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(54) Title: 5-HETEROARYLIMINO-1,2,3-DITHIAZOLES

(57) Abstract: The present invention relates to the use of novel and of known 5 -heteroarylimino- 1,2,3 -dithiazoles for controlling phytopathogenic fungi, and to methods of controlling phytopathogemc fungi in plant protection, and to plant protection compositions comprising these dithiazoles.

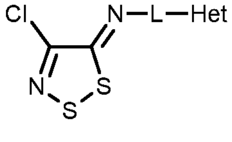
5-Heteroarylimino-1,2,3-dithiazoles

The present invention relates to the use of novel and of known 5-heteroarylimino-1,2,3-dithiazoles for controlling phytopathogenic fungi, and to methods of controlling phytopathogenic fungi in plant protection, and to plant protection compositions comprising these dithiazoles.

The 5-heteroarylimino-1,2,3-dithiazoles per se are already known and that at least some of these 5-heteroarylimino-1,2,3-dithiazoles can be used as antimycotics or antibacterial compounds (cf. *Bioorg. Med. Chem.* **2002**, *10*, 449-456; *J. Chem. Soc., Perkin Trans. 1* **1997**, 201-205; *Tetrahedron* **1998**, *54*, 9639-9650; US 2009/0163545 A). Furthermore, it is known that certain 5-heteroarylimino-1,2,3-dithiazoles are useful intermediates of plant protecting compounds [cf. DD-212387 (A3)]. Moreover, many 5-arylimino-1,2,3-dithiazoles with different activity are known (cf. US 5,688,744; DE-A 28 48 221; EP-A 0 771 527; *Bioorg. Med. Chem. Lett.* **1996**, *6*, 529-532; *Bioorg. Med. Chem. Lett.* **1996**, *6*, 2343-2348; *Eur. J. Med. Chem.* **1998**, *33*, 149-153; *Pharm. Pharmacol. Commun.* **1998**, *4*, 39-42), some of them are useful as fungicides, ovicides, insecticides or herbicides (cf. US 4,119,722 and US 4,059,590).

Since the ecological and economical demands made on modern fungicides keep getting more and more stringent, for example as regards the spectrum of action, toxicity, selectivity, application rate, formation of residues and advantageous production, and since furthermore for example resistance problems may occur, there is a constant need to develop novel fungicides which meet the abovementioned demands better, at least in some areas.

It has now been found that 5-heteroarylimino-1,2,3-dithiazoles of the general formula (I)



(I)

in which

L represents a direct bond or C_1-C_2-alkanediyl,

Het represents an optionally substituted heteroaryl,

are highly suitable for controlling phytopathogenic fungi.

The 5-heteroarylimino-1,2,3-dithiazoles of the formula (I) according to the invention and, if appropriate, their salts are highly suitable for controlling phytopathogenic harmful fungi. The abovementioned compounds according to the invention show mainly a fungicidal activity and can be used not only in plant protection, in the domestic and hygiene fields, but also in the protection of materials.

Depending on the nature of the substituents defined above, the compounds of the formula (I) have acidic or basic properties and can form salts, if appropriate also inner salts or adducts, with inorganic or organic acids or with inorganic or organic bases or with metal ions. Suitable metal ions are in particular the ions of the elements of the second main group, in particular calcium and magnesium, of the third and fourth main group, in particular aluminum, tin and lead, and also of the first to eighth transition group, in particular chromium, manganese, iron, cobalt, nickel, copper, zinc and others. Particular preference is given to the metal ions of the elements of the fourth period. Here, the metals can be present in the various valencies they can assume.

If the compounds of the formula (I) carry hydroxyl groups, carboxyl groups or other groups which induce acidic properties, these compounds can be converted with bases into salts. Suitable bases are, for example, the hydroxides, carbonates and bicarbonates of the alkali metals and the alkaline earth metals, in particular those of sodium, potassium, magnesium and calcium, furthermore ammonia, primary, secondary and tertiary amines having C_1-C_4-alkyl radicals, mono-, di- and trialkanolamines of C_1-C_4-alkanols, choline and also chlorocholine.

If the compounds of the formula (I) carry amino groups, alkylamino groups or other groups which induce basic properties, these compounds can be converted with acids into salts. Examples of inorganic acids are hydrohalic acids, such as hydrofluoric acid, hydrochloric acid, hydrobromic acid and hydroiodic acid, sulphuric acid, phosphoric acid and nitric acid, and acidic salts, such as $NaHSO_4$ and $KHSO_4$. Suitable organic acids are, for example, formic acid, carbonic acid and alkanoic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid and propionic acid, and also glycolic acid, thiocyanic acid, lactic acid, succinic acid, citric acid, benzoic acid, cinnamic acid, oxalic acid, alkylsulphonic acids (sulphonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbon atoms), arylsulphonic acids or -disulphonic acids (aromatic radicals, such as phenyl and naphthyl which carry one or two sulphonic acid groups), alkylphosphonic acids (phosphonic acids having straight-chain or branched alkyl radicals of 1 to 20 carbon atoms), arylphosphonic acids or -diphosphonic acids (aromatic radicals, such as phenyl and naphthyl, which carry one or two phosphonic acid radicals, where the alkyl radicals and aryl radicals may carry further substituents, for example p-toluenesulphonic acid, salicylic acid, p-aminosalicylic acid, 2-phenoxybenzoic acid, 2-acetoxybenzoic acid, etc.

The salts which can be obtained in this manner also have fungicidal properties.

The 5-heteroarylimino-1,2,3-dithiazoles which can be used according to the invention can, if appropriate, be present as mixtures of various possible isomeric forms, in particular of stereoisomers, such as, for example, E and Z, threo and erythro, and also optical isomers, and, if appropriate, also of tautomers. What is claimed are both the E and the Z isomers and the threo and erythro and also the optical isomers, any mixtures of these isomers, and also the possible tautomeric forms.

The formula (I) provides a general definition of the 5-heteroarylimino-1,2,3-dithiazoles which can be used according to the invention. Preferred radical definitions of the formulae given above and below are indicated below. These definitions apply both to the end products of the formula (I) and likewise to all intermediates.

L preferably represents a direct bond.
L furthermore preferably represents $-CH_2-$, $-(CH_2)_2-$ or $-CH(CH_3)-$.
L particularly preferably represents a direct bond.

Het preferably represents a five- or six-membered heteroaryl selected from the group consisting of furyl, thienyl, pyrrolyl, pyrazolyl, imidazolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, triazolyl, tetrazolyl, oxadiazolyl, thiadiazolyl, pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl and triazinyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z, whereby

Z represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy.

Het particularly preferably represents a five- or six-membered heteroaryl selected from the group consisting of 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 1-pyrrolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 1-pyrazolyl, 1H-imidazol-2-yl, 1H-imidazol-4-yl, 1H-imidazol-5-yl, 1H-imidazol-1-yl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 1H-1,2,3-triazol-1-yl, 1H-1,2,3-triazol-4-yl, 1H-1,2,3-triazol-5-yl, 2H-1,2,3-triazol-2-yl, 2H-1,2,3-triazol-4-yl, 1H-1,2,4-triazol-3-yl, 1H-1,2,4-triazol-5-yl, 1H-1,2,4-triazol-1-yl, 4H-1,2,4-triazol-3-yl, 4H-1,2,4-triazol-4-yl, 1H-tetrazol-1-yl, 1H-tetrazol-5-yl, 2H-tetrazol-2-yl, 2H-tetrazol-5-yl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,3-oxadiazol-4-yl, 1,2,3-oxadiazol-5-yl, 1,2,3-thiadiazol-4-yl, 1,2,3-thiadiazol-5-yl, 1,2,5-oxadiazol-3-yl, 1,2,5-thiadiazol-3-yl, 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl, 1,2,4-triazin-3-yl, 1,2,4-triazin-5-yl, 1,2,4-triazin-6-yl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z, whereby

Z represents halogen, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-, i-, s- or t-butoxy, methylsulfanyl, ethylsulfanyl, n-propylsulfanyl, isopropylsulfanyl, n-, i-, s- or t-butylsulfanyl, methylsulfinyl, ethylsulfinyl, methylsulfonyl, ethylsulfonyl, trifluoromethyl, trichloromethyl, difluoromethyl, dichloromethyl, difluorochloromethyl, fluorodichloromethyl, pentafluoroethyl, trifluoromethoxy, trichloromethoxy, difluoromethoxy, dichloromethoxy, pentafluoroethoxy, trifluoromethylsulfanyl, trichloromethylsulfanyl, difluoromethylsulfanyl, dichloromethylsulfanyl, pentafluoroethylsulfanyl, trifluoromethylsulfonyl, methylcarbonyl, ethylcarbonyl, methoxycarbonyl, ethoxycarbonyl, C_3-C_6-cycloalkyl, (C_3-C_6-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy.

Het very particularly preferably represents a five- or six-membered heteroaryl selected from the group consisting of 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 3-pyrazolyl, 1H-imidazol-2-yl, 2-oxazolyl, 2-thiazolyl, 3-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 5-isothiazolyl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,5-oxadiazol-3-yl, 1,2,5-thiadiazol-3-yl, 2-pyridinyl, 3-pyridinyl, 3-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z, whereby

Z represents fluorine, chlorine, bromine, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, methylsulfanyl, ethylsulfanyl, methylsulfonyl, trifluoromethyl, trifluoromethoxy, trifluoromethylsulfanyl, methoxycarbonyl, ethoxycarbonyl, cyclopentyl, cyclohexyl, cyclopentylmethyl, 1-cyclopentylethyl, cyclohexylmethyl, 1-cyclohexylethyl, or represents phenyl, which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by fluorine, chlorine, bromine, methyl, ethyl, n-propyl, isopropyl, n-, i-, s- or t-butyl, methoxy, trifluoromethyl, trifluoromethoxy.

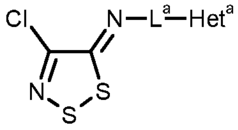
However, the general or preferred radical definitions or illustrations given above can also be combined with one another as desired, i.e. including combinations between respective ranges and preferred ranges. They apply both to the end products and, correspondingly, to precursors and intermediates. Moreover, individual definitions may not apply.

Preference is given to using those compounds of the formula (I) in which all radicals each have the meanings mentioned above as being preferred.

Particular preference is given to using those compounds of the formula (I) in which all radicals each have the meanings mentioned above as being particularly preferred.

Very particular preference is given to using those compounds of the formula (I) in which all radicals each have the meanings mentioned above as being very particularly preferred.

Novel 5-heteroarylimino-1,2,3-dithiazoles are those of the formula (I-a)



(I-a)

in which

L^a represents a direct bond or C_1-C_2-alkanediyl, Het^a represents a five- or six-membered heteroaryl selected from the group consisting of 2-furyl, 3-furyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 1-pyrrolyl, 4-pyrazolyl, 1-pyrazolyl, 1H-imidazol-2-yl, 1H-imidazol-1-yl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 1H-1,2,3-triazol-1-yl, 2H-1,2,3-triazol-2-yl, 2H-1,2,3-triazol-4-yl, 1H-1,2,4-triazol-3-yl, 1H-1,2,4-triazol-5-yl, 1H-1,2,4-triazol-1-yl, 4H-1,2,4-triazol-3-yl, 4H-1,2,4-triazol-4-yl, 1H-tetrazol-1-yl, 1H-tetrazol-5-yl, 2H-tetrazol-2-yl, 2H-tetrazol-5-yl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,3-oxadiazol-4-yl, 1,2,3-oxadiazol-5-yl, 1,2,3-thiadiazol-4-yl, 1,2,3-thiadiazol-5-yl, 1,2,5-oxadiazol-3-yl, 1,2,5-thiadiazol-3-yl, 3-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl, 1,2,4-triazin-3-yl, 1,2,4-triazin-5-yl, 1,2,4-triazin-6-yl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^a, whereby

Z^a represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^a – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a represents a five-membered heteroaryl selected from the group consisting of 5-pyrazolyl, 1H-imidazol-4-yl, 1H-imidazol-5-yl, 1H-1,2,3-triazol-4-yl and 1H-1,2,3-triazol-5-yl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^b, whereby

Z^b represents halogen, nitro, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^b – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a represents a five-membered heteroaryl selected from the group consisting of 2-thienyl and 3-pyrazolyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical

Z^c, whereby

Z^c represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^c – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a represents 2-pyridinyl, which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^d, whereby

Z^d represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^d – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

with the proviso that the 2-pyridinyl is either not unsubstituted or is not substituted by methyl or is not substituted by 5-chlorine or 5-bromine;

or

Het^a represents 4-pyridinyl, which is identically or differently monosubstituted or polysubstituted by the radical Z^e, whereby

Z^e represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^e – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy.

L^a preferably represents a direct bond.

L^a furthermore preferably represents -CH_2-, -$(CH_2)_2$- or -$CH(CH_3)$-.

L^a particularly preferably represents a direct bond.

Het^a preferably represents a five- or six-membered heteroaryl selected from the group consisting of 2-furyl, 3-furyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 1-pyrrolyl, 4-pyrazolyl, 1-pyrazolyl, 1H-imidazol-2-yl, 1H-imidazol-1-yl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 1H-1,2,3-triazol-1-yl, 2H-1,2,3-triazol-2-yl, 2H-1,2,3-triazol-4-yl, 1H-1,2,4-triazol-3-yl, 1H-1,2,4-triazol-5-yl, 1H-1,2,4-triazol-1-yl, 4H-1,2,4-triazol-3-yl, 4H-1,2,4-triazol-4-yl, 1H-tetrazol-1-yl, 1H-tetrazol-5-yl, 2H-tetrazol-2-yl, 2H-tetrazol-5-yl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,3-oxadiazol-4-yl, 1,2,3-oxadiazol-5-yl, 1,2,3-thiadiazol-4-yl, 1,2,3-thiadiazol-5-yl, 1,2,5-oxadiazol-3-yl, 1,2,5-thiadiazol-3-yl, 3-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl, 1,2,4-triazin-3-yl, 1,2,4-triazin-5-yl, 1,2,4-triazin-6-yl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^a, whereby

Z^a represents halogen, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-, i-, s- or t-butoxy, methylsulfanyl, ethylsulfanyl, n-propylsulfanyl, isopropylsulfanyl, n-, i-, s- or t-butylsulfanyl, methylsulfinyl, ethylsulfinyl, methylsulfonyl, ethylsulfonyl, trifluoromethyl, trichloromethyl, difluoromethyl, dichloromethyl, difluorochloromethyl, fluorodichloromethyl, pentafluoroethyl, trifluoromethoxy, trichloromethoxy, difluoromethoxy, dichloromethoxy, pentafluoroethoxy, trifluoromethylsulfanyl, trichloromethylsulfanyl, difluoromethylsulfanyl, dichloromethylsulfanyl, pentafluoroethylsulfanyl, trifluoromethylsulfonyl, methylcarbonyl, ethylcarbonyl, methoxycarbonyl, ethoxycarbonyl, C_3-C_6-cycloalkyl, (C_3-C_6-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^a – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a preferably represents a five-membered heteroaryl selected from the group consisting of 5-pyrazolyl, 1H-imidazol-4-yl, 1H-imidazol-5-yl, 1H-1,2,3-triazol-4-yl and 1H-1,2,3-triazol-5-yl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^b, whereby

Z^b represents halogen, nitro, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-, i-, s- or t-butoxy, methylsulfanyl, ethylsulfanyl, n-propylsulfanyl, isopropylsulfanyl, n-, i-, s- or t-butylsulfanyl, methylsulfinyl, ethylsulfinyl, methylsulfonyl, ethylsulfonyl, trifluoromethyl, trichloromethyl, difluoromethyl, dichloromethyl, difluorochloromethyl, fluorodichloromethyl, pentafluoroethyl, trifluoromethoxy, trichloromethoxy, difluoromethoxy, dichloromethoxy, pentafluoroethoxy, trifluoromethylsulfanyl, trichloromethylsulfanyl, difluoromethylsulfanyl, dichloromethylsulfanyl, pentafluoroethylsulfanyl, trifluoromethylsulfonyl, methylcarbonyl, ethylcarbonyl, methoxycarbonyl, ethoxycarbonyl, C_3-C_6-cycloalkyl, (C_3-C_6-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^b – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a preferably represents a five-membered heteroaryl selected from the group consisting of 2-thienyl and 3-pyrazolyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^c, whereby

Z^c represents halogen, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-, i-, s- or t-butoxy, methylsulfanyl, ethylsulfanyl, n-propylsulfanyl, isopropylsulfanyl, n-, i-, s- or t-butylsulfanyl, methylsulfinyl, ethylsulfinyl, methylsulfonyl, ethylsulfonyl, trifluoromethyl, trichloromethyl, difluoromethyl, dichloromethyl, difluorochloromethyl, fluorodichloromethyl, pentafluoroethyl, trifluoromethoxy, trichloromethoxy, difluoromethoxy, dichloromethoxy, pentafluoroethoxy, trifluoromethylsulfanyl, trichloromethylsulfanyl, difluoromethylsulfanyl, dichloromethylsulfanyl, pentafluoroethylsulfanyl, trifluoromethylsulfonyl, methylcarbonyl, ethylcarbonyl, C_3-C_6-cycloalkyl, (C_3-C_6-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^c – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a preferably represents 2-pyridinyl, which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^d, whereby

Z^d represents halogen, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-, i-, s- or t-butoxy, methylsulfanyl, ethylsulfanyl, n-propylsulfanyl, isopropylsulfanyl, n-, i-, s- or t-butylsulfanyl, methylsulfinyl, ethylsulfinyl, methylsulfonyl, ethylsulfonyl, trifluoromethyl, trichloromethyl, difluoromethyl, dichloromethyl, difluorochloromethyl, fluorodichloromethyl, pentafluoroethyl, trifluoromethoxy, trichloromethoxy, difluoromethoxy, dichloromethoxy, pentafluoroethoxy, trifluoromethylsulfanyl, trichloromethylsulfanyl, difluoromethylsulfanyl, dichloromethylsulfanyl, pentafluoroethylsulfanyl, trifluoromethylsulfonyl, methylcarbonyl, ethylcarbonyl, methoxycarbonyl, ethoxycarbonyl, C_3-C_6-cycloalkyl, (C_3-C_6-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^d – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

with the proviso that the 2-pyridinyl is either not unsubstituted or is not substituted by methyl or is not substituted by 5-chlorine or 5-bromine;

or

Het^a preferably represents 4-pyridinyl, which is identically or differently monosubstituted or polysubstituted by the radical Z^e, whereby

Z^e represents halogen, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-, i-, s- or t-butoxy, methylsulfanyl, ethylsulfanyl, n-propylsulfanyl, isopropylsulfanyl, n-, i-, s- or t-butylsulfanyl, methylsulfinyl, ethylsulfinyl, methylsulfonyl, ethylsulfonyl, trifluoromethyl, trichloromethyl, difluoromethyl, dichloromethyl, difluorochloromethyl, fluorodichloromethyl, pentafluoroethyl, trifluoromethoxy, trichloromethoxy, difluoromethoxy, dichloromethoxy, pentafluoroethoxy, trifluoromethylsulfanyl, trichloromethylsulfanyl, difluoromethylsulfanyl, dichloromethylsulfanyl, pentafluoroethylsulfanyl, trifluoromethylsulfonyl, methylcarbonyl, ethylcarbonyl, methoxycarbonyl, ethoxycarbonyl, C_3-C_6-cycloalkyl, (C_3-C_6-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^e – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy.

Het^a particularly preferably represents a five- or six-membered heteroaryl selected from the group consisting of 2-furyl, 3-furyl, 3-thienyl, 1H-imidazol-2-yl, 2-oxazolyl, 2-thiazolyl, 3-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 5-isothiazolyl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,5-oxadiazol-3-yl, 1,2,5-thiadiazol-3-yl, 3-pyridinyl, 3-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^a, whereby

Z^a represents fluorine, chlorine, bromine, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, methylsulfanyl, ethylsulfanyl, methylsulfonyl, trifluoromethyl, trifluoromethoxy, trifluoromethylsulfanyl, methoxycarbonyl, ethoxycarbonyl, cyclopentyl, cyclohexyl, cyclopentylmethyl, 1-cyclopentylethyl, cyclohexylmethyl, 1-cyclohexylethyl, or represents phenyl, which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^a – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a particularly preferably represents a five-membered heteroaryl selected from the group consisting of 2-thienyl and 3-pyrazolyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^c, whereby

Z^c represents fluorine, chlorine, bromine, nitro, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, methylsulfanyl, ethylsulfanyl, methylsulfonyl, trifluoromethyl, trifluoromethoxy, trifluoromethylsulfanyl, methoxycarbonyl, ethoxycarbonyl, cyclopentyl, cyclohexyl, cyclopentylmethyl, 1-cyclopentylethyl, cyclohexylmethyl, 1-cyclohexylethyl, or represents phenyl, which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^c – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

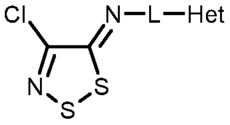
Het^a particularly preferably represents 2-pyridinyl, which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^d, whereby

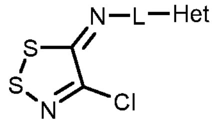
Z^d represents fluorine, chlorine, bromine, nitro, cyano, methyl, ethyl, n-propyl, isopropyl, n-, i-, s-, t-butyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, methoxy, ethoxy, methylsulfanyl, ethylsulfanyl, methylsulfonyl, trifluoromethyl, trifluoromethoxy, trifluoromethylsulfanyl, methoxycarbonyl, ethoxycarbonyl, cyclopentyl, cyclohexyl, cyclopentylmethyl, 1-cyclopentylethyl, cyclohexylmethyl, 1-cyclohexylethyl, or represents phenyl, which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

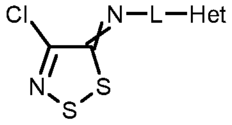
or two vicinal substituents Z^d – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

with the proviso that the 2-pyridinyl is either not unsubstituted or is not substituted by methyl or is not substituted by 5-chlorine or 5-bromine.

The compounds of the formula (I) may exist in two different tautomeric forms relative to the imino double bond. The crossed double bond means that either tautomeric form may exist. Nevertheless, for simplicity in each case only one tautomeric form is drawn. If a single tautomeric form is present only, then an additional indicator, e.g. *cis* or *trans* or *E* or *Z*, is used.







According to the invention, the following generic terms are generally used with the following meanings:

Halogen: (also in combinations such as halogenoalkyl, halogenoalkoxy etc.) fluorine, chlorine, bromine and iodine;

Alkyl: (also in combinations such as alkylsulfanyl, alkoxy etc.) saturated straight-chain or branched hydrocarbon radicals having 1 to 8 carbon atoms, for example C_1-C_6-alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, hexyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl; heptyl, octyl.

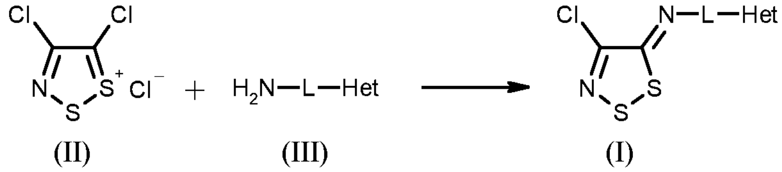
Halogenoalkyl: (also in combinations such as halogenoalkylsulfanyl, halogenalkoxy etc.) straight-chain or branched alkyl groups having 1 to 8 carbon atoms (as mentioned above), where in these groups some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above, for example C_1-C_3-haloalkyl, such as chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl and 1,1,1-trifluoroprop-2-yl.

Cycloalkyl: monocyclic saturated hydrocarbon groups having 3 to 7 carbon ring members, such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl and cycloheptyl.

Illustration of processes of preparation and intermediates

The 5-heteroarylimino-1,2,3-dithiazoles of formula (I) can be obtained in a known manner (cf. *Bioorg. Med. Chem.* **2002**, *10*, 449-456; *J. Chem. Soc., Perkin Trans. 1* **1997**, 201-205). The general process for their preparation is shown in the following scheme, wherein the radicals have the meanings given above.

Scheme 1



4,5-Dichloro-1,2,3-dithiazolium chloride of formula (II) (also known as Appel's salt) and the amines of formula (III) are known.

The process according to the invention may be carried out in a solvent (e.g. CH_2Cl_2, tetrahydrofurane, acetonitrile) and in the presence of a base (e.g. pyridine, lutidine, triethylamine, diisopropylethylamine).

The process according to the invention is generally carried out at temperatures of between 0°C and room temperature.

When carrying out the process according to the invention, generally 1 mol or an excess of the amine of formula (III) and from 1 to 3 mol of acid binder (generally 2 mol of acid binder, 3 mol in case of amine salts) are employed per mole of Appel's salt of formula (II). It is also possible to employ the reaction components in other ratios.

The present invention furthermore relates to a plant protection composition for combating/controlling undesired microorganism, in particular phytopathogenic fungi, comprising at least one 5-heteroarylimino-1,2,3-dithiazole of the formula (I). Preferably, the compositions are fungicidal compositions comprising agriculturally suitable auxiliaries, adjuvants, solvents, carriers, surfactants or extenders.

Furthermore the invention relates to a method of combating undesirable microorganisms, characterized in that the compounds according to the invention are applied to the phytopathogenic fungi and/or their habitat.

According to the invention, carrier is to be understood as meaning a natural or synthetic, organic or inorganic substance which is mixed or combined with the active substances for better applicability, in particular for application to plants or plant parts or seeds. The carrier, which may be solid or liquid, is generally inert and should be suitable for use in agriculture.

Suitable solid or liquid carriers are: for example ammonium salts and natural ground minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as finely divided silica, alumina and natural or synthetic silicates, resins, waxes, solid fertilizers, water, alcohols, especially butanol, organic solvents, mineral oils and vegetable oils, and also derivatives thereof. It is also possible to use mixtures of such carriers. Solid carriers suitable for granules are: for example crushed and fractionated natural minerals, such as calcite, marble, pumice, sepiolite, dolomite, and also synthetic granules of inorganic and organic meals and also granules of organic material, such as sawdust, coconut shells, maize cobs and tobacco stalks.

Suitable liquefied gaseous extenders or carriers are liquids which are gaseous at ambient temperture and under atmospheric pressure, for example aerosol propellants, such as halocarbons, and also butane, propane, nitrogen and carbon dioxide.

Tackifiers, such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules and latices, such as gum arabic, polyvinyl alcohol, polyvinyl acetate, or else natural phospholipids, such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other possible additives are mineral and vegetable oils.

If the extender used is water, it is also possible, for example, to use organic solvents as auxiliary solvents. Suitable liquid solvents are essentially: aromatic compounds, such as xylene, toluene or alkylnaphthalenes, chlorinated aromatic compounds or chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols, such as butanol or glycol, and also ethers and esters thereof, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and also water.

The compositions according to the invention may comprise additional further components, such as, for example, surface-active substances. Suitable surface-active substances are emulsifiers and/or foam formers, dispersants or wetting agents having ionic or nonionic properties, or mixtures of these surface-active substances. Examples of these are salts of polyacrylic acid, salts of lignosulphonic acid, salts of phenolsulphonic acid or naphthalenesulphonic acid, polycondensates of ethylene oxide with fatty alcohols or with fatty acids or with fatty amines, substituted phenols (preferably alkylphenols or arylphenols), salts of sulphosuccinic esters, taurine derivatives (preferably alkyl taurates), phosphoric esters of polyethoxylated alcohols or phenols, fatty esters of polyols, and derivatives of the compounds containing sulphates, sulphonates and phosphates, for example, alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates, protein hydrolysates, lignin-sulphite waste liquors and methylcellulose. The presence of a surface-active substance is required if one of the active substances and/or one of the inert carriers is insoluble in water and when the application takes place in water. The proportion of surface-active substances is between 5 and 40 per cent by weight of the composition according to the invention.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide, Prussian blue, and organic dyes, such as alizarin dyes, azo dyes and metal phthalocyanine dyes, and trace nutrients, such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

If appropriate, other additional components may also be present, for example protective colloids, binders, adhesives, thickeners, thixotropic substances, penetrants, stabilizers, sequestring agents, complex formers. In general, the active substances can be combined with any solid or liquid additive customarily used for formulation purposes.

In general, the formulations contain between 0.05 and 99% by weight, 0.01 and 98% by weight, preferably between 0.1 and 95% by weight, especially preferably between 0.5 and 90% by weight of active substance, very especially preferably between 10 and 70 per cent by weight.

The active substances or compositions according to the invention can be used as such or, depending on their respective physical and/or chemical properties, in the form of their formulations or the use forms prepared therefrom, such as aerosols, capsule suspensions, cold-fogging concentrates, warm-fogging concentrates, encapsulated granules, fine granules, flowable concentrates for the treatment of seed, ready-to-use solutions, dustable powders, emulsifiable concentrates, oil-in-water emulsions, water-in-oil emulsions, macrogranules, microgranules, oil-dispersible powders, oil-miscible flowable concentrates, oil-miscible liquids, foams, pastes, pesticide-coated seed, suspension concentrates, suspoemulsion concentrates, soluble concentrates, suspensions, wettable powders, soluble powders, dusts and granules, water-soluble granules or tablets, water-soluble powders for the treatment of seed, wettable powders, natural products and synthetic substances impregnated with active substance, and also microencapsulations in polymeric substances and in coating materials for seed, and also ULV cold-fogging and warm-fogging formulations.

The formulations mentioned can be prepared in a manner known per se, for example by mixing the active substances with at least one customary extender, solvent or diluent, emulsifier, dispersant and/or binder or fixing agent, wetting agent, water repellant, if appropriate siccatives and UV stabilizers and, if appropriate, dyes and pigments, defoamers, preservatives, secondary thickeners, adhesives, gibberellins and also further processing auxiliaries.

The compositions according to the invention do not only comprise ready-to-use compositions which can be applied with suitable apparatus to the plant or the seed, but also commercial concentrates which have to be diluted with water prior to use.

The active substances according to the invention, per se or in their (commercially available) formulations and in the use forms prepared from these formulations, may be present in a mixture with other (known) active substances such as insecticides, attractants, sterilants, bactericides, acaricides, nematicides, fungicides, growth regulators, herbicides, fertilisers, safeners or semiochemicals.

The treatment according to the invention of the plants and plant parts with the active substances or compositions is carried out directly or by action on their surroundings, habitat or storage space using customary treatment methods, for example by dipping, spraying, atomizing, irrigating, evaporating, dusting, fogging, broadcasting, foaming, painting, spreading-on, drenching, drip irrigating and, in the case of propagation material, in particular in the case of seeds, furthermore by dry seed treatment, by wet seed treatment, by slurry treatment, by incrusting, by coating with one or more coats, etc. It is furthermore possible to apply the active substances by the ultra-low-volume method, or to inject the active substance preparation, or the active substance itself, into the soil.

The invention furthermore comprises a method for the treatment of seed.

The invention furthermore relates to seed which has been treated in accordance with one of the methods described in the previous paragraph. The seeds according to the invention are used in methods for the protection of seed from undesirable fungi. Here, a seed treated with at least one active substance according to the invention is used.

The active substances or compositions according to the invention are also suitable for treating seed. A large part of the damage to crop plants caused by harmful organisms is triggered by the infection of the seed during storage or after sowing as well as during and after germination of the plant. This phase is particularly critical since the roots and shoots of the growing plant are particularly sensitive, and even just small damage may result in the death of the plant. Accordingly, there is great interest in protecting the seed and the germinating plant by using appropriate compositions.

The control of phytopathogenic fungi by treating the seed of plants has been known for a long time and is the subject of continuous improvements. However, the treatment of seed entails a series of problems which cannot always be solved in a satisfactory manner. Thus, it is desirable to develop methods for protecting the seed and the germinating plant which dispense with the additional application of plant protection compositions after sowing or after the emergence of the plants or which at least considerably reduce additional application. It is furthermore desirable to optimize the amount of active substance employed in such a way as to provide maximum protection for the seed and the germinating plant from attack by phytopathogenic fungi, but without damaging the plant itself by the active substance employed. In particular, methods for the treatment of seed should also take into consideration the intrinsic fungicidal properties of transgenic plants in order to achieve optimum protection of the seed and the germinating plant with a minimum of plant protection compositions being employed.

Accordingly, the present invention also relates to a method for protecting seed and germinating plants against attack by phytopathogenic fungi by treating the seed with a composition according to the invention. The invention also relates to the use of the compositions according to the invention for treating seed for protecting the seed and the germinating plant against phytopathogenic fungi. Furthermore, the invention relates to seed treated with a composition according to the invention for protection against phytopathogenic fungi.

The control of phytopathogenic fungi which damage plants post-emergence is carried out primarily by treating the soil and the above-ground parts of plants with plant protection compositions. Owing to the concerns regarding a possible impact of the plant protection compositions on the environment and the health of humans and animals, there are efforts to reduce the amount of active substances applied.

One of the advantages of the present invention is that, because of the particular systemic properties of the active substances or compositions according to the invention, treatment of the seed with these active substances or compositions not only protects the seed itself, but also the resulting plants after emergence, from phytopathogenic fungi. In this manner, the immediate treatment of the crop at the time of sowing or shortly thereafter can be dispensed with.

It is also considered to be advantageous that the active substances or compositions according to the invention can be used in particular also for transgenic seed where the plant growing from this seed is capable of expressing a protein which acts against pests. By treating such seed with the active substances or compositions according to the invention, even by the expression of the, for example, insecticidal protein, certain pests may be controlled. Surprisingly, a further synergistic effect may be observed here, which additionally increases the effectiveness of the protection against attack by pests.

The compositions according to the invention are suitable for protecting seed of any plant variety employed in agriculture, in the greenhouse, in forests or in horticulture and viticulture. In particular, this takes the form of seed of cereals (such as wheat, barley, rye, triticale, sorghum/millet and oats), maize, cotton, soya beans, rice, potatoes, sunflower, bean, coffee, beet (for example sugar beet and fodder beet), peanut, oilseed rape, poppy, olive, coconut, cacao, sugar cane, tobacco, vegetables (such as tomato, cucumbers, onions and lettuce), turf and ornamentals (see also hereinbelow). Of particular importance is the treatment of the seed of cereals (such as wheat, barley, rye, triticale and oats), maize and rice.

As also described hereinbelow, the treatment of transgenic seed with the active substances or compositions according to the invention is of particular importance. This refers to the seed of plants containing at least one heterologous gene which allows the expression of a polypeptide or protein having insecticidal properties. The heterologous gene in transgenic seed can originate, for example, from microorganisms of the species Bacillus, Rhizobium, Pseudomonas, Serratia, Trichoderma, Clavibacter, Glomus or Gliocladium. Preferably, this heterologous gene is from Bacillus sp., the gene product having activity against the European corn borer and/or the Western corn rootworm. Particularly preferably, the heterologous gene originates from Bacillus thuringiensis.

In the context of the present invention, the composition according to the invention is applied on its own or in a suitable formulation to the seed. Preferably, the seed is treated in a state in which it is sufficiently stable so that the treatment does not cause any damage. In general, treatment of the seed may take place at any point in time between harvesting and sowing. Usually, the seed used has been separated from the plant and freed from cobs, shells, stalks, coats, hairs or the flesh of the fruits. Thus, it is possible to use, for example, seed which has been harvested, cleaned and dried to a moisture content of less than 15% by weight. Alternatively, it is also possible to use seed which, after drying, has been treated, for example, with water and then dried again.

When treating the seed, care must generally be taken that the amount of the composition according to the invention applied to the seed and/or the amount of further additives is chosen in such a way that the germination of the seed is not adversely affected, or that the resulting plant is not damaged. This must be borne in mind in particular in the case of active substances which may have phytotoxic effects at certain application rates.

The compositions according to the invention can be applied directly, that is to say without comprising further components and without having been diluted. In general, it is preferable to apply the compositions to the seed in the form of a suitable formulation. Suitable formulations and methods for the treatment of seed are known to the person skilled in the art and are described, for example, in the following documents: US 4,272,417 A, US 4,245,432 A , U S 4,808,430 A, US 5,876,739 A, US 2003/0176428 A1, WO 2002/080675 A1, WO 2002/028186 A2.

The active substances which can be used according to the invention can be converted into the customary seed-dressing product formulations such as solutions, emulsions, suspensions, powders, foams, slurries and other coating compositions for seed, and ULV formulations.

These formulations are prepared in the known manner by mixing the active substances with customary additives such as, for example, customary extenders and also solvents or diluents, colorants, wetters, dispersants, emulsifiers, antifoams, preservatives, secondary thickeners, adhesives, gibberellins, and also water.

Colorants which may be present in the seed-dressing product formulations which can be used according to the invention are all colorants which are customary for such purposes. Both pigments, which are sparingly soluble in water, and dyes, which are soluble in water, may be used. Examples of colorants which may be mentioned are those known by the names Rhodamin B, C.I. Pigment Red 112 and C.I. Solvent Red 1.

Wetters which may be present in the seed-dressing product formulations which can be used according to the invention are all substances which are conventionally used for the formulation of agrochemical active substances and for promoting wetting. Alkylnaphthalenesulphonates, such as diisopropyl- or diisobutylnaphthalenesulphonates, can preferably be used.

Suitable dispersants and/or emulsifiers which may be present in the seed-dressing product formulations which can be used in accordance with the invention are all non-ionic, anionic and cationic dispersants which are conventionally used for the formulation of agrochemical active substances. Non-ionic or anionic dispersants or mixtures of non-ionic or anionic dispersants can preferably be used. Suitable non-ionic dispersants which may be mentioned are, in particular, ethylene oxide/propylene oxide block polymers, alkylphenol polyglycol ethers and tristryrylphenol polyglycol ethers, and their phosphated or sulphated derivatives. Suitable anionic dispersants are, in particular, lignosulphonates, polyacrylic acid salts and arylsulphonate/formaldehyde condensates.

Antifoams which may be present in the seed-dressing product formulations which can be used according to the invention are all foam-suppressing substances conventionally used for the formulation of agrochemical active substances. Silicone antifoams and magnesium stearate can preferably be used.

Preservatives which may be present in the seed-dressing product formulations which can be used according to the invention are all substances which can be employed in agrochemical compositions for such purposes. Examples which may be mentioned are dichlorophene and benzyl alcohol hemiformal.

Secondary thickeners which may be present in the seed-dressing product formulations which can be used according to the invention are all substances which can be employed in agrochemical compositions for such purposes. Cellulose derivatives, acrylic acid derivatives, xanthan, modified clays and highly disperse silica are preferably suitable.

Adhesives which may be present in the seed-dressing product formulations which can be used according to the invention are all customary binders which can be employed in seed-dressing products. Polyvinylpyrrolidone, polyvinyl acetate, polyvinyl alcohol and tylose may be mentioned by preference.

Gibberellins which may be present in the seed-dressing product formulations which can be used according to the invention are preferably the gibberellins A1, A3 (= gibberellic acid), A4 and A7, with gibberellic acid being particularly preferably used. The gibberellins are known (cf. R. Wegler “Chemie der Pflanzenschutz- und

Schädlingsbekämpfungsmittel" [Chemistry of Plant Protectants and Pesticides], Vol. 2, Springer Verlag, 1970, pp. 401-412).

The seed-dressing product formulations which can be used in accordance with the invention can be employed either directly or after previous dilution with water for the treatment of a wide range of seeds, including the seed of transgenic plants. In this context, additional synergistic effects may also occur as a consequence of the interaction with the substances formed by expression.

Suitable apparatuses which can be employed for treating seed with the seed-dressing product formulations which can be used in accordance with the invention, or with the preparations prepared therefrom by addition of water, are all mixing apparatuses which can usually be employed for dressing seed. Specifically, a seed-dressing procedure is followed in which the seed is placed in a mixer, the amount of seed-dressing product formulation desired in each case is added, either as such or after previously diluting it with water, and the contents of the mixer are mixed until the formulation has been distributed uniformly on the seed. If appropriate, this is followed by a drying process.

The active substances or compositions according to the invention have a potent fungicidal activity and can be employed for controlling undesired fungi in plant protection and in the protection of materials.

In crop protection, fungicides can be used for controlling Plasmodiophoromycetes, Oomycetes, Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes.

In crop protection, bactericides can be used for controlling Pseudomonadaceae, Rhizobiaceae, Enterobacteriaceae, Corynebacteriaceae and Streptomycetaceae.

The fungicidal compositions according to the invention can be employed curatively or protectively for controlling phytopathogenic fungi. The invention therefore also relates to curative and protective methods of controlling phytopathogenic fungi by using the active substances or compositions according to the invention, which are applied to the seed, the plant or plant parts, the fruits or the soil in which the plants grow.

The compositions according to the invention for controlling phytopathogenic fungi in plant protection comprise an effective, but nonphytotoxic amount of the active substances according to the invention. "Effective, but nonphytotoxic amount" means such an amount of the composition according to the invention which suffices for sufficiently controlling or fully eradicating the fungal disease of the plant while simultaneously not entailing substantial phytotoxicity symptoms. In general, this application rate can vary within a substantial range. It depends on a plurality of factors, for example on the fungus to be controlled, the plant, the climatic conditions and the constituents of the compositions according to the invention.

The good plant tolerance of the active substances at the concentrations required for controlling plant diseases permits the treatment of aerial plant parts, of rigiditive propagation material and of seed, and of the soil.

All plants and plant parts can be treated in accordance with the invention. In the present context, plants are understood as meaning all plants and plant populations, such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be plants which can be obtained by traditional breeding and optimization methods or by biotechnological and recombinant methods, or combinations of these methods, including the transgenic plants and including the plant varieties capable or not of being protected by Plant Breeders' Rights. Plant parts are understood as meaning all aerial and subterranean parts and organs of the plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stalks, stems, flowers, fruiting bodies, fruits and seeds, and also roots, tubers and rhizomes. The plant parts also include crop material and vegetative and generative propagation material, for example cuttings, tubers, rhizomes, slips and seeds.

The active substances according to the invention are suitable for the protection of plants and plant organs, for increasing the yields, for improving the quality of the harvested crop, while being well tolerated by plants, having favourable toxicity to warm-blooded species and being environmentally friendly. They can preferably be employed as plant protection compositions. They are active against normally sensitive and resistant species and against all or individual developmental stages.

Plants which can be treated in accordance with the invention and which may be mentioned are the following: cotton, flax, grapevine, fruit, vegetables, such as *Rosaceae sp.* (for example pome fruits such as apples and pears, but also stone fruits such as apricots, cherries, almonds and peaches, and soft fruits such as strawberries), *Ribesioidae sp.*, *Juglandaceae sp.*, *Betulaceae sp.*, *Anacardiaceae sp.*, *Fagaceae sp.*, *Moraceae sp.*, *Oleaceae sp.*, *Actinidaceae sp.*, *Lauraceae sp.*, *Musaceae sp.* (for example banana plants and banana plantations), *Rubiaceae sp.* (for example coffee), *Theaceae sp.*, *Sterculiceae sp.*, *Rutaceae sp.* (for example lemons, oranges and grapefruit); *Solanaceae sp.* (for example tomatoes), *Liliaceae sp.*, *Asteraceae sp.* (for example lettuce), *Umbelliferae sp.*, *Cruciferae sp.*, *Chenopodiaceae sp.*, *Cucurbitaceae sp.* (for example cucumbers), *Alliaceae sp.* (for example leeks, onions), *Papilionaceae sp.* (for example peas); major crop plants such as *Gramineae sp.* (for example maize, turf, cereals such as wheat, rye, rice, barley, oats, sorghum, millet and triticale), *Poaceae sp.* (for example sugar cane), *Asteraceae sp.* (for example sunflower), *Brassicaceae sp.* (for example white cabbage, red cabbage, broccoli, cauliflower, Brussels sprouts, pak choi, kohlrabi, small radishes, and also oilseed rape, mustard, horseradish and cress), *Fabacae sp.* (for example beans, peanuts), *Papilionaceae sp.* (for example soya beans), *Solanaceae sp.* (for example potatoes), *Chenopodiaceae sp.* (for example sugar beet, fodder beet, swiss chard, beetroot); useful plants and ornamentals in gardens and forests; and in each case genetically modified types of these plants.

As has already been mentioned above, all plants and their parts may be treated in accordance with the invention. In a preferred embodiment, plant species and plant varieties, and their parts, which grow wild or which are obtained by traditional biological breeding methods such as hybridization or protoplast fusion are treated. In a further preferred embodiment, transgenic plants and plant varieties which have been obtained by recombinant methods, if appropriate in combination with traditional methods (genetically modified organisms), and their parts are treated. The term "parts" or "parts of plants" or "plant parts" has been explained hereinabove. Plants of the plant varieties which are in each case commercially available or in use are especially preferably treated in accordance with the invention. Plant varieties are understood as meaning plants with novel traits which have been bred both by traditional breeding, by mutagenesis or by recombinant DNA techniques. They may take the form of varieties, races, biotypes and genotypes.

The method of treatment according to the invention can be used in the treatment of genetically modified organisms (GMOs), e.g. plants or seeds. Genetically modified plants (or transgenic plants) are plants in which a heterologous gene has been stably integrated into the genome. The expression "heterologous gene" essentially means a gene which is provided or assembled outside the plant and when introduced in the nuclear, chloroplastic or mitochondrial genome gives the transformed plant new or improved agronomic or other properties by expressing a protein or polypeptide of interest or by downregulating or silencing other gene(s) which are present in the plant (using for example antisense technology, cosuppression technology or RNA interference - RNAi - technology). A heterologous gene that is located in the genome is also called a transgene. A transgene that is defined by its particular location in the plant genome is called a transformation or transgenic event.

Depending on the plant species or plant varieties, their location and growth conditions (soils, climate, vegetation period, diet), the treatment according to the invention may also result in superadditive ("synergistic") effects. Thus, for example, reduced application rates and/or a widening of the activity spectrum and/or an increase in the activity of the active substances and compositions which can be used according to the invention, better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, bigger fruits, larger plant height, greener leaf colour, earlier flowering, higher quality and/or a higher nutritional value of the harvested products, higher sugar concentration within the fruits, better storage stability and/or processability of the harvested products are possible, which exceed the effects which were actually to be expected.

At certain application rates, the active substance combinations according to the invention may also have a strengthening effect in plants. Accordingly, they are suitable for mobilizing the defence system of the plant against attack by unwanted phytopathogenic fungi and/or microorganisms and/or viruses. This may, if appropriate, be one of the reasons for the enhanced activity of the combinations according to the invention, for example against fungi. Plant-strengthening (resistance-inducing) substances are to be understood as meaning, in the present context, those substances or combinations of substances which are capable of stimulating the defence system of plants in such a way that, when subsequently inoculated with unwanted phytopathogenic fungi, the treated plants display a substantial degree of resistance to these unwanted phytopathogenic fungi. Thus, the substances according to the invention can be employed for protecting plants against attack by the abovementioned pathogens within a certain period of time after the treatment. The period of time within which protection is effected generally extends from 1 to 10 days, preferably 1 to 7 days, after the treatment of the plants with the active substances.

Plants and plant varieties which are preferably to be treated according to the invention include all plants which have genetic material which imparts particularly advantageous, useful traits to these plants (whether obtained by breeding and/or biotechnological means).

Plants and plant varieties which are also preferably to be treated according to the invention are resistant against one or more biotic stresses, i.e. said plants have a better defence against animal and microbial pests, such as against nematodes, insects, mites, phytopathogenic fungi, bacteria, viruses and/or viroids.

Plants and plant varieties which may also be treated according to the invention are those plants which are resistant to one or more abiotic stresses. Abiotic stress conditions may include, for example, drought, cold temperature exposure, heat exposure, osmotic stress, waterlogging, increased soil salinity, increased exposure to minerals, exposure to ozone, exposure to strong light, limited availability of nitrogen nutrients, limited availability of phosphorus nutrients or shade avoidance.

Plants and plant varieties which may also be treated according to the invention are those plants characterized by enhanced yield characteristics. Increased yield in said plants can be the result of, for example, improved plant physiology, growth and development, such as water use efficiency, water retention efficiency, improved nitrogen use, enhanced carbon assimilation, improved photosynthesis, increased germination efficiency and accelerated maturation. Yield can furthermore be affected by improved plant architecture (under stress and non-stress conditions), including early flowering, flowering control for hybrid seed production, seedling vigour, plant size, internode number and distance, root growth, seed size, fruit size, pod size, pod or ear number, seed number per pod or ear, seed mass, enhanced seed filling, reduced seed dispersal, reduced pod dehiscence and lodging resistance. Further yield traits include seed composition, such as carbohydrate content, protein content, oil content and composition, nutritional value, reduction in anti-nutritional compounds, improved processability and better storage stability.

Plants that may be treated according to the invention are hybrid plants that already express the characteristics of heterosis, or hybrid vigour, which results in generally higher yield, vigour, health and resistance towards biotic and abiotic stress factors. Such plants are typically made by crossing an inbred male-sterile parent line (the female parent) with another inbred male-fertile parent line (the male parent). Hybrid seed is typically harvested from the male sterile plants and sold to growers. Male sterile plants can sometimes (e.g. in corn) be produced by detasseling (i.e. the mechanical removal of the male reproductive organs or male flowers) but, more typically, male sterility is the result of genetic determinants in the plant genome. In that case, and especially when seed is the desired product to be harvested from the hybrid plants, it is typically useful to ensure that male fertility in the hybrid plants, which contain the genetic determinants responsible for male sterility, is fully restored. This can be accomplished by ensuring that the male parents have appropriate fertility restorer genes which are capable of restoring the male fertility in hybrid plants that contain the genetic determinants responsible for male sterility. Genetic determinants for male sterility may be located in the cytoplasm. Examples of cytoplasmic male sterility (CMS) were for instance described in Brassica species. However, genetic determinants for male sterility can also be located in the nuclear genome. Male sterile plants can also be obtained by plant biotechnology methods such as genetic engineering. A particularly useful means of obtaining male sterile plants is described in WO 89/10396 in which, for example, a ribonuclease such as barnase is selectively expressed in the tapetum cells in the stamens. Fertility can then be restored by expression in the tapetum cells of a ribonuclease inhibitor such as barstar.

Plants or plant cultivars (obtained by plant biotechnology methods such as genetic engineering) which may be treated according to the invention are herbicide-tolerant plants, i.e. plants made tolerant to one or more given herbicides. Such plants can be obtained either by genetic transformation, or by selection of plants containing a mutation imparting such herbicide tolerance.

Herbicide-tolerant plants are for example glyphosate-tolerant plants, i.e. plants made tolerant to the herbicide glyphosate or salts thereof. For example, glyphosate-tolerant plants can be obtained by transforming the plant with a gene encoding the enzyme 5-enolpyruvylshikimate-3-phosphate synthase (EPSPS). Examples of such EPSPS genes are the AroA gene (mutant CT7) of the bacterium *Salmonella typhimurium*, the CP4 gene of the bacterium *Agrobacterium sp.*, the genes encoding a petunia EPSPS, a tomato EPSPS, or an Eleusine EPSPS. It can also be a mutated EPSPS. Glyphosate-tolerant plants can also be obtained by expressing a gene that encodes a glyphosate oxidoreductase enzyme. Glyphosate-tolerant plants can also be obtained by expressing a gene that encodes a glyphosate acetyltransferase enzyme. Glyphosate-tolerant plants can also be obtained by selecting plants containing naturally occurring mutations of the abovementioned genes.

Other herbicide-resistant plants are for example plants that are made tolerant to herbicides inhibiting the enzyme glutamine synthase, such as bialaphos, phosphinothricin or glufosinate. Such plants can be obtained by expressing an enzyme detoxifying the herbicide or a mutant glutamine synthase enzyme that is resistant to inhibition. One such efficient detoxifying enzyme is, for example, an enzyme encoding a phosphinothricin acetyltransferase (such as the bar or pat protein from Streptomyces species). Plants expressing an exogenous phosphinothricin acetyltransferase are described.

Further herbicide-tolerant plants are also plants that are made tolerant to the herbicides inhibiting the enzyme hydroxyphenylpyruvatedioxygenase (HPPD). Hydroxyphenylpyruvatedioxygenases are enzymes that catalyze the reaction in which para-hydroxyphenyl pyruvate (HPP) is transformed into homogentisate. Plants tolerant to HPPD inhibitors can be transformed with a gene encoding a naturally occurring resistant HPPD enzyme, or a gene encoding a mutated HPPD enzyme. Tolerance to HPPD inhibitors can also be obtained by transforming plants with genes encoding certain enzymes enabling the formation of homogentisate despite the inhibition of the native HPPD enzyme by the HPPD inhibitor. Tolerance of plants to HPPD inhibitors can also be improved by transforming plants with a gene encoding an enzyme of prephenate dehydrogenase in addition to a gene encoding an HPPD-tolerant enzyme.

Still further herbicide-resistant plants are plants that are made tolerant to acetolactate synthase (ALS) inhibitors. Known ALS inhibitors include, for example, sulphonylurea, imidazolinone, triazolopyrimidines, pyrimidinyloxy(thio)benzoates, and/or sulphonylaminocarbonyltriazolinone herbicides. Different mutations in the ALS enzyme (also known as acetohydroxyacid synthase, AHAS) are known to confer tolerance to different herbicides and groups of herbicides. The production of sulphonylurea-tolerant plants and imidazolinone-tolerant plants has been described in the international publication WO 1996/033270. Further sulphonylurea- and imidazolinone-tolerant plants have also been described, for example in WO 2007/024782.

Other plants tolerant to imidazolinone and/or sulphonylurea can be obtained by induced mutagenesis, selection in cell cultures in the presence of the herbicide or mutation breeding.

Plants or plant varieties (obtained by plant biotechnology methods such as genetic engineering) which may also be treated according to the invention are insect-resistant transgenic plants, i.e. plants made resistant to attack by certain target insects. Such plants can be obtained by genetic transformation, or by selection of plants containing a mutation imparting such insect resistance.

An "insect-resistant transgenic plant", as used herein, includes any plant containing at least one transgene comprising a coding sequence encoding:

1) an insecticidal crystal protein from *Bacillus thuringiensis* or an insecticidal portion thereof, such as the insecticidal crystal proteins listed online at: http://www.lifesci.sussex.ac.uk/Home/Neil_Crickmore/Bt/, or insecticidal portions thereof, e.g. proteins of the Cry protein classes Cry1Ab, Cry1Ac, Cry1F, Cry2Ab, Cry3Ae, or Cry3Bb or insecticidal portions thereof; or

2) a crystal protein from *Bacillus thuringiensis* or a portion thereof which is insecticidal in the presence of a second other crystal protein from *Bacillus thuringiensis* or a portion thereof, such as the binary toxin made up of the Cy34 and Cy35 crystal proteins; or

3) a hybrid insecticidal protein comprising parts of two different insecticidal crystal proteins from *Bacillus thuringiensis*, such as a hybrid of the proteins of 1) above or a hybrid of the proteins of 2) above, e.g. the Cry1A.105 protein produced by corn event MON98034 (WO 2007/027777); or

4) a protein of any one of 1) to 3) above wherein some, particularly 1 to 10, amino acids have been replaced by another amino acid to obtain a higher insecticidal activity to a target insect species, and/or to expand the range of target insect species affected, and/or because of changes induced into the encoding DNA during cloning or transformation, such as the Cry3Bb1 protein in corn events MON863 or MON88017, or the Cry3A protein in corn event MIR 604; or

5) an insecticidal secreted protein from *Bacillus thuringiensis* or *Bacillus cereus*, or an insecticidal portion thereof, such as the vegetative insecticidal proteins (VIP) listed at: http://www.lifesci.sussex.ac.uk/Home/Neil_Crickmore/Bt/vip.html, e.g. proteins from the VIP3Aa protein class; or

6) a secreted protein from *Bacillus thuringiensis* or *Bacillus cereus* which is insecticidal in the presence of a second secreted protein from *Bacillus thuringiensis* or *B. cereus*, such as the binary toxin made up of the VIP1A and VIP2A proteins; or

7) a hybrid insecticidal protein comprising parts from different secreted proteins from *Bacillus thuringiensis* or *Bacillus cereus*, such as a hybrid of the proteins in 1) above or a hybrid of the proteins in 2) above; or

8) a protein of any one of 1) to 3) above wherein some, particularly 1 to 10, amino acids have been replaced by another amino acid to obtain a higher insecticidal activity to a target insect species, and/or to expand the range of target insect species affected, and/or because of changes induced into the encoding DNA during cloning or transformation (while still encoding an insecticidal protein), such as the VIP3Aa protein in cotton event COT 102.

Of course, insect-resistant transgenic plants, as used herein, also include any plant comprising a combination of genes encoding the proteins of any one of the above classes 1 to 8. In one embodiment, an insect-resistant plant contains more than one transgene encoding a protein of any one of the above classes 1 to 8, to expand the range of target insect species affected or to delay insect resistance development to the plants, by using different proteins insecticidal to the same target insect species but having a different mode of action, such as binding to different receptor binding sites in the insect.

Plants or plant varieties (obtained by plant biotechnology methods such as genetic engineering) which may also be treated according to the invention are tolerant to abiotic stresses. Such plants can be obtained by genetic transformation, or by selection of plants containing a mutation imparting such stress resistance. Particularly useful stress tolerance plants include:

a. plants which contain a transgene capable of reducing the expression and/or the activity of the poly(ADP-ribose)polymerase (PARP) gene in the plant cells or plants.

b. plants which contain a stress tolerance-enhancing transgene capable of reducing the expression and/or the activity of the PARG-encoding genes of the plants or plant cells.

c. plants which contain a stress tolerance-enhancing transgene coding for a plant-functional enzyme of the nicotinamide adenine dinucleotide salvage biosynthesis pathway, including nicotinamidase, nicotinate phosphoribosyltransferase, nicotinic acid mononucleotide adenyltransferase, nicotinamide adenine dinucleotide synthetase or nicotinamide phosphoribosyltransferase.

Plants or plant varieties (obtained by plant biotechnology methods such as genetic engineering) which may also be treated according to the invention show altered quantity, quality and/or storage stability of the crop product and/or altered properties of specific ingredients of the crop product such as:

1) transgenic plants which synthesize a modified starch, which in its physical-chemical characteristics, in particular the amylose content or the amylose/amylopectin ratio, the degree of branching, the average chain length, the side chain distribution, the viscosity behaviour, the gelling strength, the starch grain size and/or the starch grain morphology, is changed in comparison with the synthesized starch in wild type plant cells or plants, so that this modified starch is better suited for special applications.

2) transgenic plants which synthesize non-starch carbohydrate polymers or which synthesize non-starch carbohydrate polymers with altered properties in comparison to wild type plants without genetic modification. Examples are plants which produce polyfructose, especially of the inulin and levan type, plants which produce alpha-1,4-glucans, plants which produce alpha-1,6 branched alpha-1,4-glucans, and plants producing alternan.

3) transgenic plants which produce hyaluronan.

Plants or plant varieties (obtained by plant biotechnology methods such as genetic engineering) which may also be treated according to the invention are plants, such as cotton plants, with altered fibre characteristics. Such plants can be obtained by genetic transformation, or by selection of plants containing a mutation imparting such altered fibre characteristics and include:

a) plants, such as cotton plants which contain an altered form of cellulose synthase genes,
b) plants, such as cotton plants which contain an altered form of rsw2 or rsw3 homologous nucleic acids;
c) plants, such as cotton plants, with an increased expression of sucrose phosphate synthase;
d) plants, such as cotton plants, with an increased expression of sucrose synthase;
e) plants, such as cotton plants, wherein the timing of the plasmodesmatal gating at the basis of the fibre cell is altered, e.g. through downregulation of fibre-selective β-1,3-glucanase;
f) plants, such as cotton plants, which have fibres with altered reactivity, e.g. through the expression of the N-acetylglucosaminetransferase gene including nodC and chitin synthase genes.

Plants or plant varieties (obtained by plant biotechnology methods such as genetic engineering) which may also be treated according to the invention are plants, such as oilseed rape or related Brassica plants, with altered oil profile characteristics. Such plants can be obtained by genetic transformation or by selection of plants containing a mutation imparting such altered oil characteristics and include:

a) plants, such as oilseed rape plants, which produce oil having a high oleic acid content;
b) plants, such as oilseed rape plants, which produce oil having a low linolenic acid content;
c) plants, such as oilseed rape plants, which produce oil having a low level of saturated fatty acids.

Particularly useful transgenic plants which may be treated according to the invention are plants which comprise one or more genes which encode one or more toxins are the following which are sold under the trade names YIELD GARD® (for example maize, cotton, soya beans), KnockOut® (for example maize), BiteGard® (for example maize), BT-Xtra® (for example maize), StarLink® (for example maize), Bollgard® (cotton), Nucotn® (cotton), Nucotn 33B® (cotton), NatureGard® (for example maize), Protecta® and NewLeaf® (potato). Examples of herbicide-tolerant plants which may be mentioned are maize varieties, cotton varieties and soya bean varieties which are sold under the trade names Roundup Ready® (tolerance to glyphosate, for example maize, cotton, soya beans), Liberty Link® (tolerance to phosphinothricin, for example oilseed rape), IMI® (tolerance to imidazolinone) and SCS® (tolerance to sulphonylurea, for example maize). Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) which may be mentioned include the varieties sold under the name Clearfield® (for example maize).

Particularly useful transgenic plants which may be treated according to the invention are plants containing transformation events, or a combination of transformation events, that are listed for example in the databases for various national or regional regulatory agencies (see for example http://gmoinfo.jrc.it/gmp_browse.aspx and http://www.agbios.com/dbase.php).

The active substances or compositions according to the invention may furthermore be employed in the protection of materials for protecting industrial materials against attack and destruction by undesired microorganisms such as, for example, fungi.

The active substances or compositions according to the invention may furthermore be employed in the protection of materials for protecting industrial materials against attack and destruction by undesired microorganisms such as, for example, fungi.

In the present context, industrial materials are understood as meaning nonlive materials which have been prepared for use in industry. Industrial materials which are intended to be protected by active substances according to the invention from change or destruction by fungi can be, for example, glues, sizes, paper, wall card and board, textiles, carpets, leather, wood, paints and plastic articles, cooling lubricants and other materials which are capable of being attacked or decomposed by microorganisms. Other materials to be protected and which can be adversely affected by the multiplication of microorganisms which may be mentioned within the scope are parts of production plants and buildings, for example cooling water circuits, cooling and heating systems and aeration and air-conditioning units. Industrial materials which may be mentioned by preference within the scope of the present invention are glues, sizes, paper and boards, leather, wood, paints, cooling lubricants and heat-transfer fluids, especially preferably wood. The active substances or compositions according to the invention can prevent disadvantageous effects such as wilting, decay, discolouration, decolouration or mould development. Moreover, the compounds according to the invention can be employed for protecting objects against being covered with growth, in particular ships' hulls, sieves, nets, buildings, jetties and signal units, which come into contact with seawater or brackish water.

The method according to the invention for controlling unwanted fungi can also be employed for protecting storage goods. Here, storage goods are to be understood as meaning natural substances of vegetable or animal origin or processed products thereof of natural origin, for which long-term protection is desired. Storage goods of vegetable origin, such as, for example, plants or plant parts, such as stems, leaves, tubers, seeds, fruits, grains, can be protected in the freshly harvested state or after processing by (pre)drying, moistening, comminuting, grinding, pressing or roasting. Storage goods also include timber, both unprocessed, such as construction timber, electricity poles and barriers, or in the form of finished products, such as furniture. Storage goods of animal origin are, for example, pelts, leather, furs and hairs. The active substances according to the invention can prevent disadvantageous effects, such as rotting, decay, discolouration, decolouration or the development of mould.

Some pathogens of fungal diseases which can be treated according to the invention may be mentioned, by way of example, but not by way of limitation:
Powdery Mildew Diseases such as Blumeria diseases caused for example by Blumeria graminis; Podosphaera diseases caused for example by Podosphaera leucotricha; Sphaerotheca diseases caused for example by Sphaerotheca fuliginea; Uncinula diseases caused for example by Uncinula necator;
Rust Diseases such as Gymnosporangium diseases caused for example by Gymnosporangium sabinae; Hemileia diseases caused for example by Hemileia vastatrix; Phakopsora diseases caused for example by Phakopsora pachyrhizi and Phakopsora meibomiae; Puccinia diseases caused for example by Puccinia recondita, Puccinia graminis, Puccinia striiformis and Puccinia triticina; Uromyces diseases caused for example by Uromyces appendiculatus;
Oomycete Diseases such as Bremia diseases caused for example by Bremia lactucae; Peronospora diseases caused for example by Peronospora pisi and Peronospora brassicae; Phytophthora diseases caused for example by Phytophthora infestans; Plasmopara diseases caused for example by Plasmopara viticola; Pseudoperonospora diseases caused for example by Pseudoperonospora humuli and Pseudoperonospora cubensis; Pythium diseases caused for example by Pythium ultimum;
Leafspot, Leaf blotch and Leaf Blight Diseases such as Alternaria diseases caused for example by Alternaria solani; Cercospora diseases caused for example by Cercospora beticola; Cladiosporium diseases caused for example by Cladiosporium cucumerinum; Cochliobolus diseases caused for example by Cochliobolus sativus (Conidiaform: Drechslera, Syn: Helminthosporium) and Cochliobolus miyabeanus; Colletotrichum diseases caused for example by Colletotrichum lindemuthianum; Cycloconium diseases caused for example by Cycloconium oleaginum; Diaporthe diseases caused for example by Diaporthe citri; Elsinoe diseases caused for example by Elsinoe fawcettii; Gloeosporium diseases caused for example by Gloeosporium laeticolor; Glomerella diseases caused for example by Glomerella cingulata; Guignardia diseases caused for example by Guignardia

bidwellii; Leptosphaeria diseases caused for example by Leptosphaeria maculans and Leptosphaeria nodorum; Magnaporthe diseases caused for example by Magnaporthe grisea; Mycosphaerella diseases caused for example by Mycosphaerella graminicola, Mycosphaerella arachidicola and Mycosphaerella fijiensis; Phaeosphaeria diseases caused for example by Phaeosphaeria nodorum; Pyrenophora diseases caused for example by Pyrenophora teres and Pyrenophora tritici repentis; Ramularia- diseases caused for example by Ramularia collo-cygni and Ramularia areola; Rhynchosporium diseases caused for example by Rhynchosporium secalis; Septoria diseases caused for example by Septoria apii and Septoria lycopersici; Typhula diseases caused for example by Thyphula incarnata; Venturia diseases caused for example by Venturia inaequalis;

Root- and Stem Diseases such as Corticium diseases caused for example by Corticium graminearum; Fusarium diseases caused for example by Fusarium oxysporum; Gaeumannomyces diseases caused for example by Gaeumannomyces graminis; Plasmodiophora diseases caused for example by Plasmodiophora brassicae; Rhizoctonia diseases caused for example by Rhizoctonia solani; Sarocladium diseases caused for example by Sarocladium oryzae; Sclerotium diseases caused for example by Sclerotium oryzae; Tapesia diseases caused for example by Tapesia acuformis; Thielaviopsis diseases caused for example by Thielaviopsis basicola;

Ear and Panicle Diseases including Maize cob such as Alternaria diseases caused for example by Alternaria spp.; Aspergillus diseases caused for example by Aspergillus flavus; Cladosporium diseases caused for example by Cladiosporium cladosporioides; Claviceps diseases caused for example by Claviceps purpurea; Fusarium diseases caused for example by Fusarium culmorum; Gibberella diseases caused for example by Gibberella zeae; Monographella diseases caused for example by Monographella nivalis;

Smut- and Bunt Diseases such as Sphacelotheca diseases caused for example by Sphacelotheca reiliana;

Tilletia diseases caused for example by Tilletia caries and Tilletia controversa; Urocystis diseases caused for example by Urocystis occulta; Ustilago diseases caused for example by Ustilago nuda and Ustilago nuda tritici;

Fruit Rot and Mould Diseases such as Aspergillus diseases caused for example by Aspergillus flavus; Botrytis diseases caused for example by Botrytis cinerea; Penicillium diseases caused for example by Penicillium expansum and Penicillium purpurogenum; Rhizopus diseases caused for example by Rhizopus stolonifer; Sclerotinia diseases caused for example by Sclerotinia sclerotiorum; Verticillium diseases caused for example by Verticillium alboatrum;

Seed- and Soilborne Decay, Mould, Wilt, Rot and Damping-off diseases Alternaria diseases caused for example by Alternaria brassicicola; Aphanomyces diseases caused for example by Aphanomyces euteiches; Ascochyta diseases caused for example by Ascochyta lentis; Aspergillus diseases caused for example by Aspergillus flavus; Cladosporium diseases caused for example by Cladosporium herbarum; Cochliobolus diseases caused for example by Cochliobolus sativus (Conidiaform: Drechslera, Bipolaris Syn: Helminthosporium); Colletotrichum diseases caused for example by Colletotrichum coccodes; Fusarium diseases caused for example by Fusarium culmorum; Gibberella diseases caused for example by Gibberella zeae; Macrophomina diseases caused for example by Macrophomina phaseolina; Microdochium diseases caused for example by Microdochium nivale; Monographella diseases caused for example by Monographella nivalis; Penicillium diseases caused for example by Penicillium expansum; Phoma diseases caused for example by Phoma lingam; Phomopsis diseases caused for example by Phomopsis sojae; Phytophthora diseases caused for example by Phytophthora cactorum; Pyrenophora diseases caused

for example by Pyrenophora graminea; Pyricularia diseases caused for example by Pyricularia oryzae; Pythium diseases caused for example by Pythium ultimum; Rhizoctonia diseases caused for example by Rhizoctonia solani; Rhizopus diseases caused for example by Rhizopus oryzae; Sclerotium diseases caused for example by Sclerotium rolfsii; Septoria diseases caused for example by Septoria nodorum; Typhula diseases caused for example by Typhula incarnata; Verticillium diseases caused for example by Verticillium dahliae;
Canker, Broom and Dieback Diseases such as Nectria diseases caused for example by Nectria galligena;
Blight Diseases such as Monilinia diseases caused for example by Monilinia laxa;
Leaf Blister or Leaf Curl Diseases including deformation of blooms and fruits such as Exobasidium diseases caused for example by Exobasidium vexans; Taphrina diseases caused for example by Taphrina deformans;
Decline Diseases of Wooden Plants such as Esca disease caused for example by Phaeomoniella clamydospora, Phaeoacremonium aleophilum and Fomitiporia mediterranea; Ganoderma diseases caused for example by Ganoderma boninense;
Diseases of Flowers and Seeds such as Botrytis diseases caused for example by Botrytis cinerea;
Diseases of Tubers such as Rhizoctonia diseases caused for example by Rhizoctonia solani; Helminthosporium diseases caused for example by Helminthosporium solani;
Diseases caused by Bacterial Organisms such as Xanthomanas species for example Xanthomonas campestris pv. oryzae; Pseudomonas species for example Pseudomonas syringae pv. lachrymans; Erwinia species for example Erwinia amylovora.

The compounds releated to this invention are preferably used to control the following soybean diseases:
Fungal Diseases of the Foliage, Upper Stems, Pods and Seeds for example Alternaria leaf spot (Alternaria spec. atrans tenuissima), Anthracnose (Colletotrichum gloeosporoides dematium var. truncatum), Brown spot (Septoria glycines), Cercospora leaf spot and blight (Cercospora kikuchii), Choanephora leaf blight (Choanephora infundibulifera trispora (Syn.)), Dactuliophora leaf spot (Dactuliophora glycines), Downy Mildew (Peronospora manshurica), Drechslera blight (Drechslera glycini), Frogeye Leaf spot (Cercospora sojina), Leptosphaerulina Leaf Spot (Leptosphaerulina trifolii), Phyllostica Leaf Spot (Phyllosticta sojaecola), Pod and Stem Blight (Phomopsis sojae), Powdery Mildew (Microsphaera diffusa), Pyrenochaeta Leaf Spot (Pyrenochaeta glycines), Rhizoctonia Aerial, Foliage, and Web Blight (Rhizoctonia solani), Rust (Phakopsora pachyrhizi, Phakopsora meibomiae), Scab (Sphaceloma glycines), Stemphylium Leaf Blight (Stemphylium botryosum), Target Spot (Corynespora cassiicola).

Fungal Disease of the Roots and Lower Stems for example Black Root Rot (Calonectria crotalariae), Charcoal Rot (Macrophomina phaseolina), Fusarium Blight or Wilt, Root Rot, and Pod and Collar Rot (Fusarium oxysporum, Fusarium orthoceras, Fusarium semitectum, Fusarium equiseti), Mycoleptodiscus Root Rot (Mycoleptodiscus terrestris), Neocosmospora (Neocosmopspora vasinfecta), Pod and Stem Blight (Diaporthe phaseolorum), Stem Canker (Diaporthe phaseolorum var. caulivora), Phytophthora Rot (Phytophthora megasperma), Brown Stem Rot (Phialophora gregata), Pythium Rot (Pythium aphanidermatum, Pythium irregulare, Pythium debaryanum, Pythium myriotylum, Pythium ultimum), Rhizoctonia Root Rot, Stem Decay, and Damping-Off (Rhizoctonia solani), Sclerotinia Stem Decay (Sclerotinia sclerotiorum), Sclerotinia Southern Blight (Sclerotinia rolfsii), Thielaviopsis Root Rot (Thielaviopsis basicola).

It is also possible to control resistant strains of the organisms mentioned above.

Microorganisms capable of degrading or changing the industrial materials which may be mentioned are, for example, bacteria, fungi, yeasts, algae and slime organisms. The active compounds according to the invention preferably act against fungi, in particular moulds, wood-discolouring and wood-destroying fungi (Basidiomycetes) and against slime organisms and algae. Microorganisms of the following genera may be mentioned as examples: Alternaria, such as Alternaria tenuis, Aspergillus, such as Aspergillus niger, Chaetomium, such as Chaetomium globosum, Coniophora, such as Coniophora puetana, Lentinus, such as Lentinus tigrinus, Penicillium, such as Penicillium glaucum, Polyporus, such as Polyporus versicolor, Aureobasidium, such as Aureobasidium pullulans, Sclerophoma, such as Sclerophoma pityophila, Trichoderma, such as Trichoderma viride, Escherichia, such as Escherichia coli, Pseudomonas, such as Pseudomonas aeruginosa, and Staphylococcus, such as Staphylococcus aureus.

When applying the compounds according to the invention the application rates can be varied within a broad range. The dose of active compound/application rate usually applied in the method of treatment according to the invention is generally and advantageously

- for treatment of part of plants, e.g. leafs (foliar treatment): from 0.1 to 10,000 g/ha, preferably from 10 to 1,000 g/ha, more preferably from 50 to 300g/ha; in case of drench or drip application, the dose can even be reduced, especially while using inert substrates like rockwool or perlite;
- for seed treatment: from 2 to 200 g per 100 kg of seed, preferably from 3 to 150 g per 100 kg of seed, more preferably from 2.5 to 25 g per 100 kg of seed, even more preferably from 2.5 to 12.5 g per 100 kg of seed;
- for soil treatment: from 0.1 to 10,000 g/ha, preferably from 1 to 5,000 g/ha.

The doses herein indicated are given as illustrative examples of the method according to the invention. A person skilled in the art will know how to adapt the application doses, notably according to the nature of the plant or crop to be treated.

The combination according to the invention can be used in order to protect plants within a certain time range after the treatment against pests and/or phytopathogenic fungi and/or microorganisms. The time range, in which protection is effected, spans in general 1 to 28 days, preferably 1 to 14 days, more preferably 1 to 10 days, even more preferably 1 to 7 days after the treatment of the plants with the combinations or up to 200 days after the treatment of plant propagation material.

Furthermore combinations and compositions according to the invention may also be used to reduce the contents of mycotoxins in plants and the harvested plant material and therefore in foods and animal feed stuff made therefrom. Especially but not exclusively the following mycotoxins can be specified: Deoxynivalenole (DON), Nivalenole, 15-Ac-DON, 3-Ac-DON, T2- und HT2- Toxins, Fumonisines, Zearalenone Moniliformine, Fusarine, Diaceotoxyscirpenole (DAS), Beauvericine, Enniatine, Fusaroproliferine, Fusarenole, Ochratoxines, Patuline, Ergotalkaloides und Aflatoxines, which are caused for example by the following fungal diseases: *Fusarium spec.*, like *Fusarium acuminatum*, *F. avenaceum*, *F. crookwellense*, *F. culmorum*, *F. graminearum*

(Gibberella zeae), F. equiseti, F. fujikoroi, F. musarum, F. oxysporum, F. proliferatum, F. poae, F. pseudograminearum, F. sambucinum, F. scirpi, F. semitectum, F. solani, F. sporotrichoides, F. langsethiae, F. subglutinans, F. tricinctum, F. verticillioides and others but also by *Aspergillus spec.*, *Penicillium spec.*, *Claviceps purpurea, Stachybotrys spec.* and others.

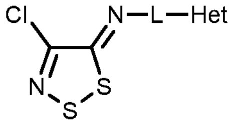
The invention is illustrated by the examples below. However, the invention is not limited to the examples.

Preparation Examples

Preparation of N-[(5Z)-4-chloro-5H-1,2,3-dithiazol-5-ylidene]-4,6-dimethylpyridin-2-amine :

To a solution of 217.8 mg (1.78 mmol) of 4,6-dimethylpyridine-2-amine in 10 ml of dichloromethane was added 371 mg (1.78 mmol) of Appel's salt. The mixture was stirred over night at room temperature and 281 mg (3.56 mmol) of pyridine were slowly added. After 1 hour, 8 ml of water were poured into the reaction mixture and the organic phase was separated over a chemelut cartridge. After evaporation and column chromatography (gradient from to 6 to 10 % ethylacetate in heptane), 190 mg of the desired product were obtained as a yellow solid [LogP 4.41, MS-(+H):258].

Table 1



(I)

Nr.	L	Het	Log P	MW measured
1	bond	1H-benzimidazol-2-yl	3,19	269
2	bond	2-chloro-pyrimidin-4-yl	2,90	265
3	bond	5-methyl-pyridin-2-yl	3,83	243,9
4	bond	1,3,4-thiadiazol-2-yl	2,11	238
5	bond	4-methyl-1,3-thiazol-2-yl	3,87	250
6	bond	3,5-dimethylpyrazin-2-yl		
7	bond	5,6-dichloro-3-(methoxycarbonyl)pyrazin-2-yl	3,81	3,81
8	bond	4,6-dimethoxypyrimidin-5-yl	2,54	291
9	bond	4,6-dichloropyrimidin-2-yl	3,37	300
10	-CH(CH$_3$)-	pyridin-2-yl	3,00	258
11	bond	3-chloro-5-(trifluoromethyl)pyridin-2-yl	4,87	331,9
12	bond	3-methylpyridin-2-yl	4,56	244
13	bond	5-bromo-3-(methoxycarbonyl)pyrazin-2-yl	3,35	368
14	bond	6-methyl-5-nitro-pyridin-2-yl	3,71	289
15	bond	3-chloro-quinoxalin-2-yl	4,51	315
16	bond	6-phenylpyridin-2-yl	4,86	306
17	bond	3,5-dibromopyrazin-2-yl		

Nr.	L	Het	Log P	MW measured
18	bond	2-methoxycarbonyl-4-nitrothiophen-3-yl	2,84	338
19	bond	4-chloropyrimidin-2-yl	2,57	265
20	bond	isoquinolin-3-yl	4,49	280
21	bond	5-chloropyrazin-2-yl	3,37	264,9
22	bond	6-ethylpyridin-2-yl	4,36	258
23	bond	6-methylpyridin-2-yl	3,78	244
24	bond	5-bromo-3-(methoxy)pyrazin-2-yl	3,96	340
25	bond	6-ethoxypyridazin-3-yl	3,33	275
26	bond	2-methoxycarbonyl-4-methylsulfonyl-thiophen-3-yl	2,33	371
27	bond	3-tert-butyl-1,2-oxazol-5-yl	4,36	276
28	bond	6-chhloropyridazin-3-yl	2,90	265
29	bond	5-methylpyrazin-2-yl	2,82	245
30	bond	pyrimidin-2-yl	1,79	231
31	bond	5-nitropyridin-2-yl	3,27	274,9
32	bond	6-chloropyridin-3-yl	2,86	264
33	bond	3,4,5,6-tetrachloropyridin-2-yl		
34	bond	6-fluoropyridin-2-yl	3,48	249
35	bond	5-phenylpyrazin-2-yl		
36	bond	3,5,6-trifluoropyridin-2-yl	3,69	284
37	bond	4-methyl-1,2,5-oxadiazol-3-yl	3,27	0
38	bond	3-ethyl-6-methylpyridin-2-yl	6,32	272
39	bond	6-methoxypyridin-2-yl	3,76	260
40	bond	4-methylpyridin-2-yl	3,80	243,9
41	bond	3-chloropyridin-2-yl	3,92	264
42	bond	1,2-oxazol-3-yl	2,51	219,9
43	bond	4-chloropyridin-2-yl	4,11	264
44	bond	6-(trifluoromethoxy)-1,3-benzothiazol-2-yl	5,48	370
45	bond	6-(1-cyclopentylethyl)pyridin-2-yl	6,56	326
46	bond	5,6-dimethylpyridin-2-yl	4,27	258
47	bond	3-methoxycarbonylpyrazin-2-yl		
48	bond	pyridin-2-yl	3,25	231
49	bond	5-chloropyridin-2-yl	4,04	264
50	bond	1H-pyrazol-3-yl	1,98	219
51	bond	6-(methyl)-1,3-benzothiazol-2-yl	5,26	300
52	bond	6-sec-butyl-pyridin-2-yl	5,35	286
53	bond	6-bromopyridin-2-yl	4,11	309

Nr.	L	Het	Log P	MW measured
54	bond	pyridin-3-yl	1,31	230
55	bond	5-bromo-3-(cyano)pyrazin-2-yl		
56	bond	4,6-dimethylpyridin-2-yl	4,41	258
57	bond	pyrazin-2-yl	2,32	231
58	bond	4-chloro-1-methyl-1H-pyrazol-3-yl	3,46	266,9
59	bond	1,3-thiazol-2-yl	3,21	235,9
60	bond	6-(3-methylbutan-2-yl)pyridin-2-yl	5,68	300
61	bond	6-(4-tert-butylphenyl)pyridin-2-yl	6,69	362
62	bond	6-chloropyridin-2-yl	3,96	265
63	bond	4,5-dimethyl-1,3-benzothiazol-2-yl	5,86	314
64	bond	5-cyanopyrimidin-2-yl		
65	bond	4,6-dimethylpyrimidin-2-yl		
66	bond	2-cyano-1-benzofuran-3-yl	3,76	294
67	bond	1-methyl-1H-pyrazol-3-yl	2,59	232,9
68	bond	quinolin-2-yl	4,54	279,9
69	bond	6-(fluoro)-1,3-benzothiazol-2-yl	4,70	304
70	bond	3-ethoxycarbonyl-4,5,6,7-tetrahydro-1-benzothiophen-2-yl	5,59	361
71	bond	2,6-difluoro-4-(trifluoromethyl)pyridin-2-yl	4,41	335
72	bond	5-cyano-6-(methyl)pyridin-2-yl	3,42	269
73	bond	6-trifluoromethylpyridin-2-yl	4,09	298

The determination of the logP values detailed in the tables and preparation examples hereinabove is carried out in accordance with EEC Directive 79/831 Annex V.A8 by means of HPLC (High Performance Liquid Chromatography) on a reversed-phase column (C 18). Temperature: 43°C.

The determination is carried out in the acidic range at pH 2.7, using 0.1% strength aqueous formic acid and acetonitrile (contains 0.1% formic acid) as eluents; linear gradient from 10% acetonitrile to 95% acetonitrile.

Calibration is carried out using unbranched alkan-2-ones (with 3 to 16 carbon atoms) with known logP values (determination of the logP values with reference to the retention times by linear interpolation between two successive alkanones).

In Table 1, M+H (or M H) means the molecular ion peak, plus or minus 1 a.m.u. (atomic mass unit) respectively, as observed in mass spectroscopy and M (ApcI+) means the molecular ion peak as it was found via positive atmospheric pressure chemical ionisation in mass spectroscopy.

Use examples

Example A: Phytophthora test (tomato) / preventive

Solvent:	49	parts by weight of N,N-dimethylformamide
Emulsifier:	1	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration. To test for preventive activity, young plants are sprayed with the preparation of active compound at the stated rate of application. One day after this treatment, the plants are inoculated with an aqueous spore suspension of *Phytophthora infestans*. The plants remain for one day in an incubation cabinet at approximately 22°C and a relative atmospheric humidity of 100 %. Then the plants are placed in an incubation cabinet at approximately 20°C and a relative atmospheric humidity of 96 %. The test is evaluated 7 days after the inoculation. 0 % means an efficacy which corresponds to that of the untreated control, while an efficacy of 100 % means that no disease is observed.

In this test the following compounds according to the invention showed efficacy of 70 % or even higher at a concentration of 1500 ppm of active ingredient: 4 (71 %), 48 (95 %), 59 (86 %), 37 (89 %), 35 (93 %), 39 (100 %), 34 (90 %), 36 (80 %), 64 (80 %), 50 (90 %), 32 (100 %), 54 (93 %), 60 (86 %), 12 (71 %), 49 (86 %), 43 (71 %), 40 (100 %), 3 (93 %), 41 (90 %), 42 (70 %), 30 (70 %), 67 (75 %), 11 (94 %), 58 (89 %), 1 (94 %).

Example B: Sphaerotheca test (cucumber) / preventive

Solvent:	49	parts by weight of N, N-dimethylformamide
Emulsifier:	1	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration. To test for preventive activity, young plants are sprayed with the preparation of active compound at the stated rate of application. One day after this treatment, the plants are inoculated with an aqueous spore suspension of *Sphaerotheca fuliginea*. Then the plants are placed in a greenhouse at approximately 23°C and a relative atmospheric humidity of approximately 70 %. The test is evaluated 7 days after the inoculation. 0 % means an efficacy which corresponds to that of the untreated control, while an efficacy of 100 % means that no disease is observed.

In this test the following compounds according to the invention showed efficacy of 70 % or even higher at a concentration of 1500 ppm of active ingredient: 48 (100%), 37 (100%), 53 (96%), 51 (100%), 39 (98%), 38 (95%), 22 (100%), 62 (100%), 34 (100%), 71 (99%), 45 (80%), 70 (93%), 16 (93%), 36 (100%), 72 (89%), 73 (100%), 64 (70%), 50 (94%), 32 (95%), 54 (70%), 71 (95%), 44 (100%), 40 (100%), 3 (95%), 41 (95%), 42 (78%), 67 (98%), 11 (95%), 58 (95%).

Example C: Venturia test (apples) / preventive

Solvent:	24,5	parts by weight of acetone
	24,5	parts by weight of dimethylacetamide
Emulsifier:	1	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration. To test for preventive activity, young plants are sprayed with the preparation of active compound at the stated rate of application. After the spray coating has dried on, the plants are inoculated with an aqueous conidia suspension of the causal agent of apple scab *(Venturia inaequalis)* and then remain for 1 day in an incubation cabinet at approximately 20°C and a relative atmospheric humidity of 100 %. The plants are then placed in a greenhouse at approximately 21°C and a relative atmospheric humidity of approximately 90 %. The test is evaluated 10 days after the inoculation. 0 % means an efficacy which corresponds to that of the untreated control, while an efficacy of 100 % means that no disease is observed.

In this test the following compounds according to the invention showed efficacy of 70 % or even higher at a concentration of 250 ppm of active ingredient: 48 (100%), 27 (100%), 37 (100%), 57 (96%), 66 (99%), 18 (81%), 55 (95%), 9 (89%), 23 (99%), 39 (99%), 22 (100%), 62 (100%), 34 (100%), 36 (100%), 73 (100%), 32 (96%), 40 (97%), 40 (100%), 3 (76%), 41 (100%), 42 (100%), 30 (93%), 67 (96%), 67 (100%), 1 (96%).

Example D: Alternaria test (tomatoes) / preventive

Solvent:	24,5	parts by weight of acetone
	24,5	parts by weight of dimethylacetamide
Emulsifier:	1	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration.

To test for preventive activity, young plants are sprayed with the preparation of active compound at the stated rate of application. After the spray coating has dried on, the plants are inoculated with an aqueous spore suspension of *Alternaria solani*. The plants are then placed in an incubation cabinet at approximately 20°C and a relative atmospheric humidity of 100 %. The test is evaluated 3 days after the inoculation. 0 % means an efficacy which corresponds to that of the untreated control while an efficacy of 100 % means that no disease is observed.

In this test the following compounds according to the invention showed efficacy of 70 % or even higher at a concentration of 250 ppm of active ingredient: 48 (96%), 27 (84%), 37 (94%), 57 (94%), 66 (89%), 55 (94%), 9 (94%), 23 (95%), 39 (95%), 22 (91%), 62 (95%), 34 (96%), 36 (95%), 73 (86%), 32 (74%), 40 (94%), 41 (95%), 42 (95%), 30 (93%), 67 (96%), 1 (95%).

Example E: Botrytis test (beans) / preventive

Solvent:	24,5	parts by weight of acetone
	24,5	parts by weight of dimethylacetamide
Emulsifier:	1	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration. To test for preventive activity, young plants are sprayed with the preparation of active compound. After the spray coating has dried on, 2 small pieces of agar covered with growth of *Botrytis cinerea* are placed on each leaf. The inoculated plants are placed in a darkened chamber at 20oC and a relative atmospheric humidity of 100 %. 2 days after the inoculation, the size of the lesions on the leaves is evaluated. 0 % means an efficacy which corresponds to that of the untreated control, while an efficacy of 100 % means that no disease is observed.

In this test the following compounds according to the invention showed efficacy of 70 % or even higher at a concentration of 500 ppm of active ingredient: 48 (98%), 27 (83%), 37 (98%), 66 (85%), 55 (94%), 22 (90%), 62 (90%), 36 (91%), 73 (90%), 40 (79%), 41 (90%), 42 (97%), 30 (78%), 67 (99%), 1 (90%).

Example F: Leptosphaeria nodorum test (wheat) / preventive

Solvent:	49	parts by weight of N,N-dimethylacetamide
Emulsifier:	1	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration. To test for preventive activity, young plants are sprayed with the preparation of active compound or active compound combination at the stated rate of application. After the spray coating has been dried, the plants are sprayed with a spore suspension of *Leptosphaeria nodorum*. The plants remain for 48 hours in an incubation cabinet at approximately 20°C and a relative atmospheric humidity of approximately 100 %. The plants are placed in the greenhouse at a temperature of approximately 22°C and a relative atmospheric humidity of approximately 80 %. The test is evaluated 8 days after the inoculation. 0 % means an efficacy which corresponds to that of the untreated control, while an efficacy of 100 % means that no disease is observed.

In this test the following compounds according to the invention showed an efficacy of 70 % or even higher at a concentration of 1000 ppm of active ingredient: 39 (100%), 34 (83%), 73 (83%), 40 (78%), 40 (71%), 41 (89%).

Example G: Septoria tritici-test (wheat) / preventive

Solvent:	49	parts by weight of N,N-dimethylacetamide
Emulsifier:	1	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound or active compound combination is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration. To test for preventive activity, young plants are sprayed with the preparation of active compound or active compound combination at the stated rate of application. After the spray coating has been dried, the plants are sprayed with a spore suspension of *Septoria tritici*. The plants remain for 48 hours in an incubation cabinet at approximately 20°C and a relative atmospheric humidity of approximately 100 % and afterwards for 60 hours at approximately 15°C in a translucent incubation cabinet at a relative atmospheric humidity of approximately 100 %. The plants are placed in the greenhouse at a temperature of approximately 15°C and a relative atmospheric humidity of approximately 80 %. The test is evaluated 21 days after the inoculation. 0 % means an efficacy which corresponds to that of the untreated control, while an efficacy of 100 % means that no disease is observed.

In this test the following compounds according to the invention showed an efficacy of 70 % or even higher at a concentration of 1000 ppm of active ingredient: 57 (70%), 53 (100%), 71 (80%), 40 (100%), 41 (80%).

Example H: Pyricularia test (rice) / protective

Solvent:	28.5	parts by weight of acetone
Emulsifier:	1.5	parts by weight of polyoxyethylene alkyl phenyl ether

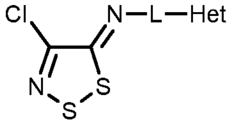
To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration.

To test for protective activity, young plants are sprayed with the preparation of active compound at the stated rate of application. One day after spraying, the plants are inoculated with an aqueous spore suspension of the causal agent of rice blast (Pyricularia oryzae). The plants are then placed in an incubator at approximately 25°C and a relative atmospheric humidity of approximately 100 % for 1 day. The test is evaluated 5 days after the inoculation. 0 % means an efficacy which corresponds to that of the control, while an efficacy of 100 % means that no disease is observed.

In this test the compounds according to the invention of the following structures showed efficacy of 80 % or even higher at a concentration of 250 ppm of active ingredient: 39 and 42.

Patent Claims

1. Use of 5-heteroarylimino-1,2,3-dithiazoles of the formula (I)



(I)

in which

L represents a direct bond or C_1-C_2-alkanediyl,

Het represents an optionally substituted heteroaryl,

or salt thereof for controlling phytopathogenic fungi.

2. Use according to Claim 1, wherein

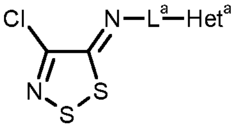
L represents a direct bond, -CH_2-, -$(CH_2)_2$- or -$CH(CH_3)$-,

Het represents a five- or six-membered heteroaryl selected from the group consisting of pyridinyl, pyridazinyl, pyrimidinyl, pyrazinyl and triazinyl, furyl, thienyl, pyrrolyl, pyrazolyl, imidazolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, triazolyl, tetrazolyl, oxadiazolyl, thiadiazolyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z, whereby

Z represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy.

3. 5-heteroarylimino-1,2,3-dithiazoles of the formula (I-a)



(I-a)

in which

L^a represents a direct bond or C_1-C_2-alkanediyl,

Het^a represents a five- or six-membered heteroaryl selected from the group consisting of 3-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 2-pyrazinyl, 1,3,5-triazin-2-yl, 1,2,4-triazin-3-yl, 1,2,4-triazin-5-yl, 1,2,4-triazin-6-yl, 2-furyl, 3-

furyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 1-pyrrolyl, 4-pyrazolyl, 1-pyrazolyl, 1H-imidazol-2-yl, 1H-imidazol-1-yl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 3-isothiazolyl, 4-isothiazolyl, 5-isothiazolyl, 1H-1,2,3-triazol-1-yl, 2H-1,2,3-triazol-2-yl, 2H-1,2,3-triazol-4-yl, 1H-1,2,4-triazol-3-yl, 1H-1,2,4-triazol-5-yl, 1H-1,2,4-triazol-1-yl, 4H-1,2,4-triazol-3-yl, 4H-1,2,4-triazol-4-yl, 1H-tetrazol-1-yl, 1H-tetrazol-5-yl, 2H-tetrazol-2-yl, 2H-tetrazol-5-yl, 1,2,4-oxadiazol-3-yl, 1,2,4-oxadiazol-5-yl, 1,2,4-thiadiazol-3-yl, 1,2,4-thiadiazol-5-yl, 1,3,4-oxadiazol-2-yl, 1,3,4-thiadiazol-2-yl, 1,2,3-oxadiazol-4-yl, 1,2,3-oxadiazol-5-yl, 1,2,3-thiadiazol-4-yl, 1,2,3-thiadiazol-5-yl, 1,2,5-oxadiazol-3-yl, 1,2,5-thiadiazol-3-yl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^a, whereby

Z^a represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^a – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a represents a five-membered heteroaryl selected from the group consisting of 5-pyrazolyl, 1H-imidazol-4-yl, 1H-imidazol-5-yl, 1H-1,2,3-triazol-4-yl and 1H-1,2,3-triazol-5-yl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^b, whereby

Z^b represents halogen, nitro, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^b – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a represents a five-membered heteroaryl selected from the group consisting of 2-thienyl and 3-pyrazolyl, each of which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^c, whereby

Z^c represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^c – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

or

Het^a represents 2-pyridinyl, which is optionally identically or differently monosubstituted or polysubstituted by the radical Z^d, whereby

Z^d represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^d – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy;

with the proviso that the 2-pyridinyl is either not unsubstituted or is not substituted by methyl or is not substituted by 5-chlorine or 5-bromine;

or

Het^a represents 4-pyridinyl, which is identically or differently monosubstituted or polysubstituted by the radical Z^e, whereby

Z^e represents halogen, nitro, cyano, C_1-C_6-alkyl, C_1-C_4-alkoxy, C_1-C_4-alkylsulfanyl, C_1-C_4-alkylsulfinyl, C_1-C_4-alkylsulfonyl, C_1-C_4-halogenoalkyl, C_1-C_4-halogenoalkoxy, C_1-C_4-halogenoalkylsulfanyl, C_1-C_4-halogenoalkylsulfinyl, C_1-C_4-halogenoalkylsulfonyl, (C_1-C_4-alkyl)carbonyl, (C_1-C_4-alkoxy)carbonyl, C_3-C_7-cycloalkyl, (C_3-C_7-cycloalkyl)-C_1-

C_2-alkyl, or represents phenyl, phenoxy or phenylthio, each of which may again be optionally identically or differently monosubstituted or polysubstituted by halogen or C_1-C_4-alkyl;

or two vicinal substituents Z^e – together with the carbon atoms to which they are bound – may form an annulated, saturated or (partly) unsaturated five- or six-membered carbocycle, which carbocycle is optionally identically or differently monosubstituted or polysubstituted by halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy, C_1-C_4-halogenoalkyl or C_1-C_4-halogenoalkoxy.

4. Composition for controlling phytopathogenic fungi, characterized in that it contains at least one 5-heteroarylimino-1,2,3-dithiazole of the formula (I-a) according to Claim 3, besides extenders and/or surface-active substances.

5. Method of controlling phytopathogenic fungi, characterized in that 5-heteroarylimino-1,2,3-dithiazoles of the formula (I-a) according to Claim 3 are applied to the fungi and/or their environment.