(I) The present invention relates to novel pyridazine derivatives of formula (I) as active ingredients which have microbiocidal activity, in particular fungicidal activity.

(II)
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The present invention relates to novel pyridazine derivatives having microbiocidal activity, in particular, fungicidal activity, to processes and intermediates for preparing them, to agricultural compositions comprising them and to methods of using the compounds 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.

Pyridazine derivatives having fungicidal activity are disclosed in international patent applications WO 2005/121104, WO 2006/001175, WO 2007/066601, WO 2007/080720, WO 2008/009405, WO 2008/009406 and WO 2008/049585. There exists a need for alternative methods of control of fungi. Preferably, new compounds may possess improved fungicidal properties, such as improved efficacy, improved selectivity, lower tendency to generate resistance or activity against a broader spectrum of fungi. Compounds may be more advantageously formulated or provide more efficient delivery and retention at sites of action, or may be more readily biodegradable. In particular there exists a need for fungicides having an improved curative action.

It has surprisingly been found that the pyridazine compounds of the present invention exhibit unexpected fungicidal activity, including unexpected curative activity, and are therefore suitable for use in agriculture as crop protection agents to combat or prevent fungal infestations.

The present invention provides a compound of formula (I)

\[
\begin{align*}
\text{R}^1 & \text{ is methyl or ethyl; } \\
\text{R}^2 & \text{ is H or chloro; }
\end{align*}
\]
The present invention includes all those possible isomeric forms and mixtures thereof for a compound of formula (I). For instance, atropisomers may occur as a result of restricted rotation about a single bond.

In a preferred embodiment:
- \( R^1 \) is methyl;
- \( R^2 \) is H or chloro;
- \( R^3 \) is fluoro;
- \( R^4 \) is fluoro or methoxy; and
- \( R^5 \) is chloro or methoxy.

In a more preferred embodiment:
- \( R^1 \) is methyl;
- \( R^2 \) is H;
- \( R^3 \) is fluoro;
- \( R^4 \) is fluoro or methoxy; and
- \( R^5 \) is chloro.

Preferred individual compounds are selected from:
- 3-chloro-5-(6-chloroethynylpyridin-3-yl)-4-(2,6-difluoro-4-methoxyphenyl)-6-methylpyridazine;
- 3-chloro-5-(6-chloroethynylpyridin-3-yl)-6-methyl-4-(2,4,6-trifluorophenyl)pyridazine;
- 3-chloro-5-(6-ethynlypyridin-3-yl)-6-methyl-4-(2,4,6-trifluorophenyl)pyridazine;
- 3-chloro-4-(2,6-difluoro-4-methoxyphenyl)-5-(6-ethynlpyridin-3-yl)-6-methylpyridazin;
- 4-(2,6-difluoro-4-methoxyphenyl)-5-(6-ethynlypyridin-3-yl)-3-methoxy-6-methylpyridazine;
- and
- 4-(6-ethynlpyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluorophenyl)pyridazine.

The compounds according to the present invention can be prepared according to the following reaction schemes, in which, unless otherwise stated, the definition of each variable \( R^1, R^2, R^3 \) and \( R^4 \) are as defined above for a compound of formula (I).
The compounds of formula (1.2) may be obtained by transformation of a compound of formula (1.1) with methanol and base or with sodium methoxide.

The compounds of formula (1.1) may be obtained by transformation of a compound of formula (1.3) with phosphorus oxychloride or thionyl chloride.

The compounds of formula (1.3) may be obtained by transformation of a compound of formula (II) with a hydrazine derivative, e.g. hydrazine hydrate.
The compounds of formula (II) may be obtained by transformation of a compound of formula (III) by oxidation with oxygen, air or 3-chloroperbenzoic acid.

\[
\begin{align*}
\text{O}_2 \text{ or } m\text{CPBA} & \quad \text{(III)} \\
\text{(II)} & \\
\end{align*}
\]

The compounds of formula (III) may be obtained by transformation of a compound of formula (IV), wherein \(R^1, R^2, R^3 \text{ and } R^4\) are as defined for formula (I), with a base, e.g. pyridine, triethylamine, diisopropylethylamine, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,8-diazabicyclo[5.4.0]undec-7-ene.

\[
\begin{align*}
\text{base} & \quad \text{(IV)} \\
\text{(III)} & \\
\end{align*}
\]

The compounds of formula (IV) may be obtained by transformation of a compound of formula (V), wherein Hal is halogen, preferably chlorine or bromine, with a compound of formula (VI) and a base, e.g. pyridine, triethylamine, diisopropylethylamine, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,8-diazabicyclo[5.4.0]undec-7-ene.

\[
\begin{align*}
\text{base} & \quad \text{(V)} + \text{(VI)} \\
\text{(IV)} & \\
\end{align*}
\]

The compounds of formula (I.3), (II), (III) and (IV) form additional aspects of the present invention.
The compounds of formula (I) can be used in unmodified form or, preferably, together with carriers and adjuvants conventionally employed in the art of formulation.

Therefore the invention additionally provides compositions for controlling and protecting against phytopathogenic micro-organisms, comprising a compound of formula (I) and an inert carrier, and to a method of controlling or preventing infestation of useful plants by phytopathogenic micro-organisms, wherein a composition, comprising a compound of formula (I) as active ingredient and an inert carrier, is applied to the plants, to parts thereof or the locus thereof.

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

To this end compounds of formula (I) and inert carriers are conveniently formulated in known manner to mollifiable concentrates, coat able pastes, directly spray able or dilatable solutions, dilute emulsions, wet table 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, 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 pacifiers as well as fertilizers, micronutrient donors or other formulations for obtaining special effects.

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.

The compounds of formula (I) or compositions, comprising a compound of formula (I) as active ingredient and an inert carrier, can be applied to the locus of the plant 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, plant growth regulators as well as insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of
these preparations, if desired together with further carriers, surfactants or application promoting adjuvants customarily employed in the art of formulation.

A preferred method of applying a compound of formula (I), or a composition, comprising a compound of formula (I) as active ingredient and an inert carrier, 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.

A formulation, i.e. a composition comprising the compound of formula (I) and, if desired, a solid or liquid adjuvant, 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).

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.

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

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 rates of application are from 10mg to 1g of active substance per kg of seeds. The rate of application for the desired action can be determined by experiments. It depends for example on the type of action, the developmental stage of the useful plant, and on the application (location, timing, application method) and can, owing to these parameters, vary within wide limits.
The invention relates to a method of controlling or preventing infestation of useful plants by phytopathogenic micro-organisms, wherein a compound of formula (I) is applied as active ingredient to the plants, to parts thereof or the locus thereof. The compounds of formula (I) according to the invention 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 useful plants. The compounds of formula (I) can be used to inhibit or destroy the diseases 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 micro-organisms.

It is also possible to use compounds of formula (I) as dressing agents for the treatment of plant propagation material, in particular of seeds (fruit, tubers, grains) and plant cuttings (e.g. rice), for the protection against fungal infections as well as against phytopathogenic fungi occurring in the soil.

Furthermore the compounds of formula (I) according to the invention may 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 or in hygiene management.

Within the scope of the invention, useful plants to be protected typically comprise the following groups of plants: cereals (wheat, barley, rye, oat, rice, maize, sorghum and related species); beets (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); cucurbit 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 ornamentals.

The term "useful plants" and / or "target crops" is to be understood as including also useful plants that have been rendered tolerant to herbicides like bromoxynil or classes of herbicides (such as, for example, HPPD inhibitors, ALS inhibitors, for example primisulfuron,
prosulfuron and trifloxysulfuron, EPSPS (5-enol-pyrovyl-shikimate-3-phosphate-synthase) inhibitors, GS (glutamine synthetase) inhibitors or PPO (protoporphyrinogen-oxidase) inhibitors) as a result of conventional methods of breeding or genetic engineering. An example of a crop that has been rendered tolerant to imidazolinones, e.g. imazamox, by conventional methods of breeding (mutagenesis) is Clearfield® summer rape (Canola). Examples of crops that have been rendered tolerant to herbicides or classes of herbicides by genetic engineering methods include glyphosate- and glufosinate-resistant maize varieties commercially available under the trade names RoundupReady®, Herculex ® and LibertyLink®.

The term "useful plants" and / or "target crops" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising one or more selectively acting toxins, such as are known, for example, from toxin-producing bacteria, especially those of the genus Bacillus.

The term "useful plants" and / or "target crops" is to be understood as including also useful plants which have been so transformed by the use of recombinant DNA techniques that they are capable of synthesising antipathogenic substances having a selective action, such as, for example, the so-called "pathogenesis-related proteins" (PRPs, see e.g. EP-A-0 392 225). Examples of such antipathogenic substances and transgenic plants capable of synthesising such antipathogenic substances are known, for example, from EP-A-0 392 225, WO 95/33818, and EP-A-0 353 191 . The methods of producing such transgenic plants are generally known to the person skilled in the art and are described, for example, in the publications mentioned above.

The term "locus" of a useful plant as used herein is intended to embrace the place on which the useful plants are growing, where the plant propagation materials of the useful plants are sown or where the plant propagation materials of the useful plants will be placed into the soil. An example for such a locus is a field, on which crop plants are growing.

The term "plant propagation material" is understood to denote generative parts of the plant, such as seeds, which can be used for the multiplication of the latter, and vegetative material, such as cuttings or tubers, for example potatoes. There may be mentioned for example seeds (in the strict sense), roots, fruits, tubers, bulbs, rhizomes and parts of plants. Germinated plants and young plants which are to be transplanted after germination or after emergence from the soil, may also be mentioned. These young plants may be protected
before transplantation by a total or partial treatment by immersion. Preferably "plant propagation material" is understood to denote seeds.

The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: The compounds of formula (I) are, for example, effective against the phytopathogenic fungi of the following classes: Fungi imperfecti (e.g. *Alternaria* spp.), Basidiomycetes (e.g. *Corticium* spp., *Ceratobasidium* spp., *Waitea* spp., *Thanatephorus* spp., *Rhizoctonia* spp., *Hemileia* spp., *Puccinia* spp., *Phakopsora* spp., *Ustilago* spp., *Tilletia* spp.), Ascomycetes (e.g. *Venturia* spp., *Blumeria* spp., *Erysiphe* spp., *Podosphaera* spp., *Uncinula* spp., *Monilinia* spp., *Sclerotinia* spp., *Colletotrichum* spp., *Glomerella* spp., *Fusarium* spp., *Gibberella* spp., *Monographella* spp., *Phaeosphaeria* spp., *Mycosphaerella* spp., *Cercospora* spp., *Pyrenophora* spp., *Rhynchosporium* spp., *Magnaporthe* spp., *Gaeumannomyces* spp., *Oculimacula* spp., *Ramularia* spp., *Botryotinia* spp.) and Oomycetes (e.g. *Phytophthora* spp., *Pythium* spp., *Plasmodora* spp., *Peronospora* spp., *Pseudoperonospora* spp. *Bremia* spp). Outstanding activity has been observed against powdery mildews (e.g. *Uncinula* necator), rusts (e.g. *Puccinia* spp.) and leaf spots (e.g. *Mycosphaerella* spp.). Furthermore, the novel compounds of formula (I) are effective against phytopathogenic gram negative and gram positive bacteria (e.g. *Xanthomonas* spp, *Pseudomonas* spp, *Erwinia* amylovora, *Ralstonia* spp.) and viruses (e.g. tobacco mosaic virus).

In a preferred embodiment of the invention, the compounds and compositions of the present invention are used against the fungal organism *Mycosphaerella graminicola*.

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

Said fungicidal compositions for controlling or protecting against phytopathogenic microorganisms, comprising as active ingredient at least one compound of formula (I) or at least one preferred individual compound as above-defined, in free form or in agrochemically usable salt form, and at least one of the above-mentioned adjuvants can be mixed with other fungicides, resulting in some cases in unexpected synergistic activities. Mixing components which are particularly preferred are:
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, pyrifoxen, prochloraz, propiconazole, simeconazole, tebuconazole, tetraconazole, triadimefon, triadimenol, triflumizole, triticonazole;
  Pyrimidinyl carbinoles, 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;
  Pyrroles, such as fenpiclonil, fludioxonil;
Benzimidazoles, such as benomyl, carbendazim, debacarb, fuberidazole, thiabendazole;
  Dicarboximides, such as chlozolinate, dichlozoline, iprodione, myclozoline, procymidine, vinclozoline;
  Carboxamides, such as boscalid, carboxin, fenfuram, flutolanil, mepronil, oxycarboxin, pentiopyrad, thifluzamide; guanidines, such as guazatine, dodine, iminoctadine;
Strobilurines, such as azoxystrobin, dimoxystrobin, enestroburin, fluoxastrobin, kresoxim-methyl, metominostrobin, trifloxystrobin, orysastrobin, picoxystrobin, pyraclostrobin;
  Dithiocarbamates, such as ferbam, mancozeb, mane, metiram, propineb, thiram, zineb, ziram;
N-halomethylthiotetrahydrophthalimides, such as captafol, captan, dichlofluanid, fluromides, folpet, tolylfluanid;
  Cu-compounds, such as Bordeaux mixture, copper hydroxide, copper oxychloride, copper sulfate, cuprous oxide, mancopper, oxine-copper;
  Nitrophenol-derivatives, such as dinocap, nitrothal-isopropyl;
Organo-phosphorus-derivatives, such as edifenphos, iprobenphos, isoprothiolane, phosphidhen, pyrazophos, tolclofos-methyl;
  Pyridazine-derivatives which are known and may be prepared by methods as described in WO 05/121104, WO 06/001175 and WO 07/066601, such as 3-chloro-5-(4-chloro-phenyl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine (formula P.1), 3-chloro-6-methyl-
5-p-tolyl-4-(2,4,6-trifluoro-phenyl)-pyridazine (formula P.2) and 3-chloro-4-(3-chloro-5-methoxy-pyridin-2-yl)-5-(4-chloro-phenyl)-6-methyl-pyridazine (formula P.3);

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-trifluorophenyl)-[1,2,4]triazolo[1,5-a]pyrimidine (formula T.1);

Carboxamide derivatives which are known and may be prepared by methods as described in WO04/035589, WO06/37632, WO03/074491 or WO03070705, such as 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (9-isopropyl)-2,3,4-tetrahydro-1,4-methano-naphthalen-5-yl)-amide (formula U.1), 3-difluoromethyl-1-methyl-1H-pyrazole-4-carboxylic acid (2-bicyclopropyl-2-yl-phenyl)-amide (formula U.2) or N-(3',4'-dichloro-5-fluoro-1,1'-biphenyl-2-yl)-3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxamide;
Benzamide derivatives which are known and may be prepared by methods as described in WO 2004/016088, such as N-(-2-[3-chloro-5-(trifluoromethyl)-2-pyridinyl]ethyl)-2-trifluoromethylbenzamide, which is also known under the name fluopyram (formula V.1);

and

various others, such as acibenzolar-S-methyl, anilazine, benthiavalcarb, blasticidin-S, chinomethionate, chloroneb, chlorothalonil, cyflufenamid, cymoxanil, dichlone, diclocymet, diclomezine, dicloran, diethofencarb, dimethomorph, flumorph, dithianon, ethaboxam, etridiazole, famoxadone, fenamidone, fenoxanil, fentin, ferimzone, fluazinam, fluopicolide, flusulfamide, fenhexamid, fosetyl-aluminium, hymexazol, iprovalicarb, cyazofamid, kasugamycin, mandipropamid, methasulfocarb, metrafenone, nicobifen, pencycuron, phthalide, polyoxins, probenazole, propamocarb, proquinazid, pyroquilon, quinoxyfen, quintozene, sulfur, tiadinil, triazoxide, tricyclazole, triforine, validamycin, zoxamide and glyphosate.

Another aspect of invention is related to the use of a compound of formula (I) or of a preferred individual compound as above-defined, of a composition comprising at least one compound of formula (I) or at least one preferred individual compound as above-defined, or of a fungicidal mixture comprising at least one compound of formula (I) or at least one preferred individual compound as above-defined, in admixture with other fungicides, as described above, for controlling or preventing infestation of plants, harvested food crops,
seeds or non-living materials by phytopathogenic microorganisms, preferably fungal organisms.

A further aspect of invention is related to a method of controlling or preventing an infestation of crop plants, harvested food crops or of non-living materials by phytopathogenic or spoilage microorganisms or organisms potentially harmful to man, especially fungal organisms, which comprises the application of a compound of formula (I) or of a preferred individual compound as above-defined as active ingredient to the plants, to parts of the plants or to the locus thereof, to seeds or to any part of the non-living materials.

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.

In the above different lists of active ingredients to be mixed with a compound of the formula (I) is preferably a compound of Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 1 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 2 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 3 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 4 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 5 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 6 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 7 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 8 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 9 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 10 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 11 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 12 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 13 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 14 of the Table 1; and more preferably, a compound selected
from the above different lists of active ingredients and the compound 15 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 16 of the Table 1; and more preferably, a compound selected from the above different lists of active ingredients and the compound 17 of the Table 1;

Table 1 below illustrates examples of individual compounds of formula (I) and intermediate (1.3) according to the invention.

![Chemical structure diagram]

<table>
<thead>
<tr>
<th>Compound No.</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>R&lt;sup&gt;3&lt;/sup&gt;</th>
<th>R&lt;sup&gt;4&lt;/sup&gt;</th>
<th>R&lt;sup&gt;5&lt;/sup&gt;</th>
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<tr>
<td>1 (1.3)</td>
<td>CH₃</td>
<td>H</td>
<td>F</td>
<td>F</td>
<td>O</td>
</tr>
<tr>
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<td>CH₃</td>
<td>H</td>
<td>F</td>
<td>F</td>
<td>C</td>
</tr>
<tr>
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<td>H</td>
<td>F</td>
<td></td>
<td>OCH₃</td>
</tr>
<tr>
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<td>F</td>
<td></td>
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<td></td>
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</table>
The following non-limiting examples illustrate the above-described invention in more detail.

Example 1: This example illustrates the preparation of 3-chloro-4-(2,6-difluoro-4-methoxyphenyl)-5-(6-ethynlypyridin-3-yl)-6-methylpyridazine (Compound No. 3)

a) Preparation of 4-(2,6-difluoro-4-methoxyphenyl)-3-methoxy-5-(6-methoxypyridin-3-yl)-6-methylpyridazine

A mixture of 3-chloro-5-(6-chloropyridin-3-yl)-6-methyl-4-(2,4,6-trifluorophenyl)pyridazine (known from WO 2009/090038, 2.0 g), sodium methoxide (30% solution in methanol, 5.3 g) and 40 ml of tetrahydrofuran is heated to 55 °C overnight. Subsequently the reaction mixture is cooled, diluted with water and extracted with ethyl acetate. The combined organic layer is washed with water and brine, dried over sodium sulfate and evaporated under reduced pressure to obtain 4-(2,6-difluoro-4-methoxyphenyl)-3-methoxy-5-(6-methoxypyridin-3-yl)-6-methylpyridazine as a brown oil.

b) Preparation of 3-chloro-5-(6-chloropyridin-3-yl)-4-(2,6-difluoro-4-methoxyphenyl)-6-methylpyridazine

A mixture of 1.0 g 4-(2,6-difluoro-4-methoxyphenyl)-3-methoxy-5-(6-methoxypyridin-3-yl)-6-methylpyridazine, 20 ml of phosphorus oxychloride and 500 mg of trimethylamine hydrochloride is heated at reflux overnight. After cooling the reaction mixture is evaporated under reduced pressure. The residue is purified by chromatography on silica gel, using a mixture of heptane / ethyl acetate 3 : 1 as eluent to obtain 3-chloro-5-(6-chloropyridin-3-yl)-4-(2,6-difluoro-4-methoxyphenyl)-6-methylpyridazine as colourless crystals, m.p. 148 - 149 °C.

c) Preparation of 3-chloro-4-(2,6-difluoro-4-methoxyphenyl)-6-methyl-5-(6-trimethylsilylalkyl)pyridazine

A mixture of 1.0 g 3-chloro-5-(6-chloropyridin-3-yl)-4-(2,6-difluoro-4-methoxyphenyl)-6-methylpyridazine, 0.58 g ethynyltrimethylsilane, 40 mg bis(triphenylphosphine)palladium(II) dichloride, 40 mg copper(I) iodide and 4 ml diisopropylamine in 10 ml tetrahydrofuran is heated at reflux for 3 h. After cooling the reaction mixture is diluted with water and extracted with ethyl acetate. The combined organic layer is washed with brine, dried over sodium sulfate and evaporated under reduced pressure. The residue is purified by chromatography on silica gel, using a mixture of heptane / ethyl acetate 4 : 1 as eluent to obtain 3-chloro-4-
(2,6-difluoro-4-methoxyphenyl)-6-methyl-5-(6-trimethylsilanylthynylpyridin-3-yl)pyridazine, m.p. 148 - 150 °C.

d) 0.41 g 3-chloro-4-(2,6-difluoro-4-methoxyphenyl)-6-methyl-5-(6-trimethylsilanylthynylpyridin-3-yl)pyridazine in 8 ml methanol is stirred with 1.4 ml 1 N potassium hydroxide for 1 h at room temperature. The reaction mixture is diluted with water and extracted with ethyl acetate. The combined organic layer is washed with brine, dried over sodium sulfate and evaporated under reduced pressure. The residue is purified by chromatography on silica gel, using a mixture of heptane / ethyl acetate 2 : 1 as eluent to obtain 3-chloro-4-(2,6-difluoro-4-methoxyphenyl)-5-(6-ethynylpyridin-3-yl)-6-methyl-pyridazine (Compound No. 3) as colourless crystals, m.p. 186-187 °C.

Example 2: This example illustrates the preparation of 3-chloro-5-(6-chloroethynylpyridin-3-yl)-4-(2,6-difluoro-4-methoxyphenyl)-6-methylpyridazine (Compound No. 7)

To an ice-cooled solution of 300 mg 3-chloro-4-(2,6-difluoro-4-methoxyphenyl)-6-methyl-5-(6-trimethylsilanylthynylpyridin-3-yl)pyridazine in 15 ml acetone were added 160 mg trichloroisocyanuric acid, 23 mg silver nitrate and 0.55 ml water. The reaction mixture was protected from light and stirred for 0.5 h at 0°C and then at 40°C overnight. Brine was added to the mixture, which was then extracted with ethyl acetate. The combined extracts were dried over sodium sulfate and concentrated in vacuo. The residue is purified by chromatography on silica gel, using a mixture of heptane / ethyl acetate 3 : 1 as eluent to obtain 3-chloro-5-(6-chloroethynylpyridin-3-yl)-4-(2,6-difluoro-4-methoxyphenyl)-6-methyl-pyridazine (Compound No. 7) as an oil, 1H-NMR (CDCl3) δ = 2.56 (s, 3H), 3.78 (s, 3H), 6.39 (d, 2H), 7.40 - 7.48 (m, 2H), 8.30 (s, 1H).

Biological examples

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

4-week old tomato plants cv. Roter Gnom were treated with the formulated test compound in a spray chamber. The test plants were inoculated by spraying them with a spore suspension two days after application. The inoculated test plants were incubated at 22/18°C (day/night) and 95% r.h in a greenhouse and the percentage leaf area covered by disease was assessed when an appropriate level of disease appears on untreated check plants (5 to 7 days after application).
Compounds 3 and 7 according to the invention at 200 ppm inhibited 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%.

*Botryotinia fuckeliana* (*Botrytis cinerea*) / tomato / preventative (Action against Botrytis on tomato)
4-week old tomato plants cv. Roter Gnom were treated with the formulated test compound in a spray chamber. The test plants were inoculated by spraying them with a spore suspension two days after application. The inoculated test plants were incubated at 20°C and 95% rh in a greenhouse and the percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (5 to 6 days after application).

Compound 3 according to the invention at 200 ppm inhibited 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%.

*Erysiphe necator* (*Uncinula necator*) / grape / preventative (Action against powdery mildew on grape)
5-week old grape seedlings cv. Gutedel were treated with the formulated test compound in a spray chamber. The test plants are inoculated by shaking plants infected with grape powdery mildew above them 1 day after application. The inoculated test plants were incubated at 24/22°C (day/night) and 70% rh under a light regime of 14/10 h (light/dark) and the percentage leaf area covered by disease was assessed when an appropriate level of disease appears on untreated check plants (7 to 9 days after application).

Compound 3 according to the invention at 200 ppm inhibited 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%.

*Magnaporthe grisea* (*Pyricularia oryzae*) / rice / preventative (Action against rice blast)
3-week old rice plants cv. Koshihikari were treated with the formulated test compound in a spray chamber. The test plants were inoculated by spraying them with a spore suspension two days after application. The inoculated test plants were incubated at 25°C and 95% rh
and the percentage leaf area covered by disease was assessed when an appropriate level of disease appears on untreated check plants (7 to 9 days after application).

Compounds 3 and 7 according to the invention at 200 ppm inhibited 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 %.

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

2-week old wheat plants cv. Riband were treated with the formulated test compound in a spray chamber. The test plants were inoculated by spraying a spore suspension on them one day after application. After an incubation period of 1 day at 22°C/21 °C (day/night) and 95% rh, the test plants were kept at 22°C/21°C (day/night) and 70% rh in a greenhouse. The percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (16 to 19 days after application).

Compounds 3 and 7 according to the invention at 200 ppm inhibited 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 %.

*Mycosphaerella graminicola (Septoria tritici) / wheat / curative (Action against Septoria leaf spot on wheat)*

2-week old wheat plants cv. Riband are inoculated by spraying them with a spore suspension. After an incubation period of 2 days at 22°C/21 °C (day/night) and 95% rh, the test plants are kept at 22°C/21°C (day/night) and 70% rh in a climate chamber. The inoculated test plants are treated with the formulated test compound in a spray chamber 5 days after inoculation. The percentage leaf area covered by disease is assessed when an appropriate level of disease appears on untreated check plants (11 to 14 days after application).

Compound 3 according to the invention at 200 ppm inhibited 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 %.

*Puccinia recondita / wheat / preventative (Action against brown rust on wheat)*
2-week old wheat plants cv. Arina were treated with the formulated test compound in a spray chamber. The test plants were inoculated by spraying them with a spore suspension one day after application. After an incubation period of 1 day at 20° C and 95% rh, the test plants were kept at 20° C / 18° C (day/night) and 60% rh in a greenhouse. The percentage leaf area covered by disease was assessed when an appropriate level of disease appears on untreated check plants (12 to 14 days after application).

Compounds 3 and 7 according to the invention at 200 ppm inhibited 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 %.

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

1-week old barley plants cv. Regina were treated with the formulated test compound in a spray chamber. The test plants were inoculated by spraying them with a spore suspension 2 days after application. The inoculated test plants were incubated at 20° C and 95% rh and the percentage leaf area covered by disease was assessed when an appropriate level of disease appears on untreated check plants (5 to 7 days after application).

Compounds 3 and 7 according to the invention at 200 ppm inhibited 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 %.
Claims

1. A compound of formula (I)

\[
\text{(I)}
\]

wherein
\( R^1 \) is methyl or ethyl;
\( R^2 \) is H or chloro;
\( R^3 \) is fluoro or chloro;
\( R^4 \) is fluoro or methoxy; and

\( R^5 \) is chloro or methoxy.

or an agrochemically usable salt form thereof.

2. A compound according to claim 1 wherein
\( R^1 \) is methyl;
\( R^2 \) is H;
\( R^3 \) is fluoro;
\( R^4 \) is fluoro or methoxy; and
\( R^5 \) is chloro.

3. A compound according to claim 1 selected from
3-chloro-5-(6-chloroethynyl-pyridin-3-yl)-4-(2,6-difluoro-4-methoxy-phenyl)-6-methyl-pyridazine;
3-chloro-5-(6-chloroethynyl-pyridin-3-yl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-5-(6-ethynyl-pyridin-3-yl)-6-methyl-4-(2,4,6-trifluoro-phenyl)-pyridazine;
3-chloro-4-(2,6-difluoro-4-methoxy-phenyl)-5-(6-ethynyl-pyridin-3-yl)-6-methyl-pyridazine;
4-(2,6-difluoro-4-methoxy-phenyl)-5-(6-ethynyl-pyridin-3-yl)-3-methoxy-6-methyl-pyridazine; and
4-(6-ethynyl-pyridin-3-yl)-6-methoxy-3-methyl-5-(2,4,6-trifluoro-phenyl)-pyridazine.
4. A fungicidal composition for controlling or protecting against phytopathogenic microorganisms, comprising as active ingredient at least one compound as defined in any one of claims 1 to 3, in free form or in agrochemically usable salt form, and at least one adjuvant.

5. A composition according to claim 4 which further comprises at least one additional fungicidally active compound, preferably selected from the group consisting of azoles, pyrimidinyl carbinoles, 2-amino-pyrimidines, morpholines, anilinopyrimidines, pyrroles, phenylamides, benzimidazoles, dicarboximides, carboxamides, strobilurines, dithiocarbamates, N-halomethylthiotetrahydrophthalimides, copper-compounds, nitrophenols, organo-phosphorus-derivatives, pyridazines, triazolopyrimidines, carboxamides and benzamides.

6. Use of a compound as defined in any one of claims 1 to 3 for controlling or preventing infestation of plants, harvested food crops, seeds or non-living materials by phytopathogenic microorganisms.

7. 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 as defined in any one of claims 1 to 3, 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.

8. A method according to claim 7 wherein the control is via curative application.

9. A method according to either claim 7 or claim 8 wherein the pathogenic microorganism is a fungal organism.

10. A method according to any one of claims 7 to 9 wherein the fungal organism is selected from Alternaria solani, Botryotinia fuckeliana, Erysiphe necator, Magnaporthe grisea, Mycosphaerella graminicola, Puccinia recondite and Pyrenophora teres.

11. A method according to claim 10 wherein the fungal organism is Mycosphaerella graminicola.
12. A process for the preparation of a compound of formula (1.1) which comprises reacting a compound of formula (1.3) with phosphorous oxychloride or thionyl chloride; wherein the compound of formula (1.3) is optionally prepared by reacting a compound of formula (II) with a hydrazine derivative; wherein the compound of formula (II) is optionally prepared by reacting a compound of formula (III)
with oxygen, air, or 3-chloroperbenzoic acid; wherein the compound of formula (III) is optionally prepared by reacting a compound of formula (IV) with a base; wherein $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in claim 1.

13. A compound selected from (I.3), (II), (III) and (IV)

wherein $R^1$, $R^2$, $R^3$ and $R^4$ are as defined in claim 1.
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/EP2011/051338

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