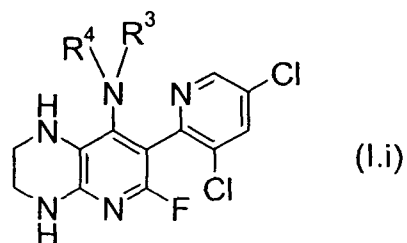
wherein R³ and R⁴ are as defined in Table 1.

e) 28 compounds of formula (I.h):



10 wherein R³ and R⁴ are as defined in Table 1.

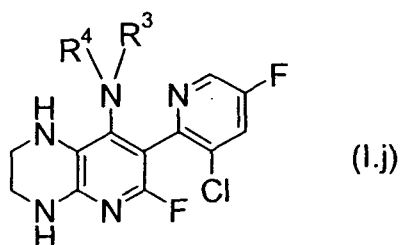
f) 28 compounds of formula (I.i):



wherein R³ and R⁴ are as defined in Table 1.

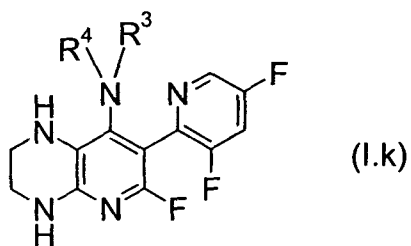
- 25 -

g) provides 28 compounds of formula (I.j):



5 wherein R³ and R⁴ are as defined in Table 1.

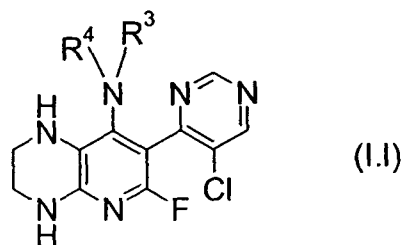
h) 28 compounds of formula (I.k):



wherein R³ and R⁴ are as defined in Table 1.

10

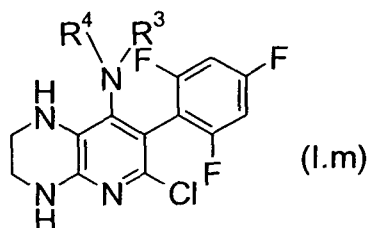
i) 28 compounds of formula (I.l):



wherein R³ and R⁴ are as defined in Table 1.

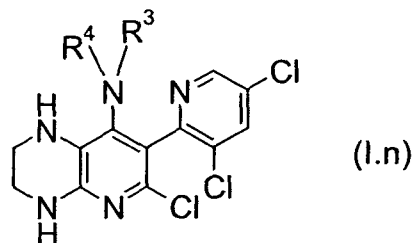
- 26 -

j) 28 compounds of formula (I.m):



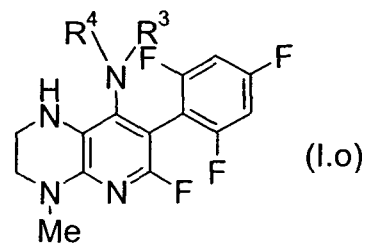
wherein R³ and R⁴ are as defined in Table 1.

5 k) 28 compounds of formula (I.n):



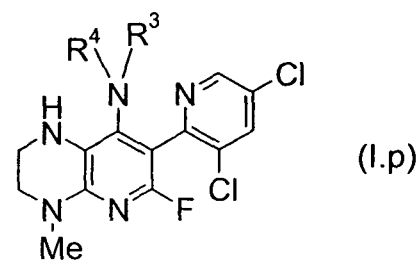
wherein R³ and R⁴ are as defined in Table 1.

l) 28 compounds of formula (I.o):



wherein R^3 and R^4 are as defined in Table 1.

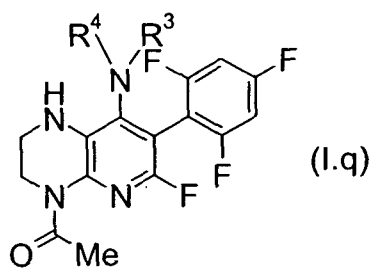
m) 28 compounds of formula (I.p):



wherein R^3 and R^4 are as defined in Table 1.

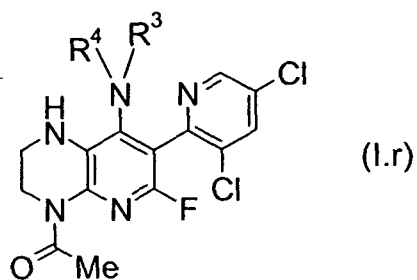
- 27 -

n) 28 compounds of formula (I.q):



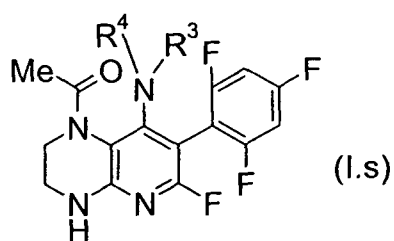
wherein R³ and R⁴ are as defined in Table 1.

5 o) 28 compounds of formula (I.r):



wherein R³ and R⁴ are as defined in Table 1.

p) 28 compounds of formula (I.s):

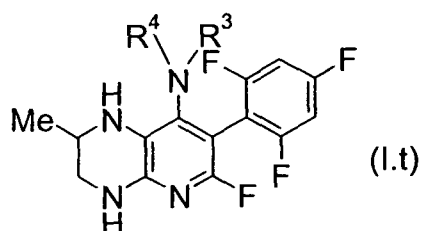


10

wherein R³ and R⁴ are as defined in Table 1.

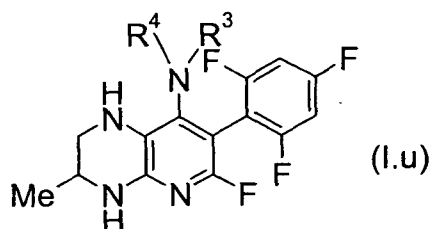
- 28 -

q) 28 compounds of formula (I.t):



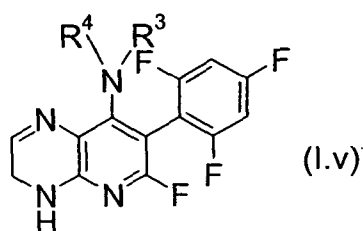
wherein R³ and R⁴ are as defined in Table 1.

5 r) 28 compounds of formula (I.u):



wherein R³ and R⁴ are as defined in Table 1.

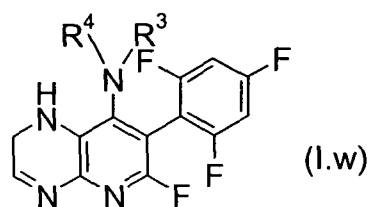
s) 28 compounds of formula (I.v):



10

wherein R³ and R⁴ are as defined in Table 1.

t) 28 compounds of formula (I.w):



15 wherein R³ and R⁴ are as defined in Table 1.

- 29 -

Throughout this description, temperatures are given in degrees Celsius; "NMR" means nuclear magnetic resonance spectrum; and "%" is percent by weight, unless corresponding concentrations are indicated in other units.

5 The following abbreviations are used throughout this description:

m.p. = Melting point	br = Broad
s = Singlet	dd = doublet of doublets
d = Doublet	dt = doublet of triplets
t = Triplet	q = Quartet
m = Multiplet	ppm = parts per million

Table 2 shows selected melting point and selected NMR data, all with CDCl₃ as the solvent (unless otherwise stated, no attempt is made to list all characterising data in all cases) for compounds of Table 1.

10

Table 2: Melting point and selected NMR data for compounds of Table 1

Compound Number	¹ H-NMR data (ppm/multiplicity/number of Hs)	m.p. (°C)
1.d.018	0.69 (d, 3H), 0.72 (d, 3H), 0.83 (d, 3H), 1.55-1.47 (m, 1H), 2.45 (s, 1H), 2.90 (septet, 1H), 3.28-3.22 (m, 2H), 3.49-3.46 (m, 2H), 4.44 (d, 1H), 4.66 (s, 1H), 6.73 (t, 2H)	148-150
1.d.027	1.32 (m, 2H), 1.44 (m, 2H), 1.50 – 1.56 (m, 4H), 3.24 (dd, 2H), 3.43 (brs, 1H), 2.45 (brs, 1H), 3.47 (brm, 2H), 4.35 (brs, 1H), 4.65 (brs, 1H), 6.68 (dd, 2H).	195-196
1.i.05	0.96 and 1.23 (d, 3H, atropisomers), 1.60 (s, 1H), 3.30-3.40 (2H, m), 3.52 and 3.60 (m, 2H), 3.59 and 4.00 (1H, m), 4.55 and 4.83 (d, 1H), 5.05 (s, 1H), 7.85 (dd, 1H), 8.62 (dd, 1H).	

Compound Number	¹ H-NMR data (ppm/multiplicity/number of Hs)	m.p. (°C)
1.d.22	-0.05 (m, 1H), 0.1 (m, 1H), 0.33 (m, 2H), 0.62 (m, 1H), 0.93 (d, 3H), 2.62 (m, 1H), 2.80 (s, 1H), 3.38 (m, 2H), 3.50 (m, 2H), 4.04 (d, 1H), 5.08 (m, 1H), 6.73 (m, 2H)	
1.d.08	0.15 (m, 1H), 0.25 (m, 1H), 0.44 (m, 1H), 0.52 (m, 1H), 0.73 (m, 1H), 3.27 (m, 3H), 3.50 (m, 2H), 4.09 (d, 1H), 5.43 (s, 1H), 6.76 (m, 2H).	

The compounds according to the present invention can be prepared according to the above-mentioned reaction schemes, in which, unless otherwise stated, the definition of each variable is as defined above for a compound of formula (I).

5

Biological examples

Alternaria solani / tomato / preventive (Action against *Alternaria* on tomato)

4 weeks old tomato plants cv. Roter Gnom are treated with the formulated test compound in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension on the test plants. After an incubation period of 4 days at 22/18° C and 95% r. h. in a greenhouse the disease incidence is assessed.

Compounds of formula I according to the invention, in particular compound I.d.018 at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Botrytis cinerea / tomato / preventive (Action against *Botrytis* on tomato)

4 weeks old tomato plants cv. Roter Gnom are treated with the formulated test compound in a spray chamber. Two days after application tomato plants are inoculated by spraying a spore suspension on the test plants. After an incubation period of 3 days at 20° C and 95% r. h. in a greenhouse the disease incidence is assessed.

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Compounds of formula I according to the invention, in particular compound I.d.018, 1.d.027, 1.i.05, 1.d.22, 1.d. 08 at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

5 *Magnaporthe grisea (Pyricularia oryzae) / rice / preventive (Action against rice blast)*

3 weeks old rice plants cv. Koshihikari are treated with the formulated test compound in a spray chamber. Two days after application rice plants are inoculated by spraying a spore suspension (1×10^5 conidia/ml) on the test plants. After an incubation period of 6 days at 25°C and 95% r. h. the disease incidence is assessed.

10

Compounds of formula I according to the invention, in particular compound I.d.018, 1.d.027, 1.i.05, 1.d.22, 1.d. 08 at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

15 *Pyrenophora teres (Helminthosporium teres) / barley / preventive (Action against net blotch on barley)*

1-week-old barley plants cv. Regina are treated with the formulated test compound in a spray chamber. Two days after application barley plants are inoculated by spraying a spore suspension (2.6×10^4 conidia/ml) on the test plants. After an incubation period of 4 days at 20° C and 95% r. h. the disease incidence is assessed.

20

Compounds of formula I according to the invention, in particular compound I.d.018, 1.d.027, 1.i.05, 1.d.22, 1.d. 08 at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

25

Septoria tritici / wheat / preventive (Action against Septoria leaf spot on wheat)

2 weeks old wheat plants cv. Riband are treated with the formulated test compound in a spray chamber. One day after application wheat plants are inoculated by spraying a spore suspension (10^6 conidia/ml) on the test plants. After an incubation period of 1 day at 22°C/21°C and 95% r. h. plants are kept at 22°C/21°C and 70% r.h. in a greenhouse. The disease incidence is assessed 16 - 18 days after inoculation.

30

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Compounds of formula I according to the invention, in particular compound I.d.018, 1.d.027, 1.i.05, 1.d.22, 1.d. 08 at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

Uncinula necator / grape / preventive (Action against powdery mildew on grape)

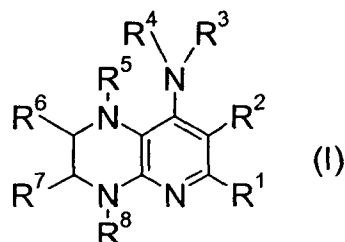
5 weeks old grape seedlings cv. Gutedel are treated with the formulated test compound in a spray chamber. One day after application grape plants are inoculated by shaking plants infected with grape powdery mildew above the test plants. After an incubation period of 7 days at 24/22° C and 70% r. h. under a light regime of 14/10 h (light/dark) the disease incidence is assessed.

Compounds of formula I according to the invention, in particular compound I.d.018 at 200 ppm inhibit fungal infestation in this test to at least 80 %, while under the same conditions untreated control plants are infected by the phytopathogenic fungi to over 80 %.

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What is claimed is:

1. A compound of formula I:



wherein

- 5 R¹ is halogen, C₁-C₆alkyl or cyano;
 R² is optionally substituted aryl or heteroaryl;
 R³ and R⁴, each independently of each other, are hydrogen, halogen, cyano, C₁-C₈alkyl, C₃-C₈cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkenyl, C₁-C₈alkynyl, C₃-C₈cycloalkyl, C₃-C₈cycloalkyl(C₁-C₆)alkyl, C₁-C₆alkoxy, C₁-C₆alkylthio, C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₁-C₆haloalkyl, C₁-C₆haloalkoxy, aryl, heteroaryl or tri(C₁-C₄)alkylsilyl; or
 R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted heterocyclic ring;
 R⁵ and R⁸, each independently of other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkylcarbonyl, C₁-C₆alkoxycarbonyl, C₂-C₆alkenyl, C₂-C₆haloalkenyl or C₁-C₆alkylsulfonyl;
 R⁶ and R⁷, each independently of each other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or cyano; or
 R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom;
 or
 R⁶ is part of an endocyclic C=C double bond together with R⁷ on the adjacent carbon atom;
 or
 R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.
- 25 2. The compound according to claim 1 in free form.
3. The compound according to claim 1 in an agrochemically usable salt form.

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4. The compound according to any one of claims 1 to 3 wherein R¹ is halogen, C₁-C₆alkyl or cyano.

5 5. The compound according to any one of claims 1 to 4 wherein R² is an optionally substituted aryl or heteroaryl.

6. The compound according to any one of claims 1 to 5 wherein R³ and R⁴, each independently of each other, are hydrogen, C₁-C₈alkyl, C₃-C₈cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₈cycloalkyl, C₃-C₈cycloalkyl(C₁-C₆)alkyl, aryl or heteroaryl.

7. The compound according to any one of claims 1 to 5 wherein R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted mono or bicyclic three- to ten-membered alkyl or alkylene ring, where one or two ring carbon atoms can be replaced by oxygen, sulphur or nitrogen.

8. The compound according to any one of claims 1 to 7 wherein R⁵ and R⁸, each independently of each other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl, C₁-C₆alkylcarbonyl or C₁-C₆alkoxycarbonyl.

9. The compound according to any one of claims 1 to 8 wherein R⁶ and R⁷, each independently of each other, are hydrogen, C₁-C₆alkyl, C₁-C₆haloalkyl or cyano.

10. The compound according to any one of claims 1 to 8 wherein R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom.

11. The compound according to any one of claims 1 to 8 wherein R⁶ is part of an endocyclic C=C double bond together with R⁷ on the adjacent carbon atom; or

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12. The compound according to any one of claims 1 to 8 wherein R^7 is part of an endocyclic C=N double bond together with R^8 on the adjacent nitrogen atom.

13. The compound according to any one of claims 1 to 12 wherein

- 5 R^1 is halogen or C_1 - C_6 alkyl;
 R^2 is optionally substituted aryl or heteroaryl;
 R^3 and R^4 , each independently of each other, are hydrogen, C_1 - C_8 alkyl, C_3 - C_8 cycloalkyl, C_1 - C_8 haloalkyl, C_1 - C_8 haloalkyl(C_3 - C_8)cycloalkyl(C_1 - C_8)alkyl, C_1 - C_8 alkyl(C_3 - C_8)cycloalkyl(C_1 - C_8)alkyl, C_3 - C_8 alkenyl, C_3 - C_8 cycloalkyl, C_3 - C_8 cycloalkyl(C_1 - C_6)alkyl, aryl or heteroaryl; or
10 R^3 and R^4 together with the nitrogen atom to which they are attached form an optionally substituted mono or bicyclic three- to ten-membered alkyl or alkylene ring, where one or two ring carbon atoms can be replaced by oxygen or nitrogen;
 R^5 and R^8 , each independently of each other, are hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl, C_1 - C_6 alkylcarbonyl or C_1 - C_6 alkoxycarbonyl;
15 R^6 and R^7 , each independently of each other, are hydrogen, C_1 - C_6 alkyl or C_1 - C_6 haloalkyl; or
 R^6 is part of an endocyclic C=N double bond together with R^5 on the adjacent nitrogen atom;
or
 R^7 is part of an endocyclic C=N double bond together with R^8 on the adjacent nitrogen atom.

20 14. The compound according to any one of claims 1 to 13 wherein

- R^1 is halogen or C_1 - C_3 alkyl;
 R^2 is optionally substituted phenyl, pyridyl or pyrimidinyl;
 R^3 and R^4 , each independently of each other, are hydrogen, C_1 - C_6 alkyl, C_3 - C_8 cycloalkyl, C_1 - C_8 haloalkyl, C_1 - C_8 haloalkyl(C_3 - C_8)cycloalkyl(C_1 - C_8)alkyl, C_1 - C_8 alkyl(C_3 - C_8)cycloalkyl(C_1 - C_8)alkyl, C_3 - C_6 alkenyl or C_3 - C_8 cycloalkyl(C_1 - C_6)alkyl; or
25 R^3 and R^4 together with the nitrogen atom to which they are attached form an optionally substituted mono or bicyclic three- to ten-membered alkyl or alkylene ring, where one or two ring carbon atoms can be replaced by nitrogen;
 R^5 and R^8 , each independently of each other, are hydrogen, C_1 - C_6 alkyl, C_1 - C_6 haloalkyl or C_1 - C_6 alkylcarbonyl;
30 R^6 and R^7 , each independently of each other, are hydrogen, C_1 - C_6 alkyl or C_1 - C_6 haloalkyl; or

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R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom;

or

R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.

5 15. The compound according to any one of claims 1 to 14 wherein

R¹ is chloro or fluoro;

R² is phenyl, pyridyl or pyrimidinyl substituted at least in one *ortho*-position with halogen;

R³ and R⁴, each independently of each other, are hydrogen, C₁-C₆alkyl, C₃-C₈cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-

10 C₈)alkyl or C₃-C₈cycloalkyl(C₁-C₆)alkyl; or

R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally substituted mono or bicyclic three- to ten-membered alkyl or alkylene ring, where one or two ring carbon atoms can be replaced by nitrogen;

R⁵ and R⁸, each independently of each other, are hydrogen or C₁-C₆alkyl or C₁-

15 C₆alkylcarbonyl;

R⁶ and R⁷, each independently of each other, are hydrogen or C₁-C₆alkyl; or

R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom;

or

R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.

20

16. The compound of formula I according to any one of claims 1 to 15 wherein

R¹ is fluoro;

R² is 2,4,6-trifluorophenyl, 2,6-difluoro-4-methoxyphenyl, 2,6-difluorophenyl, 2-chloro-6-fluorophenyl, 3,5-difluoropyridin-2-yl, 3-chloro-5-fluoropyridin-2-yl, 3,5-dichloropyridin-2-yl or

25 5-chloro-pyrimidin-4-yl;

R³ and R⁴, each independently of each other, are hydrogen, C₁-C₆alkyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl, C₁-C₈haloalkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl, C₁-C₈alkyl(C₃-C₈)cycloalkyl(C₁-C₈)alkyl; or

R³ and R⁴ together with the nitrogen atom to which they are attached form an optionally

30 substituted monocyclic three- to eight-membered alkyl ring, where one or two ring carbon atoms can be replaced by nitrogen;

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R⁵ and R⁸, each independently of each other, are hydrogen, methyl or C₁-C₄alkylcarbonyl;
R⁶ and R⁷, each independently of each other, are hydrogen or methyl; or
R⁶ is part of an endocyclic C=N double bond together with R⁵ on the adjacent nitrogen atom;
or

5 R⁷ is part of an endocyclic C=N double bond together with R⁸ on the adjacent nitrogen atom.

17. A compound selected from:

[6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2,2,2-trifluoro-1-methylethyl)-amine (Compound No. I.d.05),

10 (1-cyclopropyl-2,2,2-trifluoroethyl)-[6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. 1.d.08),

[6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2-methyl-1-trifluoromethylpropyl)-amine (Compound No. I.d.011),

(2,2-dimethyl-1-trifluoromethylpropyl)-[6-fluoro-7-((S)-2,4,6-trifluorophenyl)-1,2,3,4-

15 tetrahydropyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.d.014),

(1,2-dimethylpropyl)-[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.d.018),

[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(1,2,2-trimethylpropyl)-amine (Compound No. I.d.021),

20 (1-cyclopropyl-ethyl)-[6-fluoro-7-(2,4,6-trifluoro-phenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. 1.d.022),

(1-cyclopropylethyl)-[6-fluoro-7-((R)-2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.d.024),

cyclopentyl-[6-fluoro-7-(2,4,6-trifluorophenyl)-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. 1.d.027),

25 [7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2,2,2-trifluoro-1-methylethyl)-amine (Compound No. I.i.05),

(1-cyclopropyl-2,2,2-trifluoroethyl)-[7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.i.08),

30 [7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2-methyl-1-trifluoromethylpropyl)-amine (Compound No. I.i.011),

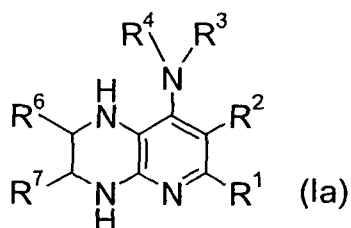
- 38 -

[7-((S)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(2,2-dimethyl-1-trifluoromethylpropyl)-amine (Compound No. I.i.014),

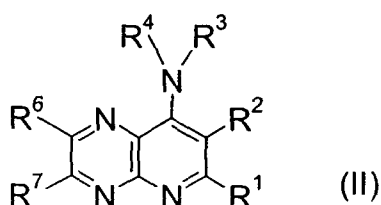
[7-((R)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(1,2-dimethylpropyl)-amine (Compound No. I.i.018),

- 5 [7-((R)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydropyrido[2,3-b]pyrazin-8-yl]-(1,2,2-trimethylpropyl)-amine (Compound No. I.i.021), and
 (1-cyclopropylethyl)-[7-((R)-3,5-dichloropyridin-2-yl)-6-fluoro-1,2,3,4-tetrahydro-pyrido[2,3-b]pyrazin-8-yl]-amine (Compound No. I.i.024).

- 10 18. A process for the preparation of a compound of formula Ia,

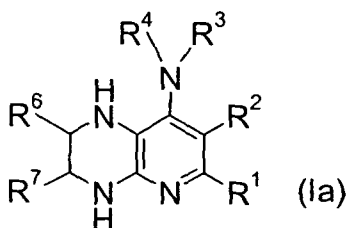


wherein R^1 , R^2 , R^3 , R^4 , R^6 and R^7 are as defined for compound formula I, which comprises reacting a compound of formula II,



- 15 wherein R^1 , R^2 , R^3 , R^4 , R^6 and R^7 are as defined for compound of formula I, with a reducing agent.

19. A process for the preparation of a compound of formula I as defined in claim 1, which comprises reacting a compound of formula Ia



- 39 -

wherein R^1 , R^2 , R^3 , R^4 , R^6 and R^7 are as defined for compound of formula I, with an alkylating agent.

20. A fungicidal composition for controlling or protecting against phytopathogenic
5 microorganisms, comprising as active ingredient at least one compound of formula I defined in claim 1, in free form or in agrochemically usable salt form, and at least one adjuvant.

21. A composition according to claim 20, which comprises at least one additional fungicidally
10 active compound, preferably selected from the group consisting of azoles, pyrimidinyl carbinols, 2-amino-pyrimidines, morpholines, anilinopyrimidines, pyrroles, phenylamides, benzimidazoles, dicarboximides, carboxamides, strobilurines, dithiocarbamates, N-halomethylthiotetrahydrophthalimides, copper-compounds, nitrophenols, organo-phosphor-derivatives, pyridazines, triazolopyrimidines or benzamides.

15 22. The use of a compound of formula I as defined in claim 1 for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms.

20 23. The use according to claim 22, wherein the phytopathogenic microorganisms are fungal organisms.

24. A method of controlling or preventing an infestation of crop plants, harvested food crops or non-living materials by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, which comprises the application of a compound of formula I as
25 defined any one of claims 1 to 16, as active ingredient to the plant, to parts of the plants or to the locus thereof, to seeds or to any part of the non-living materials.

25. A method according to claim 24, wherein the phytopathogenic microorganisms are fungal organisms.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/000876

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D471/04 A01N43/90

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)
C07D

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 practical, search terms used)

EPO-Internal, WPI Data, BIOSIS, BEILSTEIN 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 2004/056825 A (SYNGENTA LTD [GB]; SYNGENTA PARTICIPATIONS AG [CH]; CROWLEY PATRICK JE) 8 July 2004 (2004-07-08) * examples * claim 1	1-25
X	WO 2005/123733 A (SYNGENTA PARTICIPATIONS AG [CH]; CROWLEY PATRICK JELF [GB]; MUELLER UR) 29 December 2005 (2005-12-29) * examples * claim 1	1-25
X	WO 2005/123698 A (SYNGENTA PARTICIPATIONS AG [CH]; CROWLEY PATRICK JELF [GB]; MUELLER UR) 29 December 2005 (2005-12-29) * examples * claim 1	1-25



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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- * & * document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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