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(54) Title: PYRAZINOTHIAZINES HAVING HERBICIDAL ACTION

(57) Abstract: Substituted pyridazines of the formula I in which the variables are defined according to the description, processes and intermediates for preparing the compounds of the formula I and their N oxides, their agriculturally useful salts, compositions comprising them and their use as herbicides, and also a method for controlling unwanted vegetation.

$$\text{(I)}$$
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PYRAZINOTHIAZINES HAVING HERBICIDAL ACTION

Description

The present invention relates substituted pyridazines of the formula I

in which the variables have the following meaning:

- **R** is 0-R^A, S(0) or 0-S(0) - R^A;
- **R^A** is hydrogen, c - alkyl, Z-C3-C6-cycloalkyl, c - haloalkyl, C2:C6-alkenyl, Z-C3-C6-cycloalkenyl, C2-C6-alkynyl, Z-(tri-c1-c4 -alkyl)silyl, Z-C(=0)-R, Z-NR-C(=O)-NR'R, Z-P(=O)(R)2, NR'R, a 3- to 7-membered monocyclic or 9- or 10-membered bicyclic saturated, unsaturated or aromatic heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S, where the cyclic groups are unsubstituted or substituted by 1, 2, 3 or 4 groups **R^B**;
- **R^B** and **R^C** independently of one another are hydrogen, c - alkyl, c - haloalkyl, c - alkyl, Z-C3-C6-cycloalkyl, Z-c1-c8-alkoxy, Z-c1-c8-alkoxy, Z-c1-c8-alkenyloxy, NR'R', C1-ce-alkylsulfonyl, Z-(tri-c1-c4-alkyl)silyl, Z-phenyl, Z-phenoxy, Z-phenylamino or a 5- or 6-membered monocyclic or 9- or 10-membered bicyclic heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S and which is attached via **Z**;
- **R^1** and **R^2** together with the nitrogen atom to which they are attached may also form a 5- or 6-membered monocyclic or 9- or 10-membered bicyclic heterocycle which contains 1, 2, 3 or
4 heteroatoms selected from the group consisting of O, N and S;

Z is a covalent bond or c \( \ce{C4} \)-alkylene;

\[ n \] is 0, 1 or 2;

R^1 is cyano, halogen, nitro, c \( \ce{C6} \)-alkyl, c \( \ce{C6} \)-alkenyl, c \( \ce{C6} \)-alkynyl, c \( \ce{C6} \)-halo-

alkyl, Z-\( \ce{C1-C6} \)-alkoxy, Z-\( \ce{C1-C4} \)-alkoxy-\( \ce{C1-C4} \)-alkoxy, Z-\( \ce{C1-C4} \)-alkylthio, Z-

\( \ce{C1-C4} \)-alkylthio-\( \ce{C1-C4} \)-alkylthio, c \( \ce{C6} \)-alkenyl, c \( \ce{C6} \)-alkynyl, c \( \ce{C6} \)-haloalkoxy,

c \( \ce{C1-C4} \)-haloalkoxy-\( \ce{C1-C4} \)-alkoxy, S(0)_nR^{\text{bb}}, Z-phenoxy, Z-heterocyclyloxy, where

heterocyclyl is a 5- or 6-membered monocyclic or 9- or 10-membered bicyclic

saturated, partially unsaturated or aromatic heterocycle which contains 1, 2, 3 or

4 heteroatoms selected from the group consisting of O, N and S, where cyclic

groups are unsubstituted or partially or fully substituted by R^{\text{bb}};

R^{\text{bb}} is C\( \text{I}-\text{Cs} \)-alkyl, C\( \text{I}-\text{C6} \)-alkenyl, C\( \text{I}-\text{C6} \)-alkynyl, C\( \text{I}-\text{C6} \)-haloalkenyl, C\( \text{I}-\text{C6} \)-halo-

alkenyl or c \( \ce{C6} \)-haloalkyl and n is 0, 1 or 2;

A is N or C-\( \text{R}^{2} \);

R\( ^{2} \) is \( Z^{1} \)-heterocyclyl, where heterocyclyl is a 5- or 6-membered monocyclic or 9-

or 10-membered bicyclic saturated, partially unsaturated or aromatic heterocycle which

contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S, where cyclic groups are unsubstituted or partially or fully substituted by R^{\text{bb}};

- is phenyl which is attached via \( Z^{1} \) or oxygen and is unsubstituted or substituted by c \( \ce{C4} \)-alkyl, c \( \ce{C4} \)-alkoxy, c \( \ce{C4} \)-haloalkyl, c \( \ce{C4} \)-alkoxy-\( \ce{C1-C4} \)-alkyl or c \( \ce{C4} \)-alkoxy-\( \ce{C1-C4} \)-alkoxy;

- is C\( \text{I}-\text{Cs} \)-alkyl, C\( \text{I}-\text{C6} \)-haloalkyl, c \( \text{I}-\text{C4} \)-alkoxy-\( \text{C1-C4} \)-alkyl, C\( \text{I}-\text{C8} \)-alkenyl, C\( \text{I}-\text{C8} \)-alkynyl, c \( \text{C8} \)-haloalkenyl, c \( \text{C8} \)-haloalkynyl, c \( \text{C6} \)-alkoxy, Z-\( \text{C1-C4} \)-alkoxy-

c \( \text{C1-C4} \)-alkoxy, Z-\( \text{C1-C4} \)-haloalkoxy-\( \text{C1-C4} \)-alkoxy, Z-\( \text{C1-C6} \)-haloalkoxy, c \( \text{C8} \)-alkenyoxy, c \( \text{C8} \)-alkynloxy, Z-\( \text{C1-C4} \)-alkylthio, Z-\( \text{C1-C6} \)-haloalkylthio, Z-C(=0)-

R^{a} or S(0)_nR^{\text{bb}};

Z\( ^{1} \) is a covalent bond, c \( \ce{C4} \)-alkyleneoxy, c \( \ce{C4} \)-oxyalkylene or c \( \ce{C4} \)-alkyleneoxy-c\( \text{C1-C4} \)-alkylene;

R\( ^{b} \) independently of one another are Z-CN, Z-OH, Z-\( \text{NO} \_2 \), Z-halogen, oxo

(=O), =N-\( \text{R}^{a} \), c\( \text{I}-\text{Cs} \)-alkyl, c\( \text{I}-\text{C4} \)-haloalkyl, C\( \text{I}-\text{C8} \)-alkenyl, C\( \text{I}-\text{C8} \)-alkynyl, Z-\( \text{C1-C8} \)-alkoxy, Z-\( \text{C1-C8} \)-haloalkoxy, Z-C\( \text{C3-C10} \)-cycloalkyl,

0-Z-\( \text{C1-C3} \)-cycloalkyl, Z-C(=0)-R \( ^{a} \), NR\( ^{a} \), Z-(\( \text{tri-C1-C4} \)-alkyl)silyl, Z-phenyl or S(0)_nR^{\text{bb}}, where

R\( ^{2} \) together with the group attached to the adjacent carbon atom may also form a five-
to ten-membered saturated or partially or fully unsaturated mono- or bicyclic ring which, in addition to carbon atoms, may contain 1, 2 or 3 heteroatoms selected from the group consisting of O, N and S and may be substituted by additional groups R\( ^{b} \);

R\( ^{3} \) is hydrogen, cyano, halogen, nitro, c \( \text{I}-\text{C4} \)-alkyl, c \( \text{I}-\text{C4} \)-haloalkyl, c \( \text{I}-\text{C4} \)-alkoxy, c \( \text{I}-\text{C4} \)-haloalkoxy, c \( \text{I}-\text{C5} \)-alkenyl, c \( \text{I}-\text{C4} \)-alkynyl, c \( \text{I}-\text{C4} \)-alkynloxy, c \( \text{I}-\text{C4} \)-alkynloxy or S(0)_nR^{\text{bb}};
R^4 is hydrogen, halogen or C_1-C_4-haloalkyl;
R^5, R^6 independently of one another are hydrogen, halogen or C_1-C_4-alkyl;
R^k is C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkoxy -C_1-C_2-alkyl, C_2-C_6-alkenyl, C_2-C_6-
haloalkenyl, C_3-C_6 -alkynyl, C_3-C_6 -haloalkynyl or Z-phenyl which is unsubstituted
or substituted by 1 to 5 groups R^e;

where in the groups R^A and their subsstituents, the carbon chains and/or the cyclic
groups may be partially or fully substituted by groups R^e,
or a N-oxide or an agriculturally suitable salt thereof.

Moreover, the invention relates to processes and intermediates for preparing the
pyridazines of the formula I and the N-oxides thereof, the agriculturally usable salts
thereof, and also to active compound combinations comprising them, to compositions
comprising them and to their use as herbicides, i.e. for controlling harmful plants, and
also to a method for controlling unwanted vegetation which comprises allowing a
herbicidally effective amount of at least one pyridazine compound of the formula I or of
an agriculturally suitable salt of I to act on plants, their seed and/or their habitat.

Further embodiments of the present invention can be found in the claims, the
description and the examples. It is to be understood that the features mentioned above
and those still to be illustrated below of the subject matter of the invention can be
applied not only in the respective given combination but also in other combinations
without leaving the scope of the invention.

WO 2008/063180 and WO 2010/029311 describe herbicidal pyridopyrazines;
however, their herbicidal action at low application rates and/or their compatibility with
crop plants leave scope for improvement.

It is an object of the present invention to provide compounds having herbicidal
action. To be provided are in particular active compounds having strong herbicidal
action, in particular even at low application rates, whose compatibility with crop plants
is sufficient for commercial application.

These and further objects are achieved by the compounds of the formula I defined at
the outset and by their N-oxides and also their agriculturally suitable salts.

The compounds according to the invention can be prepared analogously to the
synthesis routes described in the documents mentioned above according to standard
processes of organic chemistry, for example according to the following synthesis route:

Pyridazinecarboxylic acids of the formula II can be reacted with carbonyl compounds
of the formula III to give compounds of the formula IV. In the formulae II and III, the
variables have the meaning given for formula I. The group Hal is a halogen atom or
another suitable nucleophilic leaving group, such as alkoxy or phenoxy.
This reaction is usually carried out at temperatures of from -78°C to 120°C, preferably from -20°C to 50°C, in an inert organic solvent in the presence of a base, such as, for example, triethylamine (cf. J. Agric. and Food Chem. 1994, 42(4), 1019-1025), a catalyst, such as, for example, dicyclohexylcarbodiimide (cf. Egyptian Journal of Chemistry 1994, 37(3), 273-282) or other known coupling agents.

Suitable solvents are aliphatic hydrocarbons, such as pentane, hexane, cyclohexane and petroleum ether, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene, ethers, such as diethyl ether, diisopropyl ether, tert-butyl methyl ether, dioxane, anisole and tetrahydrofuran, nitriles, such as acetonitrile and propionitrile, ketones, such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, and also dimethyl sulfoxide, dimethylformamide and dimethylacetamide, particularly preferably halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene. It is also possible to use mixtures of the solvents mentioned.

Suitable bases are, in general, inorganic compounds, such as lithium oxide, sodium oxide, calcium oxide and magnesium oxide, alkali metal and alkaline earth metal hydrides, such as lithium hydride, sodium hydride, potassium hydride and calcium hydride, alkali metal and alkaline earth metal carbonates, such as lithium carbonate, potassium carbonate and calcium carbonate, and also alkali metal bicarbonates, such as sodium bicarbonate, organometallic compounds, in particular alkali metal alkyls, such as methyl lithium, butyllithium and phenyllithium, alkylmagnesium halides, such as methylmagnesium chloride, and also alkali metal and alkaline earth metal alkoxides, such as sodium methoxide, sodium ethoxide, potassium ethoxide, potassium tert-butoxide and dimethoxy magnesium, moreover organic bases, for example tertiary amines, such as trimethylamine, triethylamine, tributylamine, diisopropylethylamine and N-methylpiperidine, pyridine, substituted pyridines, such as collidine, lutidine and 4-dimethylaminopyridine, and also bicyclic amines. Particular preference is given to tertiary amines such as trimethylamine, triethylamine, tributylamine, diisopropylethylamine as well as to alkali metal and alkaline earth metal carbonates such as lithium carbonate, potassium carbonate and calcium carbonate. The bases are generally employed in equimolar amounts; however, they can also be used in catalytic amounts, in excess or, if appropriate, as solvents.

The starting materials are generally reacted with one another in equimolar amounts.

The compounds of the formula IV are activated by introducing a leaving group L'. Suitable leaving groups L' are, in general, groups which increase the electrophilicity of
the carbonyl group, for example O-alkyl, O-aryl, halides, activated esters or aldehydes (such as, for example, Weinreb amide), in particular pentafluorophenoxy.

This reaction is usually carried out at temperatures of from -78°C to 120°C, preferably from -20°C to 50°C, in an inert organic solvent in the presence of a base, such as, for example, triethylamine (cf. J. Agric. and Food Chem. 1994, 42(4), 1019-1025), a catalyst, such as, for example, dicyclohexylcarbodiimide (cf. Egyptian Journal of Chemistry 1994, 37(3), 273-282) or other known coupling agents.

Suitable solvents are aliphatic hydrocarbons, such as pentane, hexane, cyclohexane and petroleum ether, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene, ethers, such as diethyl ether, diisopropyl ether, tert-butyl methyl ether, dioxane, anisole and tetrahydrofuran, nitriles, such as acetonitrile and propionitrile, ketones, such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, and also dimethyl sulfoxide, dimethylformamide and dimethylacetamide, particularly preferably methylene chloride and toluene. It is also possible to use mixtures of the solvents mentioned.

Suitable bases are, in general, inorganic compounds, such as alkali metal and alkaline earth metal oxides, such as lithium oxide, sodium oxide, calcium oxide and magnesium oxide, alkali metal and alkaline earth metal hydrides, such as lithium hydride, sodium hydride, potassium hydride and calcium hydride, alkali metal and alkaline earth metal carbonates, such as lithium carbonate, potassium carbonate and calcium carbonate, and also alkali metal bicarbonates, such as sodium bicarbonate, organometallic compounds, in particular alkali metal alkyls, such as methylolithium, butyllithium and phenyllithium, alkylmagnesium halides, such as methylmagnesium chloride, and also alkali metal and alkaline earth metal alkoxides, such as sodium methoxide, sodium ethoxide, potassium ethoxide, potassium tert-butoxide and dimethoxymagnesium, moreover organic bases, for example tertiary amines, such as trimethylamine, triethylamine, tributylamine, diisopropylethylamine and N-methylpiperidine, pyridine, substituted pyridines, such as collidine, lutidine and 4-dimethylaminopyridine, and also bicyclic amines. Particular preference is given to alkali metal and alkaline earth metal carbonates, such as lithium carbonate, potassium carbonate, calcium carbonate, cesium carbonate and rubidium carbonate. The bases are generally employed in catalytic amounts; however, they can also be used in equimolar amounts, in excess or, if appropriate, as solvents.

The starting materials are generally reacted with one another in equimolar amounts.
Suitable agents H-L\(^1\) are alcohols, optionally subst. phenols, N,0-dialkyl-hydroxylamine, in particular pentafluorophenol or N,0-dimethylhydroxylamine.

The compounds of the formula V are cyclized to give the compounds of the formula I.

This reaction is usually carried out at temperatures of from -78\(^\circ\)C to 120\(^\circ\)C, preferably from -20\(^\circ\)C to 50\(^\circ\)C, in an inert organic solvent in the presence of a base or a Lewis acid or a catalyst [cf. Silverman, Richard B. J. Am. Chem. Soc. 1981, 103(13), 3910].

Suitable solvents are aliphatic hydrocarbons, such as pentane, hexane, cyclohexane and petroleum ether, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene, ethers, such as diethyl ether, diisopropyl ether, tert-butyl methyl ether, dioxane, anisole and tetrahydrofuran, nitriles, such as acetonitrile and propionitrile, ketones, such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, and also dimethyl sulfoxide, dimethylformamide and dimethylacetamide, particularly preferably acetonitrile and dimethylformamide. It is also possible to use mixtures of the solvents mentioned.

Suitable bases are, in general, inorganic compounds, such as alkali metal and alkaline earth metal oxides, such as lithium oxide, sodium oxide, calcium oxide and magnesium oxide, alkali metal and alkaline earth metal hydrides, such as lithium hydride, sodium hydride, potassium hydride and calcium hydride, alkali metal and alkaline earth metal carbonates, such as lithium carbonate, potassium carbonate, calcium carbonate, cesium carbonate and rubidium carbonate, and also alkali metal bicarbonates, such as sodium bicarbonate, organometallic compounds, in particular alkali metal alkyls, such as methyl lithium, butyllithium and phenyllithium, alkyl magnesium halides, such as methyl magnesium chloride, and also alkali metal and alkaline earth metal alkoxides, such as sodium methoxide, sodium ethoxide, potassium ethoxide, potassium tert-butoxide and dimethoxymagnesium, moreover organic bases, for example tertiary amines, such as trimethylamine, triethylamine, tributylamine, diisopropylethylamine and N-methylpiperidine, pyridine, substituted pyridines, such as collidine, lutidine and 4-dimethylaminopyridine, and also bicyclic amines. Particular preference is given to alkali metal and alkaline earth metal carbonates, such as lithium carbonate, potassium carbonate, calcium carbonate, cesium carbonate and rubidium
carbonate.

The bases are generally employed in catalytic amounts; however, they can also be used in equimolar amounts, in excess or, if appropriate, as solvents.

The starting materials are generally reacted with one another in equimolar amounts.

Alternatively, the compounds of the formula I can also be obtained via a reverse reaction sequence, i.e. the reaction of the compounds of the formula II with compounds H-L\(^1\) gives the activated derivatives of the formula VI.

\[
\text{OH} \quad \begin{array}{c} \text{II} \quad \text{H-L}^1 \quad \text{VI} \\
R^6 \quad N \quad N \quad NH \quad R^x \end{array}
\]

Per se, this reaction is carried out under the conditions mentioned for the reaction of the formula IV with H-L\(^1\).

The compounds of the formula VI can then be reacted with compounds III to give the derivatives of the formula V.

\[
\begin{array}{c} \text{VI} \\
R^6 \quad N \quad N \quad NH \quad R^x \end{array} \quad + \quad \begin{array}{c} \text{III} \\
O \quad S \quad \text{Hal} \quad \text{R}^3 \quad \text{R}^1 \quad \text{A} \quad \text{R}^4 \quad \text{R}^2 \quad \text{A}
\end{array} \quad \text{base} \quad \begin{array}{c} \text{V} \\
\text{R}^6 \quad N \quad N \quad \text{S} \quad \text{SO}_2 \quad \text{A} \quad \text{R}^1 \quad \text{R}^4 \quad \text{R}^2 \quad \text{R}^3 \quad \text{A}
\end{array}
\]

Per se, this reaction is carried out under the conditions mentioned for the reaction of the formula II with III.


The reaction mixtures are worked up in a customary manner, for example by mixing with water, separating the phases and, if appropriate, chromatographic purification of the crude products. Some of the intermediates and end products are obtained in the form of colorless or slightly brownish viscous oils which are purified or freed from
volatile components under reduced pressure and at moderately elevated temperature. If the intermediates and end products are obtained as solids, the purification can also be carried out by recrystallization or digestion.

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

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

The organic moieties mentioned for the substituents of the compounds according to the invention are collective terms for individual enumerations of the individual group members. All hydrocarbon chains, such as alkyl, haloalkyl, alkenyl, alkynyl, and the alkyl moieties and alkenyl moieties in alkoxy, haloalkoxy, alkylamino, dialkylamino, N-alkylsulfonylamino, alkenyloxy, alkynlyoxy, alkoxyamino, alkyaminosulfonylamino, dialkylaminosulfonylamino, alkenylamino, alkynlyamino, N-(alkenyl)-N-(alkyl)amino, N-(alkenyl)-N-(alkyl)amino, N-(alkoxy)-N-(alkyl)amino, N-(alkoxy)-N-(alkoxy)amino or N-(alkenyl)-N-(alkoxy)amino can be straight-chain or branched.

The prefix C\(_n\)-C\(_m\) indicates the respective number of carbons of the hydrocarbon unit. Unless indicated otherwise, halogenated substituents preferably carry one to five identical or different halogen atoms, in particular fluorine atoms or chlorine atoms. The meaning halogen denotes in each case fluorine, chlorine, bromine or iodine.

Examples of other meanings are:

alkyl and the alkyl moieties for example in alkoxy, alkylamino, dialkylamino: saturated straight-chain or branched hydrocarbon radicals having one or more carbon atoms, for example 1 or 2, 1 to 4 or 1 to 6 carbon atoms, for example C\(_1\)-C\(_8\) -alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethylyl, pentyly, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 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, 1-ethyl-2-methylpropyl. In one embodiment according to the invention, alkyl denotes small alkyl groups, such as C\(_1\)-C\(_4\) -alkyl.

In another embodiment according to the invention, alkyl denotes relatively large alkyl groups, such as C\(_5\)-C\(_8\) -alkyl.

Haloalkyl: an alkyl radical as mentioned above, some or all of whose hydrogen atoms are substituted by halogen atoms, such as fluorine, chlorine, bromine and/or iodine, for example chloromethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 2-fluoroethyl, 2-chloroethyl, 2-bromoethyl, 2-iodoethyl, 2,2-difluoroethyl, 2,2,2-trifluoro-
ethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl, 2-fluoropropyl, 3-fluoropropyl, 2,2-difluoropropyl, 2,3-difluoropropyl, 2-chloropropyl, 3-chloropropyl, 2,3-dichloropropyl, 2-bromopropyl, 3-bromopropyl, 3,3,3-trifluoropropyl, 3,3,3-trichloropropyl, 2,2,3,3,3-pentafluoropropyl, heptafluoropropyl, 1-(fluoromethyl)-2-fluoroethyl, 1-(chloromethyl)-2-chloroethyl, 1-(bromomethyl)-2-bromoethyl, 4-fluorobutyl, 4-chlorobutyl, 4-bromobutyl and nonafluorobutyl.

Cycloalkyl and the cycloalkyl moieties for example in cycloalkoxy or cycloalkylcarbonyl: monocyclic saturated hydrocarbon groups having three or more carbon atoms, for example 3 to 6 carbon ring members, such as cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

Alkenyl and the alkenyl moieties for example in alkenyloxy: monounsaturated straight-chain or branched hydrocarbon radicals having two or more carbon atoms, for example 2 to 4, 2 to 6 or 3 to 6 carbon atoms, and a double bond in any position, for example C2-C6-alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1-methyl-4-butenyl, 2-methyl-4-butenyl, 3-methyl-4-butenyl, 4-methyl-4-butenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butyl, 1,2-dimethyl-2-butyl, 1,2-dimethyl-3-butyl, 1,3-dimethyl-1-butyl, 1,3-dimethyl-2-butyl, 1,3-dimethyl-3-butyl, 1,4-dimethyl-2-butyl, 1,4-dimethyl-3-butyl, 2,2-dimethyl-3-butyl, 2,3-dimethyl-1-butyl, 2,3-dimethyl-2-butyl, 2,3-dimethyl-3-butyl, 3,3-dimethyl-1-butyl, 3,3-dimethyl-2-butyl, 3,3-dimethyl-3-butyl, 1-ethyl-1-butyl, 1-ethyl-2-butyl, 1-ethyl-3-butyl, 2-ethyl-1-butyl, 2-ethyl-2-butyl, 2-ethyl-3-butyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl, 1-ethyl-2-methyl-2-propenyl.

Cycloalkenyl: monocyclic monounsaturated hydrocarbon groups having 3 to 6, preferably 5 or 6, carbon ring members, such as cyclopenten-1-yl, cyclopenten-3-yl, cyclohexen-1-yl, cyclohexen-3-yl, cyclohexen-4-yl.

Alkynyl and the alkynyl moieties for example in alkynyloxy, alkynylamino: straight-chain or branched hydrocarbon groups having two or more carbon atoms, for example 2 to 4, 2 to 6 or 3 to 6 carbon atoms, and a triple bond in any position, for example C2-C6-alkynyl, such as ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl, 1-pentynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 1-methyl-3-butynyl, 2-methyl-3-butynyl, 3-methyl-1-butynyl, 1,1-dimethyl-2-propenyl, 1-ethyl-2-propynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-
pentynyl, 1-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-3-pentynyl, 2-methyl-4-pentynyl, 3-methyl-1-pentynyl, 3-methyl-4-pentynyl, 4-methyl-1-pentynyl, 4-methyl-2-pentynyl, 1,1-dimethyl-2-butynyl, 1,1-dimethyl-3-butynyl, 1,2-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl, 3,3-dimethyl-1-butynyl, 1-ethyl-2-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl, 1-ethyl-1-methyl-2-propynyl.

Alkoxy: alkyl as defined above which is attached via an oxygen atom, for example methoxy, ethoxy, n-propoxy, 1-methylethoxy, butoxy, 1-methylpropoxy, 2-methylpropoxy or 1,1-dimethylethoxy, pentoxy, 1-methylbutoxy, 2-methylbutoxy, 3-methylbutoxy, 1,1-dimethylpropoxy, 1,2-dimethylpropoxy, 2,2-dimethylpropoxy, 1-ethylpropoxy, hexoxy, 1-methylpent oxy, 2-methylpent oxy, 3-methylpent oxy, 4-methylpent oxy, 1,1-dimethylbutoxy, 1,2-dimethylbutoxy, 1,3-dimethylbutoxy, 2,2-dimethylbut oxy, 2,3-dimethylbutoxy, 3,3-dimethylbutoxy, 1-ethylbutoxy, 2-ethylbutoxy, 1,1,2-trimethylpropoxy, 1,2,2-trimethylpropoxy, 1-ethyl-1-methylpropoxy or 1-ethyl-2-methylpropoxy.

3- to 7-membered monocyclic or 9- or 10-membered bicyclic saturated, unsaturated or aromatic heterocycle which contains 1, 2, 3, or 4 heteroatoms selected from the group consisting of O, N and S and which can be attached via C or N. Preferred from among these are 5- or 6-membered heterocycles.

Saturated or unsaturated heterocyclic groups which are attached via N or C, such as: pyridazin-3-yl, pyridazin-4-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrazin-2-yl, isoxazol ine-3-yl, isoxazoline-4-yl, isoxazolin 5-yl, isothiazol-3-yl, isothiazol-4-yl, isothiazol-5-yl, imidazol-1-yl, imidazol-2-yl, imidazol-4-yl, oxazol-2-yl, oxazolin 2-yl, thiazolin-2-yl and morpholinyl.

Heteroaromatic groups which are attached via N or C, such as: pyrazol-3-yl, 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, pyrazol-1-yl, pyrazol-3-yl, pyrazol-4-yl, isoxazol-3-yl, isoxazol-4-yl, isoxazol-5-yl, imidazol-5-yl, oxazol-2-yl, oxazol-4-yl, oxazol-5-yl, thiazol-2-yl, thiazol-4-yl, thiazol-5-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrimidin-5-yl, pyrazin-4-yl, pyrazin-2-yl, [1H]-tetrazol-5-yl and [2H]-tetrazol-5-yl.

The compounds of the formula I may, depending on the substitution pattern, contain one or more further centers of chirality. Accordingly, the compounds according to the invention can be present as pure enantiomers or diastereomers or as enantiomer or diastereomer mixtures. The invention provides both the pure enantiomers or diastereomers and their mixtures.

The compounds of the formula I may also be present in the form of the N-oxides and/or of their agriculturally useful salts, the type of salt generally not being important. Suitable salts are generally the salts of those cations or the acid addition salts of those acids whose cations and anions, respectively, have no adverse effect on the herbicidal activity of the compounds I.
Suitable cations are in particular ions of the alkali metals, preferably lithium, sodium or potassium, of the alkaline earth metals, preferably calcium or magnesium, and of the transition metals, preferably manganese, copper, zinc or iron. Another cation that may be used is ammonium, where, if desired, one to four hydrogen atoms may be replaced by \(\text{Cl}_4\)-alkyl, hydroxy-\(\text{Cl}_4\)-alkyl, \(\text{Cl}_4\)-alkoxy-\(\text{Cl}_4\)-alkyl, hydroxy-\(\text{Cl}_4\)-alkoxy-\(\text{Cl}_4\)-alkyl, phenyl or benzyl, preferably ammonium, dimethylammonium, diisopropylammonium, tetramethylammonium, tetrabutylammonium, 2-(2-hydroxyeth-1-oxy)eth-1-ylammonium, di(2-hydroxyeth-1-yl)ammonium, trimethylbenzlammonium. Another suitable ammonium cation is the pyridine nitrogen atom of the formula I quaternized by alkylation or arylation. Also suitable are phosphonium ions, sultonium ions, preferably tri(\(\text{Cl}_4\)-alkyl)sulfoxonium, or sulfoxonium ions, preferably tri(\(\text{Cl}_4\)-alkyl)sulfoxonium.

Anions of suitable acid addition salts are primarily chloride, bromide, fluoride, hydrogensulfate, sulfate, dihydrogenphosphate, hydrogenphosphate, nitrate, bicarbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate and also the anions of \(\text{Cl}_4\)-alkanoic acids, preferably formate, acetate, propionate, butyrate or trifluoroacetate.

With respect to the variables, the particularly preferred embodiments of the intermediates correspond to those of the groups of the formula I.

In a particular embodiment, the variables of the compounds of the formula I have the following meanings, these meanings, both on their own and in combination with one another, being particular embodiments of the compounds of the formula I:

In one preferred embodiment of the compounds of the formula I, \(R\) is 0-R^\(a\), in which \(R^a\) is H, \(\text{Cs}-\text{Cs}\)-alkenyl, \(C_3-C_6\)-haloalkenyl, \(C_3-C_6\)-alkynyl, \(C_3-C_6\)-haloalkynyl, \(\text{Cl}_4\)-alkylcarbonyl, such as \(C(0)\text{CH}_3\), \(C(0)\text{CH}_2\text{CH}_3\), \(C(0)\text{CH}(CH_3)_2\) or \(C(0)\text{C}(_{3}\text{CH}_3\text{)}\); \(\text{Cl}_4\)-cycloalkylcarbonyl, such as cyclopropylcarbonyl, cyclopentylcarbonyl or cyclohexylcarbonyl; \(C_2-C_6\)-alkenylcarbonyl, such as \(C(0)\text{CH} = \text{CH}_2\) or \(C(0)\text{CH}_{2}\text{CH} = \text{CH}_2\), optionally subst. benzoyl, such as \(C(0)\text{C}_6\text{H}_5\), \(C(0)[2\text{-CH}_3\text{-C}_6\text{H}_4]\), \(C(0)[4\text{-CH}_3\text{-C}_6\text{H}_4]\).

\(C(0)[2\text{-F-C}_6\text{H}_4]\), \(C(0)[4\text{-F-C}_6\text{H}_4]\), or optionally subst. heteroaryl, such as pyridyl, which is attached via a carbonyl group. Particularly preferably, \(R^a\) is H, \(C_3-C_4\)-alkenyl, \(C_3-C_4\)-alkynyl or \(\text{Cl}_4\)-alkylcarbonyl. Especially particularly preferably, \(R^a\) is selected from the group consisting of H, \(\text{CH}_2\text{CH} = \text{CH}_2\), \(\text{CH}_2\text{C} = \text{CH}_2\), \(\text{CH}_3\), \(C(0)\text{CH}_3\), \(C(0)\text{CH}_2\text{CH}_3\), \(C(0)\text{CH}(_{3}\text{CH}_3\text{)}\), \(C(0)\text{C}(_{3}\text{CH}_3\text{)}\), \(C(0)\text{-C}_6\text{H}_5\), \(C(0)\text{-C}_6\text{H}_5\), \(C(0)\text{-CH}_2\text{C}_6\text{H}_5\), \(C(0)\text{-CH}_2\text{C}_6\text{H}_5\), \(C(0)\text{-Cl}\), \(C(0)\text{CF}_3\), \(C(0)\text{CH}(_{3}\text{OCH}_2)\), \(C(0)\text{N}(\text{CH}_3)_2\) and \(C(0)\text{OCH}(_{2}\text{CH}_3)\).

In a further preferred embodiment of the compounds of the formula I, \(R\) is \(\text{OS}(0)_n\)-\(R^a\), where \(n\) is preferably 0 or 2, in particular 2, such as, for example, \(\text{OS}(0)\text{-CH}_3\), \(\text{OS}(0)\text{-C}_2\text{H}_5\), \(\text{OS}(0)\text{-C}_3\text{H}_7\), \(\text{OS}(0)\text{-C}_6\text{H}_5\) or \(\text{OS}(0)\text{-}(4\text{-CH}_3\text{-C}_6\text{H}_4)\).

In a further preferred embodiment, \(R^1\) is 0-\(S(0)_n\)-NR\(R^a\), which has in particular the groups NR\(R^a\) mentioned below as being preferred.

\(R^a\) and \(R^a\) are preferably \(\text{Cs}\)-alkyl, \(\text{Cl}_4\)-haloalkyl, \(Z\)-\(C_3-C_6\)-cycloalkyl, \(Z\)-\(\text{Cl}_4\)-alkyl.
alkoxy, Z-\textit{ci}-Cs-haloalkoxy, Z-phenyl, Z-C(=0)-R or Z-hetaryl. Here, preference is given to CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}, n-propyl, CH(CH\textsubscript{3})\textsubscript{2}, butyl, 2-chloroethyl, cyclopentyl, cyclohexyl, 2-ethoxyethyl, 2-chloroethoxy, phenyl, pyrimidines or triazines whose rings are unsubstituted or substituted. Here, preferred substituents are c \textit{\&}C\textsubscript{4} -alkylcarbonyl or c \textit{\&}C\textsubscript{1}-C\textsubscript{2}-haloalkylcarbonyl, in particular C(=0)-CH\textsubscript{3}, C(=0)-C\textsubscript{2}H\textsubscript{5}, C(=0)-CH(CH\textsubscript{3})\textsubscript{2}, C(=0)-butylcarbonyl and C(=0)-Ci-C\textsubscript{2}Cl. Particularly preferred aspects of the group NR'R" are N(di-c\textit{\&}C\textsubscript{4}-alkyl), in particular N(CH\textsubscript{3})\textsubscript{2}, N(CH\textsubscript{2})\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}, N(CH\textsubscript{3})\textsubscript{2}C\textsubscript{2}H\textsubscript{5} and N(CH\textsubscript{3})\textsubscript{2}CH(CH\textsubscript{3})\textsubscript{2}.

Further particularly preferred aspects of NR'R" are NH-aryl, where aryl is preferably phenyl which is substituted - in particular in the 2- and 6-position - by one to three identical or different halogen, CH\textsubscript{3}, halo-c\textit{\&}C\textsubscript{1}-c\textsubscript{2}-alkyl, halo-c\textit{\&}C\textsubscript{1}-c\textsubscript{2}-alkoxy and carboxyl groups, such as 2-Cl\textsubscript{2}-COOH-C\textsubscript{6}H\textsubscript{5}, 2,6-Cl\textsubscript{2}-C\textsubscript{6}H\textsubscript{5}, 2,6-F\textsubscript{2}-C\textsubscript{6}H\textsubscript{5}, 2,6-Cl\textsubscript{2} 3-C\textsubscript{6}H\textsubscript{5}, 2-CF\textsubscript{3} 6-CH\textsubscript{2}CF\textsubscript{2}C\textsubscript{6}H\textsubscript{5}, 2-CF\textsubscript{3} 6-OOCF\textsubscript{3}C\textsubscript{6}H\textsubscript{5} and 2-CF\textsubscript{3} 6-CH\textsubscript{2}CHF\textsubscript{2}C\textsubscript{6}H\textsubscript{5}.

In a further preferred embodiment of the invention, R\textsuperscript{a} is a 5- or 6-membered heterocycle optionally substituted by R\textsuperscript{b} as defined above, which preferably has either 1, 2, 3 or 4 nitrogen atoms or 1 oxygen or 1 sulfur atom and if appropriate 1 or 2 nitrogen atoms as ring members and which is unsubstituted or may have 1 or 2 substituents selected from R\textsuperscript{b}. Preference is given to saturated or unsaturated groups attached via nitrogen, such as, for example:

Heteroaromatic groups: pyrazidin-3-yl, pyridazin-4-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrimidin-5-yl, pyrazin-2-yl, 2-furyl, 3-furyl, 2-thieryl, 3-thieryl, pyrazol-1-yl, pyrazol-3-yl, pyrazol-4-yl, isoxazol-3-yl, isoxazol-4-yl, isoxazol-5-yl, isothiazol-3-yl, isothiazol-4-yl, isothiazol-5-yl, imidazol-1-yl, imidazol-2-yl, imidazol-4-yl, oxazol-2-yl, oxazol-4-yl, oxazol-5-yl, thiazol-2-yl, thiazol-4-yl and thiazol-5-yl;

In another aspect, R\textsuperscript{a} is a heteroaromatic group attached via carbon, such as pyrazol-3-yl, imidazol-5-yl, oxazol-2-yl, thiazol-2-yl, thiazol-4-yl, thiazol-5-yl, pyridin-2-yl, pyridin-3-yl, pyridin-4-yl, pyrimidin-2-yl, pyrimidin-4-yl, pyrimidin-5-yl, pyridazin-4-yl, pyrazin-2-yl, [1 H]-tetroazol-5-yl and [2 H]-tetroazol-5-yl, where each of the heterocycles mentioned here in an exemplary manner may have 1 or 2 substituents selected from R\textsuperscript{b}. Preferred groups R\textsuperscript{b} are, in this case, in particular F, Cl, CN, N\textsubscript{2}, CH\textsubscript{3}, C\textsubscript{2}H\textsubscript{5}, OCH\textsubscript{3}, OC\textsubscript{2}H\textsubscript{5}, OCHF\textsubscript{2}, OCF\textsubscript{3} and CF\textsubscript{3}.

In particular preferred embodiments of the compounds of the formula I, R is selected from the group consisting of OH, OCH\textsubscript{2}CH=CH\textsubscript{2}, OCH\textsubscript{2}C=CH, OCH\textsubscript{3}, OC(0)CH\textsubscript{3}, OC(0)CH\textsubscript{2}CH\textsubscript{3}, OC(0)CH(\textsubscript{2})\textsubscript{2}, OC(0)C(\textsubscript{2})\textsubscript{3}, OC(0)-c-C\textsubscript{3}H\textsubscript{5}, OC(0)-C\textsubscript{6}H\textsubscript{5}, OC(0)-CH\textsubscript{2}C\textsubscript{6}H\textsubscript{5}, OC(0)-CH\textsubscript{2}C\textsubscript{6}H\textsubscript{5}, OC(0)-CH\textsubscript{2}Cl, OC(0)-CF\textsubscript{3}, OC(0)-CH\textsubscript{2}OCH\textsubscript{3}, OC(0)-N(CH\textsubscript{3})\textsubscript{2} and OC(0)-OCH\textsubscript{2}CH\textsubscript{3}.

Groups R\textsuperscript{b} preferred for the compounds of the formula I are selected from the group consisting of OH, c\textsubscript{1}-c\textsubscript{2}-alkyl, c \textit{\&}C\textsubscript{4}-haloalkyl, C\textsubscript{3}-c\textsubscript{4}-alkenyl, C\textsubscript{3}-c\textsubscript{5}-alkynyl, Z-c\textsubscript{1}-c\textsubscript{6}-alkoxy, Z-c\textsubscript{1}-C\textsubscript{4}-haloalkoxy, Z-C\textsubscript{3}-C\textsubscript{5}-alkenyloxy, Z-C\textsubscript{3}-C\textsubscript{5}-alkynyloxy and NR'R".

For the compounds of the formula I, the groups R\textsuperscript{b} are preferably selected from the
group consisting of halogen, oxo (=O), =N-R, C1-C4-alkyl, C1-C4-haloalkyl, C2-C6-alkenyl, C2-C6-alkynyl, Z-C1-C4-haloalkoxy, C1-C4-alkoxy-C1-C4-alkyl, C1-C4-alkylthio-C1-C4-alkyl, C1-C4-alkoxy-C1-C4-alkyl, S(0)4, where Rf is preferably C1-C4-alkyl or C1-C4-haloalkyl and n is 0, 1 or 2.

Particularly preferably, R is a group selected from the group consisting of halogen, C1-C4-alkyl, C1-C4-haloalkyl, C1-C4-alkoxy, C1-C4-alkylthio, C1-C4-alkoxy-C1-C4-alkyl, C1-C4-alkylthio-C1-C4-alkyl, C1-C4-haloalkoxy, C3-C4-alkenyl, C3-C4-alkynyl and =N-C1-C4-alkoxy.

Two groups Rf together may form a ring which preferably has three to seven ring members and, in addition to carbon atoms, may also contain heteroatoms from the group consisting of O, N and S and which may be unsubstituted or substituted by further groups Rf. These substituents Rf are preferably selected from the group consisting of halogen, C1-C4-alkyl, C1-C4-alkoxy and C1-C4-haloalkyl.

Groups R and Rf are selected independently of one another if a plurality of such groups is present.

In a preferred embodiment of the compounds of the formula I, Rf is halogen, CN, N02, C1-C4-alkyl, C1-C4-haloalkyl, C1-C4-alkoxy-C1-C4-alkyl, C1-C4-alkylthio-C1-C4-alkyl, C1-C4-alkoxy-C1-C4-alkyl, C1-C4-alkylthio-C1-C4-alkyl, C1-C4-alkoxy-C1-C4-alkyl, C1-C4-haloalkoxy, C3-C4-alkenyl, C3-C4-alkynyl, C1-C4-haloalkoxy-C1-C4-alkoxy, C1-C4-alkoxy-C1-C4-alkoxy, S(0)4, C1-C4-alkyl and S(0)4-C1-C4-halolalkyl. Particularly preferably, Rf is selected from the group consisting of F, Cl, Br, N02, CH3, CF3, OCH3, OCF3, SCF3, SO2CH3, OCH2CH2OCH3, CH2OCH2CH2OCH3, CH2OCH2CF3.

In a further preferred embodiment of the compounds of the formula I, A is C-R2. These compounds correspond to the formula I.1

where the variables have the meanings defined at the outset and preferably the meanings mentioned as preferred.

Particularly preferably, in the compounds of the formula I.1, the group Rf is halogen, C1-C4-alkyl, C1-C4-haloalkyl, C1-C4-alkoxy-C1-C4-alkyl, C1-C4-alkoxy-
c 1-4-alkoxy-1-4-alkyl, c 1-4-alkoxy, c 1-4-haloalkoxy, c 1-4-alkylthio, c 1-4-haloalkylthio or c 1-4-alkylsulfonyl, in particular F, Cl, Br, N02, CH3, CF3, OCH3, OCF3, OCH F2, SCFs SCHF2, SO2CH3, CH2OCH2CH2OCH3;

R3 is H, halogen, CN, N02, c 1-4-alkyl, c 1-4-haloalkyl, c 1-4-alkoxy, c 1-4-alkylthio, c 1-4-alkylsulfonyl, in particular H, F, Cl, CN, N02, CH3, CH2CH3, CF3, CHF2, OCH3, OCF3, OCHF2, SCH2, SO2CH3 or S02CH2CH3;

R4 is H or halogen, in particular H, F or Cl.

R2 is preferably a 3- to 7-membered monocyclic or 9- or 10-membered bicyclic saturated, partially unsaturated or aromatic heterocycle which is attached via Z1 and contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S, where the cyclic groups are unsubstituted or partially or fully substituted by groups Rb.

In a further preferred aspect of the compounds of the formula 1.1, R2 is a 3- to 7-membered monocyclic or 9- or 10-membered bicyclic saturated, partially unsaturated or aromatic heterocycle which is attached directly or via c 1-4-alkyleneoxy, C1-C4-oxyalkylene or c 1-4-alkyleneoxy -c1-C4-alkylene, which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S and which may be substituted as defined at the outset.

A preferred aspect of group R2 relates to five- or six-membered saturated or partially unsaturated heterocycles, such as, for example, isoxazoline, tetrazolone, 1,2-dihydro-tetrazolone, 1,4-dihydropyrazolone, tetrahydrofuran, dioxolane, piperidine, morpholine and pyrazine. Particular preference is given to 3-isoxazoline, 5-isoxazoline, 1-tetrazolone, 2-tetrazolone, 1,3-dioxolane-2 and N-morpholine. Especially preferred are: 4,5-dihydroisoxazole-3, unsubstituted or substituted by 5-CH3, 5-CH2F or 5-CH F2; 4,5-dihydroisoxazole-5, unsubstituted or substituted by 3-CH3, 3-OCH3, 3-CH2OCH3, 3-CH2SCH3; 1-methyl-5-oxo-1,5-dihydropyrazole-2; 4-methyl-5-oxo-4,5-dihydropyrazole-1 and N-morpholine.

A further preferred aspect of group R2 relates to five- or six-membered aromatic heterocycles, such as, for example, isoxazole, pyrazole, thiazole, furyl, pyridine, pyrimidine and pyrazine. Particular preference is given to 3-isoxazole, 5-isoxazole, 3-pyrazole, 5-pyrazole, 2-thiazole, 2-oxazole, 2-furyl. Especially preferred are: 3-isoxazole, 5-methyl-3-isoxazole, 5-isoxazole, 3-methyl-5-isoxazole, 1-methyl-1H-pyrazole-3, 2-methyl-2H-pyrazole-3 and thiazole-2.

In a preferred aspect of heterocyclic groups R2, the groups Rb are preferably C1-C4-alkyl, c 1-4-haloalkyl, c 1-4-alkoxy, c 1-4-alkoxy -c1-C4-alkyl, c 1-4-alkylthio -c1-C4-alkyl, c 1-4-alkylthio or c 1-4-alkylsulfonyl. Especially preferred are CH3, C2H5, CH2F, CF2H, CF3, OCH3, CH2OCH3, CH2SCH3, SCH3 and SO2CH3.

In a preferred aspect, the group Z1 is a covalent bond.

In a further preferred aspect, the group Z1 is c 1-4-alkyleneoxy, in particular OCH2 or OCH2CH2.

In a further preferred aspect, the group Z1 is c 1-4-oxyalkylene, in particular CH2O or CH2CH2O.
In a further preferred aspect, the group $Z^i$ is $\text{Ci-C4-alkyleneoxy -Ci-C4-alkylene}$, in particular $\text{OCH}_2\text{OCH}_2$ or $\text{OCH}_2\text{CH}_2\text{OCH}_2$.

Particularly preferred aspects of heterocycles attached via $Z^i$ include tetrahydrofuran-2-ylmethoxymethyl and $[\text{1,3}]$dioxolan-2-ylmethoxy.

In a further preferred aspect of the compounds of the formula $1,1$, $R^2$ is phenyl which may be partially or fully substituted - preferably mono-, di- or trisubstituted, in particular monosubstituted - by groups $R^6$. Groups $R^6$ preferred for this aspect include: $\text{Cl-C}_2$-alkyl, $\text{Cl-C4-alkoxy}$, $\text{Cl-C}_2$-haloalkyl, $\text{Cl-C}_2$-alkoxy-$\text{Cl-C}_2$-alkyl or $\text{Cl-C}_2$-alkoxy-$\text{Cl-C}_2$-alkoxy. Particular preference is given to $\text{CH}_3$, $\text{C}_2\text{H}_5$, $\text{OCH}_3$, $\text{OC}_2\text{H}_5$, $\text{CHF}_2$, $\text{CF}_3$, $\text{OCHF}_2$, $\text{OCF}_3$, $\text{OCH}_2\text{OCH}_3$ and $\text{OCH}_2\text{CH}_2\text{OCH}_3$. Special preference is given to alkoxyl, such as $\text{OCH}_3$ or $\text{OC}_2\text{H}_5$. A group $R^6$ is preferably in position 4. A particularly preferred phenyl group $R^2$ is a group $P$:

\[
\begin{array}{c}
\text{R}^3 \quad \text{R}^4 \\
\text{#} \quad \text{R}^4 \quad \text{R}^4
\end{array}
\]

in which # denotes the bond via which the group $R^2$ is attached and the substituents are selected from $R^6$ and are in particular:

$R^3 = \text{H}$ or $\text{OCH}_3$; and

$R^4 = \text{H, CH}_3$, $\text{CF}_3$, $\text{OCH}_3$, $\text{OCH}_2\text{OCH}_3$ or $\text{OCH}_2\text{CH}_2\text{OCH}_3$.

In a further preferred aspect of the compounds of the formula $1,1$, $R^2$ is an aliphatic group selected from the group consisting of $\text{Cl-C}_6$-alkyl, $\text{Cl-C4-alkoxy}$-$\text{Cl-C4}$-alkyl, $\text{Cl-C4}$-haloalkoxy-$\text{Cl-C4}$-alkyl, $\text{Cl-C}_2$-alkenyl, $\text{Cl-C}_2$-alkynyl, $\text{Cl-C}_2$-alkoxy, $\text{Cl-C}_4$-haloalkoxy, $\text{Cl-C}_2$-alkenylcarbonyl, $\text{Cl-C}_2$-alkoxy-carbonyl and $S(0)_2$-$\text{Cl-C4}$-alkyl and $S(0)_2$-$\text{Cl-C8}$-haloalkyl.

Particularly preferred aliphatic groups $R^2$ include $\text{C}_2$-$\text{c-C4}$-alkenyl, $\text{C}_2$-$\text{c-C4}$-alkynyl, $\text{Cl-C}_2$-haloalkoxy-$\text{Cl-C}_2$-alkyl, $\text{c-C}_2$-alkenylcarbonyl or $\text{c-C}_2$-alkoxy-carbonyl and $S(0)_2$-$\text{Cl-C4}$-alkyl. Special preference is given to $\text{CH}_2$, $\text{CH}=$ $\text{CHCH}_3$, $\text{CH}_2\text{OCH}_2\text{CF}_3$, $\text{OC}_2\text{H}_5$, $\text{OCH}_2\text{CH}=$ $\text{CH}_2$, $\text{OCH}_2\text{C}=$ $\text{CH}$, $\text{OCH}_2\text{CH}_2\text{OCH}_3$, $\text{COOCH}_3$, $\text{COOC}_2\text{H}_5$ and $\text{S0}_2$ $\text{C}_2$ $\text{H}_5$ and $\text{S0}_2$ $\text{CH}($ $\text{CH}_3)_2$.

In a further preferred aspect, $R^2$ together with $R^1$ or $R^3$ forms a five- to ten-membered mono- or bicyclic saturated or partially unsaturated ring which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S and which may be partially or fully substituted by groups $R^6$. Together with the phenyl group which carries the groups $R^1$ to $R^5$, a nine- to fifteen-membered bi- or tricyclic, optionally heterocyclic, ring system results. Suitable are, for example, the following: 2,3-dihydrobenzo[b]thiophene 1,1-dioxide, thiochroman 1,1-dioxide, 2,3-dihydrobenzo-
[1,4]dithiin 1,1,4,4-tetraoxide, 3H-benzothiazol-2-one, quinoline and saccharin.

Preferably, R² together with R¹ or R³ forms a five- or six-membered monocyclic, saturated or partially unsaturated ring.

Preferred bicyclic ring systems comprising the phenyl group attached to the dioxo-dihydrothiatriazanaphthalene skeleton and R¹ and R² are, for example, groups A to D:

\[
\begin{align*}
A & \quad B \\
R^4 & \quad R^4 \\
R^3 & \quad R^3 \\
\# & \quad \# \\
(R^b)_{0-3} & \quad (R^b)_{0-3}
\end{align*}
\]

# denotes the bond to the skeleton.

Preferred bi- and tricyclic ring systems comprising the phenyl group attached to the dioxodihydrothiatriazanaphthalene skeleton and R² and R³ contain one or two sulfur atoms and optionally one nitrogen atom. Preferred are groups E to L:

\[
\begin{align*}
E & \quad F \\
R^4 & \quad R^4 \\
\# & \quad \# \\
(R^b)_{0-4} & \quad (R^b)_{0-5}
\end{align*}
\]

\[
\begin{align*}
G & \quad H \\
R^4 & \quad R^4 \\
\# & \quad \# \\
(R^b)_{0-6} & \quad (R^b)_{0-9}
\end{align*}
\]

\[
\begin{align*}
I & \quad J \\
R^4 & \quad R^4 \\
\# & \quad \# \\
(R^b)_{0-4} & \quad (R^b)_{0-5}
\end{align*}
\]

\[
\begin{align*}
K & \quad L \\
R^4 & \quad R^4 \\
\# & \quad \# \\
(R^b)_{0-6} & \quad (R^b)_{0-6}
\end{align*}
\]
In groups A to L, the groups $R^b$ independently of one another are preferably halogen, $C_1$-$C_4$-alkyl, $C_1$-$C_4$-alkoxy, $C_1$-$C_4$-alkoxycarbonyl, $C_1$-$C_4$-alkyl carbonyl, $C_1$-$C_4$-alkylthio, $C_1$-$C_4$-haloalkyl, $C_1$-$C_4$-haloalkoxy, $C_1$-$C_4$-haloalkylthio, $C_3$-$C_4$-alkenyl, $C_3$-$C_4$-alkynyl, $=N$-$C_1$-$C_4$-alkoxy.

The compounds of the formula I in which $R^2$ is one of the groups A to L correspond to the formulae I A and I L.

In the formulae I A to I L, $R^i$ is preferably halogen, $C_1$-$C_4$-alkyl, $C_1$-$C_4$-alkoxy or $C_1$-$C_4$-haloalkyl.

The following examples represent particularly preferred groups A to L:

$R^{3A}, R^{3B}, R^{3C}$ and $R^{3D}$ are preferably halogen, $C_1$-$C_4$-alkyl, $C_1$-$C_4$-haloalkyl, $C_1$-$C_4$-alkoxycarbonyl, in particular $F, Cl, Br, CH_3, CF_3$ or $OCH_3$.

$R^{bE1}, R^{bE2}$ are preferably $H, C_1$-$C_4$-alkyl or $C_1$-$C_4$-alkoxy, in particular $R^{bE1}$ is $H$ or $CH_3$;

$R^{bE2}$ is $H$, $CH_3$ or $OCH_3$.

$R^{bL}$ is preferably $C_1$-$C_4$-haloalkoxy, in particular $OCH_2CH_2F$.

$R^{bJ1}$ is preferably $C_1$-$C_4$-alkoxy, in particular $OCH_3$ or $OCH_2CH_3$.

$R^{bJ2}$ is preferably $C_1$-$C_4$-alkoxy, in particular $OCH_3$ or $OCH_2CH_3$.

$R^{bL}$ is preferably $C_1$-$C_4$-alkyl or $C_3$-$C_4$-alkenyl, in particular $CH_3$, $CH_2CH_3$, $CH_2CH_2CH_3$, $CH(CH_3)_2$ or $CH_2CH=CH_2$.

In a further preferred embodiment of the compounds of the formula I, A is $N$. These compounds correspond to formula 1.2
in which the variables have the meanings defined at the outset and preferably those mentioned above. Especially preferably, in compounds of the formula I the group

\[ \text{R}^1 \text{ is nitro, } \text{C}_1-\text{C}_4-\text{alkyl, } \text{C}_1-\text{C}_4-\text{haloalkyl, } \text{C}_1-\text{C}_4-\text{alkoxy-} \text{C}_1-\text{C}_4-\text{alkyl, } \text{C}_1-\text{C}_4-\text{alkoxy-} \text{C}_1-\text{C}_4-\text{haloalkoxy, } \text{C}_1-\text{C}_4-\text{haloalkylthio} \text{ or } \text{C}_1-\text{C}_4-\text{alkylsulfonyl, in particular NO}_2, \text{CH}_3, \text{CF}_3, \text{CH}_2\text{OCH}_2\text{CH}_2\text{OCF}_3, \text{OCH}_3, \text{OCF}_3, \text{OCH}_2\text{F}_2, \text{SCF}_3, \text{SCH}_2\text{F}_2, \text{SO}_2\text{CH}_3; } \]

\[ \text{R}^3 \text{ is H, CN, NO}_2, \text{C}_1-\text{C}_4-\text{alkyl, } \text{C}_1-\text{C}_4-\text{haloalkyl, } \text{C}_1-\text{C}_4-\text{alkoxy-} \text{C}_1-\text{C}_4-\text{haloalkoxy, } \text{S}(0)_{n-\text{C}_1-\text{C}_4-\text{haloalkyl}, \text{where } n \text{ is preferably } 0 \text{ or } 1. \text{Particularly preferably, } \text{R}^3 \text{ is selected from the group consisting of } \text{H, F, Cl, Br, CN, NO}_2, \text{CH}_3, \text{CF}_3, \text{CHF}_2, \text{OCH}_3, \text{OCF}_3, \text{OCH}_2\text{F}_2, \text{SCH}_3, \text{SCF}_3, \text{SCH}_2\text{F}_2, \text{SO}_2\text{CH}_3, \text{SO}_2\text{CF}_2\text{CH}_3. } \]

In a further preferred embodiment of the compounds of the formula I, the group \( \text{R}^4 \) is hydrogen or halogen, particularly preferably \( \text{H, F or Cl, in particular H. } \)

In a further preferred embodiment of the compounds of the formula I, at least one of the groups \( \text{R}^5 \) and \( \text{R}^6 \), preferably both groups, is/are hydrogen.

\[ \text{R}^x \text{ is preferably H, C}_1-\text{C}_6-\text{alkyl, such as } \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{CH(Ch}_3)_2, \text{n-C}_3\text{H}_9, \text{or C(CH}_3)_3; \text{C}_3-\text{C}_6-\text{cycloalkyl-} \text{C}_1-\text{C}_4-\text{alkyl, such as cyclopropylmethyl, } \text{C}_3-\text{C}_6-\text{alkenyl, such as CH}_2\text{CH=CH}_2, \text{CH}_2\text{C(CH}_3)\text{=CH}_2, \text{CH}_2\text{CH}_2\text{H=CH}_2, \text{CH}_2\text{CH}_2\text{C(CH}_3)\text{-CH}_2, } \text{CH}_2\text{CH}_2\text{CH}_2=\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}=\text{C(CH}_3)\text{-CH}_2, \text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}=\text{C(CH}_3)\text{-CH}_2, \text{or optionally subst. phenyl, such as C}_6\text{H}_5, 4-\text{CH}_3\text{-C}_6\text{H}_4, 4-\text{F-CH}_3\text{-C}_6\text{H}_4 \text{or S(0)H, where } \text{R}^N \text{ is C}_1-\text{C}_6-\text{haloalkyl, such as CH}_2\text{CF}_3, \text{CH}_2\text{CH}_2\text{F}_2. \text{Especially preferably, } \text{R}^x \text{ is } \text{C}_1\text{-alkyl } \text{or } \text{C}_1-\text{C}_4-\text{haloalkyl. } \]

A further embodiment relates to the N-oxides of the compounds of the formula I.

A further embodiment relates to salts of the compounds of the formula I, in particular those which are obtainable by quaternization of a pyridazine nitrogen atom, which may preferably take place by alkylation or arylation of the compounds of the formula I.
Preferred salts of the compounds are thus the N-alkyl salts, in particular the N-methyl salts, and the N-phenyl salts.

In particular with a view to their use, preference is given to the compounds of the formula I compiled in the tables below, which compounds correspond to the formulae 1.1 A and 1.2A. The groups mentioned for a substituent in the tables are furthermore per se, independently of the combination in which they are mentioned, a particularly preferred aspect of the substituent in question.

Table 1
Compounds of the formula I in which R^x is CH3, R is OH, R^5 is H and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A

Table 2
Compounds of the formula I in which R^x is CH3, R is OCH2CH=CH2, R^5 is H and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A

Table 3
Compounds of the formula I in which R^x is CH3, R is OCH2C≡ CH, R^5 is H and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A

Table 4
Compounds of the formula I in which R^x is CH3, R is OH, R^5 is CH3 and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A

Table 5
Compounds of the formula I in which R^x is CH3, R is OCH2CH=CH2, R^5 is CH3 and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A

Table 6
Compounds of the formula I in which R^x is CH3, R is OCH2C≡ CH, R^5 is CH3 and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A

Table 7
Compounds of the formula I in which R^x is CH3, R is OH, R^5 is CH2CH3 and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A

Table 8
Compounds of the formula I in which R^x is CH3, R is OCH2CH=CH2, R^5 is CH2CH3 and the combination of R^1, R^3 and, if appropriate, R^2 for a compound corresponds in each case to one row of Table A
Table 9
Compounds of the formula I in which R is CH₃, R is OCH₂C≡CH, R₅ is CH₂CH₃ and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 10
Compounds of the formula I in which R is CH₃, R is OH, R₅ is OCH₃ and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 11
Compounds of the formula I in which R is CH₃, R is OCH₂CH=CH₂, R₅ is OCH₃ and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 12
Compounds of the formula I in which R is CH₃, R is OCH₂C≡CH, R₅ is OCH₃ and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 13
Compounds of the formula I in which R is CH₃, R is OH, R₅ is SCH₃ and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 14
Compounds of the formula I in which R is CH₃, R is OCH₂CH=CH₂, R₅ is SCH₃ and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 15
Compounds of the formula I in which R is CH₃, R is OCH₂C≡CH, R₅ is SCH₃ and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 16
Compounds of the formula I in which R is CH₂CH₃, R is OH, R₅ is H and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 17
Compounds of the formula I in which R is CH₂CH₃, R is OCH₂CH=CH₂, R₅ is H and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 18
Compounds of the formula I in which R is CH₂CH₃, R is OCH₂C≡CH, R₅ is H and the combination of R¹, R³ and, if appropriate, R² for a compound corresponds in each case to one row of Table A

Table 19
Compounds of the formula I in which R is CH₂CH₃, R is OH, R₅ is CH₃ and the
combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 20

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OCH}_2\text{CH=CH}_2 \), \( R^5 \) is \( \text{CH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 21

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OCH}_2\text{CH=CH}_2 \), \( R^5 \) is \( \text{CH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 22

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OH} \), \( R^5 \) is \( \text{CH}_2\text{CH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 23

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OCH}_2\text{CH=CH}_2 \), \( R^5 \) is \( \text{CH}_2\text{CH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 24

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OH} \), \( R^5 \) is \( \text{OCH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 25

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OH} \), \( R^5 \) is \( \text{OCH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 26

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OCH}_2\text{CH=CH}_2 \), \( R^5 \) is \( \text{OCH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 27

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OCH}_2\text{CH=CH}_2 \), \( R^5 \) is \( \text{OCH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 28

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OH} \), \( R^5 \) is \( \text{SCH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 29

Compounds of the formula I in which \( R^x \) is \( \text{CH}_2\text{CH}_3 \), \( R \) is \( \text{OCH}_2\text{CH=CH}_2 \), \( R^5 \) is \( \text{SCH}_3 \) and the combination of \( R^1, R^3 \) and, if appropriate, \( R^2 \) for a compound corresponds in each case to one row of Table A

Table 30
Table 3
Compounds of the formula I in which $R^x$ is CH$_2$CH$_3$, $R$ is OCH$_2$C=CH, $R^5$ is SCH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 4
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OH, $R^5$ is OCH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 5
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$CH=CH, $R^5$ is H and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 6
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$C=CH, $R^5$ is H and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 7
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OH, $R^5$ is CH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 8
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$CH=CH, $R^5$ is CH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 9
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OH, $R^5$ is CH$_2$CH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 10
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$CH=CH, $R^5$ is CH$_2$CH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 11
Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OH, $R^5$ is OCH$_3$ and the
combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 4.1

Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$CH=CH$_2$, $R^5$ is OCH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 4.2

Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$C≡CH, $R^5$ is OCH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 4.3

Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OH, $R^5$ is SCH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 4.4

Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$CH=CH$_2$, $R^5$ is SCH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table 4.5

Compounds of the formula I in which $R^x$ is CH$_2$CHF$_2$, $R$ is OCH$_2$C≡CH, $R^5$ is SCH$_3$ and the combination of $R^1$, $R^3$ and, if appropriate, $R^2$ for a compound corresponds in each case to one row of Table A

Table A

Compounds of the formula I which correspond to the formula 1.1A and 1.2A

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<th>No.</th>
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<th>$R^2$</th>
<th>$R^3$</th>
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| A-93 | I.1A    | Cl           | CsH&lt;sub&gt;5&lt;/sub&gt; | Cl          |
| A-94 | I.1A    | Cl           | CsH&lt;sub&gt;5&lt;/sub&gt; | CH&lt;sub&gt;3&lt;/sub&gt; |
| A-95 | I.1A    | Cl           | CsH&lt;sub&gt;5&lt;/sub&gt; | CF&lt;sub&gt;3&lt;/sub&gt; |
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| A-97 | I.1A    | Cl           | CsH&lt;sub&gt;5&lt;/sub&gt; | OCH&lt;sub&gt;3&lt;/sub&gt; |
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The compounds I and their agriculturally useful salts are suitable, both as isomer mixtures and in the form of the pure isomers, as herbicides. They are suitable as such or as an appropriately formulated composition. The herbicidal compositions comprising the compound I, in particular the preferred aspects thereof, control vegetation on non-crop areas very efficiently, especially at high rates of application. They act against broad-leaved weeds and weed grasses in crops such as wheat, rice, corn, soybeans and cotton without causing any significant damage to the crop plants. This effect is mainly observed at low rates of application.

Depending on the application method in question, the compounds I, in particular the preferred aspects thereof, or compositions comprising them can additionally be employed in a further number of crop plants for eliminating unwanted plants. Examples of suitable crops are the following:


The term "crop plants" also includes plants which have been modified by breeding.
mutagenesis or genetic engineering. Genetically modified plants are plants whose
genetic material has been modified in a manner which does not occur under natural
conditions by crossing, mutations or natural recombination (i.e. reassembly of the
genetic information). Here, in general, one or more genes are integrated into the
genetic material of the plant to improve the properties of the plant.

Accordingly, the term "crop plants" also includes plants which, by breeding and
genetic engineering, have acquired tolerance to certain classes of herbicides, such as
hydroxyphenyl pyruvate dioxygenase (HPPD) inhibitors, acetalactate synthase (ALS)
inhibitors, such as, for example, sulfonylureas (EP-A-0257993, US 5,013,659) or
imidazolinones (see, for example, US 6,222,100, WO 01/82685, WO 00/26390,
WO 97/41218, WO 98/02526, WO 98/02527, WO 04/106529, WO 05/20673,
WO 03/14357, WO 03/13225, WO 03/14356, WO 04/16073), enolpyruvylshikimate 3-
phosphate synthase (EPSPS) inhibitors, such as, for example, glyphosate (see, for
example, WO 92/00377), glutamine synthetase (GS) inhibitors, such as, for example,
glufosinate (see, for example, EP-A-0242236, EP-A-242246), or oxynil herbicides (see,
for example, US 5,559,024).

Numerous crop plants, for example Clearfield® oilseed rape, tolerant to
imidazolinones, for example imazamox, have been generated with the aid of classic
breeding methods (mutagenesis). Crop plants such as soybeans, cotton, corn, beet
and oilseed rape, resistant to glyphosate or glufosinate, which are available under the
tradenames RoundupReady® (glyphosate) and Liberty Link® (glufosinate) have been
generated with the aid of genetic engineering methods.

Accordingly, the term "crop plants" also includes plants which, with the aid of genetic
engineering, produce one or more toxins, for example those of the bacterial strain
Bacillus ssp. Toxins which are produced by such genetically modified plants include,
for example, insecticidal proteins of Bacillus spp., in particular B. thuringiensis, such as
the endotoxins Cry1Ab, Cry1Ac, Cry1 F, Cry1 Fa2, Cry2Ab, Cry3A, Cry3Bb1, Cry9c,
Cry34Ab1 or Cry35Ab1; or vegetative insecticidal proteins (VIPS), for example VIP1,
VIP2, VIP3, or VIP3A; insecticidal proteins of nematode-colonizing bacteria, for
example Photorhabdus spp. or Xenorhabdus spp.; toxins of animal organisms, for
example wasp, spider or scorpion toxins; fungal toxins, for example from
Streptomyces; plant lectins, for example from peas or barley; agglutinins; proteinase
inhibitors, for example trypsin inhibitors, serine protease inhibitors, patatin, cystatin or
papain inhibitors, ribosome-inactivating proteins (RIPs), for example ricin, corn-RIP,
abrin, luffin, saporin or bryodin; steroid-metabolizing enzymes, for example 3-
hydroxysteroid oxidase, ecysteroid-IDP glycosyl transferase, cholesterol oxidase,
ecdysone inhibitors, or HMG-CoA reductase; ion channel blockers, for example
inhibitors of sodium channels or calcium channels; juvenile hormone esterase;
receptors of the diuretic hormone (helicokinin receptors); stilbene synthase, bibenzyl
synthase, chitinases and glucanases. In the plants, these toxins may also be produced as pretoxins, hybrid proteins or truncated or otherwise modified proteins. Hybrid proteins are characterized by a novel combination of different protein domains (see, for example, WO 2002/015701). Further examples of such toxins or genetically modified plants which produce these toxins are disclosed in EP-A 374 753, WO 93/007278, WO 95/34656, EP-A 427 529, EP-A 451 878, WO 03/018810 and WO 03/052073. The methods for producing these genetically modified plants are known to the person skilled in the art and disclosed, for example, in the publications mentioned above. Numerous of the toxins mentioned above bestow, upon the plants by which they are produced, tolerance to pests from all taxonomic classes of arthropods, in particular to beetles (Coleoptera), dipterans (Diptera) and butterflies (Lepidoptera) and to nematodes (Nematoda).

Genetically modified plants which produce one or more genes coding for insecticidal toxins are described, for example, in the publications mentioned above, and some of them are commercially available, such as, for example, YieldGard® (corn varieties producing the toxin Cry1Ab), YieldGard® Plus (corn varieties which produce the toxins CrylAb and Cry3Bb1), Starlink® (corn varieties which produce the toxin Cry9c), Herculex® RW (corn varieties which produce the toxins Cry34Ab1, Cry35Ab1 and the enzyme phosphinothricin-N-acetyltransferase [PAT]); NuCOTN® 33B (cotton varieties which produce the toxin CrylAc), Bollgard® I (cotton varieties which produce the toxin CrylAc), Bollgard® II (cotton varieties which produce the toxins CrylAc and Cry2Ab2); VIPCOT® (cotton varieties which produce a VIP toxin); NewLeaf® (potato varieties which produce the toxin Cry3A); Bt-Xtra®, NatureGard®, KnockOut®, BiteGard®, Protecta®, Bt1 1 (for example Agrisure® CB) and Bt176 from Syngenta Seeds SAS, France (cotton varieties which produce the toxin CrylAb and the PAT enzyme), MIR604 from Syngenta Seeds SAS, France (corn varieties which produce a modified version of the toxin Cry3A, see WO 03/018810), MON 863 from Monsanto Europe S.A., Belgium (corn varieties which produce the toxin Cry3Bb1), IPC 531 from Monsanto Europe S.A., Belgium (cotton varieties which produce a modified version of the toxin CrylAc) and 1507 from Pioneer Overseas Corporation, Belgium (corn varieties which produce the toxin Cry1 F and the PAT enzyme).

Accordingly, the term "crop plants" also includes plants which, with the aid of genetic engineering, produce one or more proteins which are more robust or have increased resistance to bacterial, viral or fungal pathogens, such as, for example, pathogenesis-related proteins (PR proteins, see EP-A 0 392 225), resistance proteins (for example potato varieties producing two resistance genes against Phytophthora infestans from the wild Mexican potato Solanum bulbocastanum) or T4 lysozyme (for example potato cultivars which, by producing this protein, are resistant to bacteria such as Erwinia amylovora).
Accordingly, the term "crop plants" also includes plants whose productivity has been improved with the aid of genetic engineering methods, for example by enhancing the potential yield (for example biomass, grain yield, starch, oil or protein content), tolerance to drought, salt or other limiting environmental factors or resistance to pests and fungal, bacterial and viral pathogens.

The term "crop plants" also includes plants whose ingredients have been modified with the aid of genetic engineering methods in particular for improving human or animal diet, for example by oil plants producing health-promoting long-chain omega 3 fatty acids or monounsaturated omega 9 fatty acids (for example Nexera® oilseed rape).

The term "crop plants" also includes plants which have been modified with the aid of genetic engineering methods for improving the production of raw materials, for example by increasing the amylopectin content of potatoes (Amflora® potato).

Furthermore, it has been found that the compounds of the formula I are also suitable for the defoliation and/or desiccation of plant parts, for which crop plants such as cotton, potato, oilseed rape, sunflower, soybean or field beans, in particular cotton, are suitable. In this regard, there have been found compositions for the desiccation and/or defoliation of plants, processes for preparing these compositions and methods for desiccating and/or defoliating plants using the compounds of the formula I.

As desiccants, the compounds of the formula I are particularly suitable for desiccating the above-ground parts of crop plants such as potato, oilseed rape, sunflower and soybean, but also cereals. This makes possible the fully mechanical harvesting of these important crop plants.

Also of economic interest is to facilitate harvesting, which is made possible by concentrating within a certain period of time the dehiscence, or reduction of adhesion to the tree, in citrus fruit, olives and other species and varieties of pomaceous fruit, stone fruit and nuts. The same mechanism, i.e. the promotion of the development of abscission tissue between fruit part or leaf part and shoot part of the plants is also essential for the readily controllable defoliation of useful plants, in particular cotton.

Moreover, a shortening of the time interval in which the individual cotton plants mature leads to an increased fiber quality after harvesting.

The compounds I, or the herbicidal compositions comprising the compounds I, can be used, for example, in the form of ready-to-spray aqueous solutions, powders, suspensions, also highly concentrated aqueous, oily or other suspensions or dispersions, emulsions, oil dispersions, pastes, dusts, materials for broadcasting, or granules, by means of spraying, atomizing, dusting, spreading, watering or treatment of the seed or mixing with the seed. The use forms depend on the intended purpose; in each case, they should ensure the finest possible distribution of the active ingredients according to the invention.
The herbicidal compositions comprise a herbicidally effective amount of at least one compound of the formula I or an agriculturally useful salt of I, and auxiliaries which are customary for the formulation of crop protection agents.

Examples of auxiliaries customary for the formulation of crop protection agents are inert auxiliaries, solid carriers, surfactants (such as dispersants, protective colloids, emulsifiers, wetting agents and tackifiers), organic and inorganic thickeners, bactericides, antifreeze agents, antifoams, if appropriate colorants and, for seed formulations, adhesives.

Examples of thickeners (i.e. compounds which impart to the formulation modified flow properties, i.e. high viscosity in the state of rest and low viscosity in motion) are polysaccharides, such as xanthan gum (Kelzan® from Kelco), Rhodopol® 23 (Rhone Poulenc) or Veegum® (from R.T. Vanderbilt), and also organic and inorganic sheet minerals, such as Attaclay® (from Engelhardt).

Examples of antifoams are silicone emulsions (such as, for example, Silikon® SRE, Wacker or Rhodorsil® from Rhodia), long-chain alcohols, fatty acids, salts of fatty acids, organofluorine compounds and mixtures thereof.

Bactericides can be added for stabilizing the aqueous herbicidal formulation. Examples of bactericides are bactericides based on diclorophen and benzyl alcohol hemiformal (Proxel® from ICI or Acticide® RS from Thor Chemie and Kathon® MK from Rohm & Haas), and also isothiazolinone derivates, such as alkylisothiazolinones and benzisothiazolinones (Acticide MBS from Thor Chemie).

Examples of antifreeze agents are ethylene glycol, propylene glycol, urea or glycerol.

Examples of colorants are both sparingly water-soluble pigments and water-soluble dyes. Examples which may be mentioned are the dyes known under the names Rhodamin B, C.I. Pigment Red 112 and C.I. Solvent Red 1, and also pigment blue 15:4, pigment blue 15:3, pigment blue 15:2, pigment blue 15:1, pigment blue 80, pigment yellow 1, pigment yellow 13, pigment red 112, pigment red 48:2, pigment red 48:1, pigment red 57:1, pigment red 53:1, pigment orange 43, pigment orange 34, pigment orange 5, pigment green 36, pigment green 7, pigment white 6, pigment brown 25, basic violet 10, basic violet 49, acid red 51, acid red 52, acid red 14, acid blue 9, acid yellow 23, basic red 10, basic red 108.

Examples of adhesives are polyvinylpyrrolidone, polyvinyl acetate, polyvinyl alcohol and tylose.

Suitable inert auxiliaries are, for example, the following: mineral oil fractions of medium to high boiling point, such as kerosene and diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example paraffin, tetrahydronaphthalene, alkylated naphthalenes and their derivatives, alkylated benzenes and their derivatives, alcohols such as methanol, ethanol, propanol, butanol and cyclohexanol, ketones such as cyclohexanone or strongly polar solvents, for example amines such as N-methylpyrrolidone, and water.
Solid carriers are mineral earths such as silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate and magnesium oxide, ground synthetic materials, fertilizers such as ammonium sulfate, ammonium phosphate, ammonium nitrate and ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders, or other solid carriers.

Suitable surfactants (adjuvants, wetting agents, tackifiers, dispersants and also emulsifiers) are the alkali metal salts, alkaline earth metal salts and ammonium salts of aromatic sulfonic acids, for example lignosulfonic acids (e.g. Borrespers-types, Borregaard), phenolsulfonic acids, naphthalenesulfonic acids (Morwet types, Akzo Nobel) and dibutylnaphthalenesulfonic acid (Nekal types, BASF SE), and of fatty acids, alkyl- and alkyaryl sulfonates, alkyl sulfates, lauryl ether sulfates and fatty alcohol sulfates, and salts of sulfated hexa-, hepta- and octadecanols, and also of fatty alcohol glycol ethers, condensates of sulfonated naphthalene and its derivatives with formaldehyde, condensates of naphthalene or of the naphthalenesulfonlic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- or nonylphenol, alklyphenyl or tributylphenyl polyglycol ether, alkyaryl polyether alcohols, isodecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypolyethylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors and proteins, denatured proteins, polysaccharides (e.g. methylcellulose), hydrophobically modified starches, polyvinyl alcohol (Mowiol types Clariant), polycarboxylates (BASF SE, Sokalan types), polyalkoxylates, polyvinylamine (BASF SE, Lupamine types), polyethyleneimine (BASF SE, Lupasol types), polyvinylpyrrolidone and copolymers thereof.

Powders, materials for broadcasting and dusts can be prepared by mixing or grinding the active ingredients together with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active ingredients to solid carriers.

Aqueous use forms can be prepared from emulsion concentrates, suspensions, pastes, wettable powders or water-dispersible granules by adding water. To prepare emulsions, pastes or oil dispersions, the compounds of the formula I or Ia, either as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetting agent, tackifier, dispersant or emulsifier. Alternatively, it is also possible to prepare concentrates comprising active substance, wetting agent, tackifier, dispersant or emulsifier and, if desired, solvent or oil, which are suitable for dilution with water.

The concentrations of the compounds of the formula I in the ready-to-use preparations can be varied within wide ranges. In general, the formulations comprise from 0.001 to 98% by weight, preferably 0.01 to 95% by weight of at least one active compound. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The formulations or ready-to-use preparations may also contain acids, bases or
buffer systems, these include, for example, phosphoric acid or sulfuric acid and/or urea or ammonia.

The compounds I of the invention can for example be formulated as follows:

1. Products for dilution with water

A Water-soluble concentrates

10 parts by weight of active compound are dissolved in 90 parts by weight of water or a water-soluble solvent. As an alternative, wetters or other adjuvants are added. The active compound dissolves upon dilution with water. This gives a formulation with an active compound content of 10% by weight.

B Dispersible concentrates

20 parts by weight of active compound are dissolved in 70 parts by weight of cyclohexanone with addition of 10 parts by weight of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion. The active compound content is 20% by weight.

C Emulsifiable concentrates

15 parts by weight of active compound are dissolved in 75 parts by weight of an organic solvent (e.g. alkylaromatics) with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5 parts by weight). Dilution with water gives an emulsion. The formulation has an active compound content of 15% by weight.

D Emulsions

25 parts by weight of active compound are dissolved in 35 parts by weight of an organic solvent (e.g. alkylaromatics) with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5 parts by weight). This mixture is introduced into 30 parts by weight of water by means of an emulsifier (e.g. Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion. The formulation has an active compound content of 25% by weight.

E Suspensions

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

F Water-dispersible granules and water-soluble granules

50 parts by weight of active compound are ground finely with addition of 50 parts by weight of dispersants and wetters and made into water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound. The formulation has an active compound content of 50% by weight.

G Water-dispersible powders and water-soluble powders

75 parts by weight of active compound are ground in a rotor-stator mill with addition
of 25 parts by weight of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound. The active compound content of the formulation is 75% by weight.

H Gel formulations

In a ball mill, 20 parts by weight of active compound, 10 parts by weight of dispersant, 1 part by weight of gelling agent and 70 parts by weight of water or of an organic solvent are ground to give a fine suspension. Dilution with water gives a stable suspension with active compound content of 20% by weight.

2. Products to be applied undiluted

I Dusts

5 parts by weight of active compound are ground finely and mixed intimately with 95 parts by weight of finely divided kaolin. This gives a dusting powder with an active compound content of 5% by weight.

J Granules (GR, FG, GG, MG)

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

K ULV solutions (UL)

10 parts by weight of active compound are dissolved in 90 parts by weight of an organic solvent, for example xylene. This gives a product to be applied undiluted with an active compound content of 10% by weight.

The compounds I or the herbicidal compositions comprising them can be applied pre- or post-emergence, or together with the seed of a crop plant. It is also possible to apply the herbicidal compositions or active compounds by applying seed, pretreated with the herbicidal compositions or active compounds, of a crop plant. If the active compounds are less well tolerated by certain crop plants, application techniques may be used in which the herbicidal compositions are sprayed, with the aid of the spraying equipment, in such a way that as far as possible they do not come into contact with the leaves of the sensitive crop plants, while the active compounds reach the leaves of undesirable plants growing underneath, or the bare soil surface (post-directed, lay-by).

In a further embodiment, the compounds of the formula I or the herbicidal compositions can be applied by treating seed.

The treatment of seed comprises essentially all procedures familiar to the person skilled in the art (seed dressing, seed coating, seed dusting, seed soaking, seed film coating, seed multilayer coating, seed encrusting, seed dripping and seed pelleting) based on the compounds of the formula I according to the invention or the compositions prepared therefrom. Here, the herbicidal compositions can be applied diluted or undiluted.

The term seed comprises seed of all types, such as, for example, corns, seeds,
fruits, tubers, cuttings and similar forms. Here, preferably, the term seed describes
corns and seeds.
The seed used can be seed of the useful plants mentioned above, but also the seed
of transgenic plants or plants obtained by customary breeding methods.

The rates of application of active compound are from 0.001 to 3.0, preferably 0.01 to
1.0, kg/ha of active substance (a.s.), depending on the control target, the season, the
target plants and the growth stage. To treat the seed, the compounds I are generally
employed in amounts of from 0.001 to 10 kg per 100 kg of seed.

It may also be advantageous to use the compounds of the formula I in combination
with safeners. Safeners are chemical compounds which prevent or reduce damage to
useful plants without substantially affecting the herbicidal action of the compounds
of the formula I on unwanted plants. They can be used both before sowing (for example in
the treatment of seed, or on cuttings or seedlings) and before or after the emergence of
the useful plant. The safeners and the compounds of the formula I can be used
simultaneously or in succession. Suitable safeners are, for example, (quinolin-8-oxy)acetic acids, 1-phenyl-5-haloalkyl-1/-1,2,4-triazole-3-carboxylic acids, 1-phenyl-4,5-dihydro-5-alkyl-1-H-pyrazole-3,5-dicarboxylic acids, 4,5-dihydro-5,5-diaryl-3-isoxazolcarboxylic acids, dichloroacetamides, alpha-oximinophenylacetanilides, acetonaphthene oximes, 4,6-dihalo-2-phenylpyrimidines, N-[4-(aminocarbonyl)phenyl]-sulfonyl]-2-benzamides, 1,8-naphthalic anhydride, 2-halo-4-(haloalkyl)-5-thiazolecarboxylic acids, phosphorothiolates and O-phenyl N-alkylcarbamates and their agriculturally useful salts and, provided that they have an acid function, their
agriculturally useful derivatives, such as amides, esters and thioesters.

To broaden the activity spectrum and to obtain synergistic effects, the compounds
of the formula I can be mixed and jointly applied with numerous representatives of other
herbicidal or growth-regulating groups of active compounds or with safeners. Suitable
mixing partners are, for example, 1,2,4-thiadiazoles, 1,3,4-thiadiazoles, amides,
aminophosphoric acid and its derivatives, aminotriazoles, anilides, aryloxy/heteroaryl-
oxalkanoic acids and their derivatives, benzoic acid and its derivatives, benzothiadiazinones, 2-(hetaroyl/arylo1)-1,3-cyclohexanediones, heteroaryl aryl
ketones, benzylisoxazolidinones, meta-CF3-phenyl derivatives, carbamates, quinoline
-carboxylic acid and its derivatives, chloroacetanilides, cyclohexenoxime ether
derivatives, diazines, dichloropropionoic acid and its derivatives, dihydrobenzofurans,
dihydrofuran-3-ones, dinitroanilines, dinitrophenols, diphenyl ethers, dipyrdyls,
halocarboxylic acids and their derivatives, ureas, 3-phenyluracils, imidazoles,
imidazolinones, N-phenyl-3,4,5,6-tetrahydrophthalimides, oxadiazoles, oxiranes,
phenols, aryloxy- and heteroaryloxyphenoxypionic esters, phenylactic acid and its
derivatives, 2-phenylpropionic acid and its derivatives, pyrazoles, phenylpyrazoles,
pyridazines, pyridinecarboxylic acid and its derivatives, pyrimidyl ethers, sulfonamides,
sulfonylureas, triazines, triazinones, triazolinones, triazolecarboxamides, uracils and
also phenylpyrazolines and isoxazolines and their derivatives.

Moreover, it may be useful to apply the compounds I alone or in combination with other herbicides or else also mixed with further crop protection agents, jointly, for example with compositions for controlling pests or phytopathogenic fungi or bacteria.

Also of interest is the miscibility with mineral salt solutions which are employed for alleviating nutritional and trace element deficiencies. Other additives such as nonphytotoxic oils and oil concentrates may also be added.

Examples of herbicides which can be used in combination with the pyridine compounds of the formula I according to the present invention are:

b1) from the group of the lipid biosynthesis inhibitors:
- aloxydim, aloxydim-sodium, butoxydim, clethodim, clodinafop, clodinafop-propargyl, cycloxydim, cyhalofop, cyhalofop-butyl, diclofop, diclofop-methyl, fenoxaprop, fenoxaprop-ethyl, fenoxaprop-P, fenoxaprop-P-ethyl, fluazifop, fluazifop-butyl, fluazifop-P, fluazifop-P-butyl, haloxyfop, haloxyfop-methyl, haloxyfop-P, haloxyfop-P-methyl, metamifop, pinoxaden, profoxydim, propaquizafop, quizalofop, quizalofop-ethyl, quizalofop-tefuryl, quinclorac, quinclorac-tefuryl, sethoxydim, tepraloxydim, tralkoxydim, butylate, cycloate, dalapon, dimepiperate, EPTC, esprocarb, ethofumesate, fluroxypyr, molinate, oryzencarb, pebulate, prosulfocarb, TCA, thiobencarb, tiocarbazil, triallate and vernolate;

b2) from the group of the ALS inhibitors:
- amidosulfuron, azimsulfuron, bensulfuron, bensulfuron-methyl, bispyribac, bispyribac-sodium, chlorimuron, chlorimuron-ethyl, chlorosulfuron, cinosulfuron, cloransulam, cloransulam-methyl, cyclosulfamuron, diclosulam, ethamsulfuron, ethamsulfuron-methyl, ethoxysulfuron, flazasulfuron, florasulam, flucarbazone, flucarbazone-sodium, flucetosulfuron, flumetsulam, flupyradifurone, flupyradifurone-methyl-sodium, foramsulfuron, halosulfuron, halosulfuron-methyl, imazamethabenz, imazamethabenz-methyl, imazamox, imazapic, imazaquin, imazethapyr, imazosulfuron, iodosulfuron, iodosulfuron-methyl-sodium, mesosulfuron, metosulam, metsulfuron, metsulfuron-methyl, nicosulfuron, orthosulfuron, oxasulfuron, penoxsulam, primisulfuron, primisulfuron-methyl, propoxycarbazone, propoxycarbazone-sodium, prosulfuron, pyrazosulfuron, pyrazosulfuron-ethyl, pyribenzoxim, pyrimisulfuron, pyrifenyl, pyriminobac, pyriminobac-methyl, pyrithiobac, pyrithiobac-sodium, pyrroxsulam, rimsulfuron, sulfometuron, sulfometuron-methyl, sulfosulfuron, thiencarbazone, thiencarbazone-methyl, thifensulfuron, thifensulfuron-methyl, triasulfuron, tribenuron, tribenuron-methyl, trifloxysulfuron, triflusulfuron, triflusulfuron-methyl and tritosulfuron;

b3) from the group of the photosynthesis inhibitors:
- ametyn, amicarbazone, atrazine, bentazone, bentazone-sodium, bromacil, bromofenoxim, bromoxynil and its salts and esters, chlorobromuron, chloridazon, chlorotoluon, chloroxuron, cyanazine, desmedipham, desmetryn, dimefuron, dimethametryn, diquat, diquat-dibromide, diuron, fluometuron, hexazinone, ioxynil and
its salts and esters, isoproturon, isouron, karbutilate, lenacil, linuron, metamitron, methabenzthiazuron, metobenzuron, metoloxuron, metribuzin, monolinuron, neburon, paraquat, paraquat-dichloride, paraquat-dimethylsulfate, pentanochlor, phenmedipham, phenmedipham-ethyl, prometon, prometryn, propanil, propazine, pyridafol, pyridate, siduron, simazine, simetryn, tebuthiuron, terbacil, terbumeton, terburmeton, terbuthylazine, terbutryn, thidiazuron and trietazine;
b4) from the group of the protoporphyrinogen-IX oxidase inhibitors:
  acifluorfen, acifluorfen-sodium, azafenidin, bencarbazone, benzofendizone, benzoxadin, butafenacil, carfentrazone, carfentrazone-ethyl, chlomethoxyfen, cinidon-ethyl, fluazolate, flufenpyr, flufenpyr-ethyl, flumiclorac, flumiclorac-pentyl, flumioxazin, fluoroglycofen, fluoroglycofen-ethyl, fluthiacet, fluthiacet-methyl, fomesafen, halosafen, lactofen, oxadiargyl, oxadiazon, oxyfluorfen, pentoxazone, profloxazol, pyraclonil, pyraflufen, pyraflufen-ethyl, saflufenacil, sulfentrazone, thidiazimin, 2-chloro-5-[3,6-dihydro-3-methyl-2,6-dioxo-4-(trifluoromethyl)-1 (2/-)-pyrimidinyl]-4-fluoro-N-[(isopropyl)-methylsulfamoyl]benzamide (H-1; CAS 3721 37-35-4), ethyl [3-[2-chloro-4-fluoro-5-(1-methyl-6-trifluoromethyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-3-yl)phenoxy]-2-pyridyloxy]acetate (H-2; CAS 353292-31-6), N-ethyl-3-(2,6-dichloro-4-trifluoromethoxyphenoxy)-5-methyl-1 H-pyrazole-1-carboxamide (H-3; CAS 452098-92-9), N-tetrahydrofurfuryl-3-(2,6-dichloro-4-trifluoromethylphenoxy)-5-methyl-1 H-pyrazole-1-carboxamide (H-4; CAS 915396-43-9), N-ethyl-3-(2-chloro-6-fluoro-4-trifluoromethylphenoxy)-5-methyl-1/-/-pyrazole-1-carboxamide (H-5; CAS 452099-05-7), N-tetrahydrofurfuryl-3-(2-chloro-6-fluoro-4-trifluoromethylphenoxy)-5-methyl-1 H-pyrazole-1-carboxamide (H-6; CAS 45100-03-7), 3-[7-fluoro-3-oxo-4-(prop-2-ynyl)-3,4-dihydro-2H-benzo[1,4]oxazin-6-yl]-1.5-dimethyl-6-thioxo-[1,3,5]triazinane-2,4-dione, 1,5-dimethyl-6-thioxo-3-(2,2,7-trifluoro-3-oxo-4-(prop-2-ynyl)-3,4-dihydro-2H-benzo[b][1,4]oxazin-6-yl)-1,3,5-triazinane-2,4-dione, 2-(2,2,7-Trifluoro-3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-benzo[1,4]oxazin-6-yl)-4,5,6,7-tetrahydro-isoindele-1,3-dione and 1-Methyl-6-trifluoromethyl-3-(2,2,7-trifluoro-3-oxo-4-prop-2-ynyl-3,4-dihydro-2H-benzo[1,4]oxazin-6-yl)-1 H-pyrimidine-2,4-dione;
b5) from the group of the bleacher herbicides:
  aclonifen, amitrol, befflobutamid, benzobicyclon, benzofenap, clomazone, diflufenican, fluridone, flurochloridone, flurtamone, isoxaflutole, mesotrione, norflurazon, picolinolen, pyrasulfotole, pyrazolynate, pyrazoxyfen, sulcotrione, tefuryltrione, tembotrione, topramezone, 4-hydroxy-3-[[2-[2-methoxyethoxy]methyl]-6-(trifluoromethyl)-3-pyridy]carbonyl]bicyclo[3.2.1]oct-3-en-2-one (H-7; CAS 352010-68-5) and 4-(3-trifluoromethylphenoxy)-2-(4-trifluoromethylphenyl)pyrimidine (H-8; CAS 180608-33-7);
b6) from the group of the EPSP synthase inhibitors:
  glyphosate, glyphosate-isopropylammonium and glyphosate-trimesium (sulfosate);
b7) from the group of the glutamine synthase inhibitors:
  bilanaphos (bialaphos), bilanaphos-sodium, glufosinate and glufosinate-ammonium;
b8) from the group of the DHP synthase inhibitors:
asulam;
b9) from the group of the mitose inhibitors:
amiprophos, amiprophos-methyl, benfluralin, butamiphos, butralin, carbetamide, chlorpropham, chlorthal, chlorthal-dimethyl, dinitramine, dithiopyr, ethalfluralin, fluchloralin, oryzalin, pendimethalin, pro diamine, pro pham, propyzamide, tebutam, thiazopyr and trifluralin;

b10) from the group of the VLCFA inhibitors:
acethochlor, alachlor, anilofos, butachlor, caf enstrole, dimethachlor, dimethanamid, dimethenamid-P, diphenamid, fentrazamide, flufenacet, mefenacet, metazachlor, metolachlor, metolachlor-S, naproanilide, napropamide, pethoxamid, piperophos, pretilachlor, propachlor, propisochlor, pyroxasulfone (KIH-485) and thenylchlor;

Compounds of the formula 2:

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{R}^{21} \quad \text{R}^{22} \quad \text{O}_{2}(\text{X})_n \\
\text{H}_3\text{C} & \quad \text{O} \quad \text{N} \quad \text{R}^{23} \quad \text{R}^{24}
\end{align*}
\]

in which the variables have the following meanings:
Y is phenyl or 5- or 6-membered heteroaryl as defined at the outset, which radicals may be substituted by one to three groups \( \text{R}^{25} \); \( \text{R}^{21}, \text{R}^{22}, \text{R}^{23}, \text{R}^{24} \) are H, halogen or Ci-C\(_4\)-alkyl; X is O or NH; N is 0 or 1.

Compounds of the formula 2 have in particular the following meanings:

\[
\begin{align*}
\text{Y} & \quad \text{N} \quad \text{R}^{25} \quad \text{R}^{26} \quad \text{N} \quad \text{R}^{25} \\
(\text{R}^{28})_n & \quad \text{(R}^{28})_n
\end{align*}
\]

where # denotes the bond to the skeleton of the molecule; and
\( \text{R}^{21}, \text{R}^{22}, \text{R}^{23}, \text{R}^{24} \) are \( \text{H, C, F, or CH}_3 \); \( \text{R}^{25} \) is halogen, Ci-C\(_4\)-alkyl or Ci-C\(_4\)-haloalkyl; \( \text{R}^{26} \) is Ci-C\(_4\)-alkyl; \( \text{R}^{27} \) is halogen, Ci-C\(_4\)-alkoxy or Ci-C\(_4\)-haloalkoxy; \( \text{R}^{28} \) is H, halogen, Ci-C\(_4\)-alkyl, Ci-C\(_4\)-haloalkyl or Ci-C\(_4\)-haloalkoxy; M is 0, 1, 2 or 3; X is oxygen; N is 0 or 1.

Preferred compounds of the formula 2 have the following meanings:

\[
\begin{align*}
\text{Y} & \quad \text{N} \quad \text{F}_3\text{C} \quad \text{N} \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{OCH}_2\text{CF}_3 & \quad \text{OCH}_2\text{CF}_3 \quad \text{OCH}_2\text{CF}_3 \quad \text{CF}_3 \quad \text{F}
\end{align*}
\]

\( \text{R}^{21} \) is H; \( \text{R}^{22}, \text{R}^{23} \) are F; \( \text{R}^{24} \) is H or F; X is oxygen; N is 0 or 1.

Particularly preferred compounds of the formula 2 are:
Examples of preferred safeners C are benoxacor, cloquintocet, cyometrinil, cyprosulfamide, dichlorim, dicyclonone, dietholate, fenchlorazole, fenclozir, flurazole,
fluxofenim, furilazole, isoxadifen, mepenpyr, mephenate, naphthelic anhydride, oxabetrinil, 4-(dichloroacetyl)-1-oxa-4-azaspiro[4.5]decane (H-11; MON4660, CAS 71526-07-3) and 2,2,5-trimethyl-3-(dichloroacetyl)-1,3-oxazolidine (H-12; R-29148, CAS 52836-31-4).

The active compounds of groups b1) to b15) and the safeners C are known herbicides and safeners, see, for example, The Compendium of Pesticide Common Names (http://www.alanwood.net/pesticides/); B. Hock, C. Fedtke, R. R. Schmidt, Herbicide [Herbizide], Georg Thieme Verlag, Stuttgart, 1995. Further herbicidally active compounds are known from WO 96/26202, WO 97/41 116, WO 97/41 117, WO 97/41 118, WO 01/83459 and WO 2008/074991 and from W. Kramer et al. (ed.) "Modern Crop Protection Compounds", Vol. 1, Wiley VCH, 2007 and the literature quoted therein.

The invention also relates to compositions in the form of a crop protection composition formulated as a 1-component composition comprising an active compound combination comprising at least one pyridine compound of the formula I and at least one further active compound, preferably selected from the active compounds of groups b1 to b15, and at least one solid or liquid carrier and/or one or more surfactants and, if desired, one or more further auxiliaries customary for crop protection compositions.

The invention also relates to compositions in the form of a crop protection composition formulated as a 2-component composition comprising at least one pyridine compound of the formula I, a solid or liquid carrier and/or one or more surfactants and a second component comprising at least one further active compound selected from the active compounds of groups b1 to b15, a solid or liquid carrier and/or one or more surfactants, where additionally both components may also comprise further auxiliaries customary for crop protection compositions.

In binary compositions comprising at least one compound of the formula I as component A and at least one herbicide B, the weight ratio of the active compounds A:B is generally in the range of from 1:1000 to 1000:1, preferably in the range of from 1:500 to 500:1, in particular in the range of from 1:250 to 250:1 and particularly preferably in the range of from 1:75 to 75:1.

In binary compositions comprising at least one compound of the formula I as component A and at least one safener C, the weight ratio of the active compounds A:C is generally in the range of from 1:1000 to 1000:1, preferably in the range of from 1:500 to 500:1, in particular in the range of from 1:250 to 250:1 and particularly preferably in the range of from 1:75 to 75:1.

In ternary compositions comprising both at least one compound of the formula I as component A, at least one herbicide B and at least one safener C, the relative parts by weight of the components A:B are generally in the range of from 1:1000 to 1000:1, preferably in the range of from 1:500 to 500:1, in particular in the range of from 1:250 to
250:1 and particularly preferably in the range of from 1:75 to 75:1; the weight ratio of the components A:C is generally in the range of from 1:1000 to 1000:1, preferably in the range of from 1:500 to 500:1, in particular in the range of from 1:250 to 250:1 and particularly preferably in the range of from 1:75 to 75:1; and the weight ratio of the components B:C is generally in the range of from 1:1000 to 1000:1, preferably in the range of from 1:500 to 500:1, in particular in the range of from 1:250 to 250:1 and particularly preferably in the range of from 1:75 to 75:1. Preferably, the weight ratio of the components A + B to the component C is in the range of from 1:500 to 500:1, in particular in the range of from 1:250 to 250:1 and particularly preferably in the range of from 1:75 to 75:1.

Examples of particularly preferred compositions according to the invention comprising in each case one individualized compound of the formula I and one mixing partner or a mixing partner combination are given in Table B below.

A further aspect of the invention relates to the compositions B-1 to B-1236 listed in Table B below, where in each case one row of Table B corresponds to a herbicidal composition comprising one of the compounds of the formula I individualized in the above description (component 1) and the further active compound from groups b1) to b15) and/or safener C stated in each case in the row in question (component 2). The active compounds in the compositions described are in each case preferably present in synergistically effective amounts.

<table>
<thead>
<tr>
<th>Herbicide(s) B</th>
<th>Safener C</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-1 clodinafop-propargyl</td>
<td>—</td>
</tr>
<tr>
<td>B-2 cycloxydim</td>
<td>—</td>
</tr>
<tr>
<td>B-3 cyhalofop-butyl</td>
<td>—</td>
</tr>
<tr>
<td>B-4 fenoxaprop-P-ethyl</td>
<td>—</td>
</tr>
<tr>
<td>B-5 pinoxaden</td>
<td>—</td>
</tr>
<tr>
<td>B-6 profoxydim</td>
<td>—</td>
</tr>
<tr>
<td>B-7 tepraloxydim</td>
<td>—</td>
</tr>
<tr>
<td>B-8 tralkoxydim</td>
<td>—</td>
</tr>
<tr>
<td>B-9 esprocarb</td>
<td>—</td>
</tr>
<tr>
<td>B-10 prosulfocarb</td>
<td>—</td>
</tr>
<tr>
<td>B-11 thiobencarb</td>
<td>—</td>
</tr>
<tr>
<td>B-12 triallate</td>
<td>—</td>
</tr>
<tr>
<td>B-13 bensulfuron-methyl</td>
<td>—</td>
</tr>
<tr>
<td>B-14 bispyribac-sodium</td>
<td>—</td>
</tr>
<tr>
<td>B-15 cyclosulfamuron</td>
<td>—</td>
</tr>
<tr>
<td>B-16 flumetsulam</td>
<td>—</td>
</tr>
<tr>
<td>B-17 flupyr-sulfuron-methyl-sodium</td>
<td>—</td>
</tr>
<tr>
<td>B-18 foramsulfuron</td>
<td>—</td>
</tr>
<tr>
<td>B-19 imazamox</td>
<td>—</td>
</tr>
<tr>
<td>Herbicide(s) B</td>
<td>Safener C</td>
</tr>
<tr>
<td>--------------</td>
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</tr>
<tr>
<td>B-20 imazapic</td>
<td></td>
</tr>
<tr>
<td>B-21 imazapyr</td>
<td></td>
</tr>
<tr>
<td>B-22 imazaquin</td>
<td></td>
</tr>
<tr>
<td>B-23 imazethapyr</td>
<td></td>
</tr>
<tr>
<td>B-24 imazosulfuron</td>
<td></td>
</tr>
<tr>
<td>B-25 iodosulfuron-methyl-sodium</td>
<td></td>
</tr>
<tr>
<td>B-26 mesosulfuron</td>
<td></td>
</tr>
<tr>
<td>B-27 nicosulfuron</td>
<td></td>
</tr>
<tr>
<td>B-28 penoxsulam</td>
<td></td>
</tr>
<tr>
<td>B-29 propoxycarbazone-sodium</td>
<td></td>
</tr>
<tr>
<td>B-30 pyrazosulfuron-ethyl</td>
<td></td>
</tr>
<tr>
<td>B-31 pyroxsulam</td>
<td></td>
</tr>
<tr>
<td>B-32 rimsulfuron</td>
<td></td>
</tr>
<tr>
<td>B-33 sulfosulfuron</td>
<td></td>
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<tr>
<td>B-34 thienocarbazone-methyl</td>
<td></td>
</tr>
<tr>
<td>B-35 tritosulfuron</td>
<td></td>
</tr>
<tr>
<td>B-36 2,4-D and its salts and esters</td>
<td></td>
</tr>
<tr>
<td>B-37 aminopyralid and its salts and esters</td>
<td></td>
</tr>
<tr>
<td>B-38 clopyralid and its salts and esters</td>
<td></td>
</tr>
<tr>
<td>B-39 dicamba and its salts and esters</td>
<td></td>
</tr>
<tr>
<td>B-40 fluroxypyr-meptyl</td>
<td></td>
</tr>
<tr>
<td>B-41 quinclorac</td>
<td></td>
</tr>
<tr>
<td>B-42 quinmerac</td>
<td></td>
</tr>
<tr>
<td>B-43 H-9</td>
<td></td>
</tr>
<tr>
<td>B-44 diflufenzopyr</td>
<td></td>
</tr>
<tr>
<td>B-45 diflufenzopyr-sodium</td>
<td></td>
</tr>
<tr>
<td>B-46 clomazone</td>
<td></td>
</tr>
<tr>
<td>B-47 diflufenican</td>
<td></td>
</tr>
<tr>
<td>B-48 flurochloridone</td>
<td></td>
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<tr>
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<td>B-97 atrazine + nicosulfuron</td>
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<td>Herbicide(s) B</td>
<td>Safener C</td>
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<td>B-102 diflufenican + fenoxaprop-P-ethyl</td>
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<td>B-103 diflufenican + flupyrsulfuron-methyl-sodium</td>
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<td>B-107 diflufenican + pyroxulam</td>
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<td>B-117 metazachlor + nicosulfuron</td>
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<td>B-122 pendimethalin + clodinafop-propargyl</td>
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<td>B-126 pendimethalin + mesosulfuron-methyl</td>
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<td>B-136 terbuthylazin + H-1</td>
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<td>2,4-D and its salts and esters</td>
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<td>B-189</td>
<td>aminopyralid and its salts and esters</td>
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<td>Herbicide(s) B</td>
<td>Safener C</td>
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<tr>
<td><strong>B-253</strong> diflufenican + fenoxaprop-P-ethyl</td>
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<td>Herbicide(s) B</td>
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<td>aminopyralid and its salts and esters cloquintocet</td>
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<td>B-409 metazachlor + mesotrione</td>
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<td>Safener C</td>
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<td>B-682 diflufenican + mesosulfuron-methyl</td>
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<td>Safener C</td>
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<tr>
<td>B-707 pendimethalin + pyroxsulam</td>
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<td>Herbicide(s) B</td>
<td>Safener C</td>
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<td>B-759 dicamba and its salts and esters</td>
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The compounds I and the compositions according to the invention may also have a plant-strengthening action. Accordingly, they are suitable for mobilizing the defense system of the plants against attack by unwanted microorganisms, such as harmful fungi, but also viruses and bacteria. Plant-strengthening (resistance-inducing) substances are to be understood as meaning, in the present context, those substances which are capable of stimulating the defense system of treated plants in such a way that, when subsequently inoculated by unwanted microorganisms, the treated plants display a substantial degree of resistance to these microorganisms.

The compounds I can be employed for protecting plants against attack by unwanted microorganisms within a certain period of time after the treatment. The period of time within which their protection is effected generally extends from 1 to 28 days, preferably from 1 to 14 days, after the treatment of the plants with the compounds I, or, after treatment of the seed, for up to 9 months after sowing.

The compounds I and the compositions according to the invention are also suitable for increasing the harvest yield.

Moreover, they have reduced toxicity and are tolerated well by the plants.

Hereinbelow, the compounds of the formula I are illustrated by way of examples, without limiting the subject matter of the present invention to the examples shown.

### i. Synthesis examples

With appropriate modification of the starting materials, the procedures given in the synthesis examples below were used to obtain further compounds I. The compounds obtained in this manner are listed in the table that follows, together with physical data.

The products shown below were characterized by determination of the melting point, by NMR spectroscopy or by the masses ([m/z]) or retention time (RT; [min.]) determined by HPLC-MS spectrometry.

HPLC-MS = high performance liquid chromatography coupled with mass spectrometry; HPLC column:
RP-18 column (Chromolith Speed ROD from Merck KgaA, Germany), 50’4.6 mm; mobile phase: acetonitrile + 0.1% trifluoroacetic acid (TFA)/water + 0.1% TFA, using a gradient from 5:95 to 100:0 over 5 minutes at 40°C, flow rate 1.8 ml/min.

MS: quadrupole electrospray ionization, 80 V (positive mode).

Ac: Acetyl; THF: tetrahydrofuran; DMF: dimethylformamide; TEA: triethylamine; dppf: 1,1'-bis(diphenylphosphino)ferrocene; dba: dibenzylidenacetone; PE: petrol ether; EtOAc: acetic acid ethyl ester; Et.20: diethyl ether; DCM: dichloromethane; NCS: N-chlorosuccinimide; LiHMDS: lithium-hexamethyldisilazane; AcOH: acetic acid; MeOH: methanol; m-CPBA: m-chloroperbenzoic acid.

Example 1: Preparation of 1-(2,2-difluoroethyl)-3-[3-(2-methoxyethoxy)-2-(trifluoromethyl)phenyl]-2,2-dioxo-pyrazino[2,3-c]thiazin-4-ol (hereinafter also referred to as compound 10 which corresponds to compound I-6 in the Table I below)

Step 1: To a solution of 2-methoxy-ethanol (2.83 g, 37.2 mmol) in DMF (30 ml) was added sodium hydride (1.49 g, 37.2 mmol) in portions at 0°C under nitrogen. After stirred at room temperature for one hour, compound 1 (3.0 g, 12.4 mmol) was added in one portion. The resulting solution was stirred at room temperature for one hour. The mixture was quenched with water, and then poured into EtOAc and water. The solution was separated and the organic phase was washed with brine. It was dried and concentrated in vacuum to give the crude compound 2 (3.1 g, 83.5%) as a colorless syrup without further purification.

Step 2: To a solution of compound 2 (5.3 g, 17.7 mmol) in toluene/ methanol (300 ml/ 100 ml) was added TEA (8.95 g, 88.5 mmol, 5 eq) and Pd(dppf)Cl₂ (2.5 g, 50% wt). The resulting solution was stirred at 80°C under carbon monoxide atmosphere (50 Psi.)
for two days. After cooled to room temperature, the mixture was concentrated in vacuum. The residue was purified by column (PE: EtOAc = 30 : 1) to give compound 3 (4.64 g, 94.3%) as a yellow syrup.

1H NMR: CDCl₃ 400 MHz 57.50 (t, J = 8.0 Hz, 1H), 7.12 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 4.21 (t, J = 4.8 Hz, 2H), 3.90 (s, 3H), 3.78 (t, J = 4.8 Hz, 2H), 3.45 (s, 3H).

Step 3: To a solution of compound 3 (4.64 g, 16.7 mmol) in dry THF (50 ml) was added lithium borohydride (0.74 g, 33.4 mmol) in portions at 0°C under nitrogen. The resulting solution was stirred at 70 °C for overnight. The mixture was added dropwise with water. The resulting solution was extracted with EtOAc. The organic phase was dried and concentrated in vacuum to give compound 4 (4.0 g, 95.8%) as a yellow syrup used directly without further purification.

1H NMR: CDCl₃ 400 MHz 57.47 (t, J = 8.0 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 4.86 (s, 2H), 4.18 (t, J = 4.8 Hz, 2H), 3.78 (t, J = 5.2 Hz, 2H), 3.46 (s, 3H).

Step 4: To a solution of compound 4 (4.0 g, 16.0 mmol) in dry DCM (50 ml) was added dropwise a solution of phosphorus tribromide (6.5 g, 24.0 mmol) in DCM at 0°C. The resulting solution was stirred at room temperature for two hours. The mixture was washed with saturated aqueous sodium bicarbonate and extracted with DCM. The organic phase was dried and concentrated in vacuum to give the crude compound 5 (3.0 g, 59.9%) as a yellow solid used directly without further purification.

1H NMR: CDCl₃ 400 MHz 5 7.42 (t, J = 8.0 Hz, 1H), 7.05-7.00 (m, 2H), 4.63 (s, 2H), 4.18 (t, J = 4.8 Hz, 2H), 3.78 (t, J = 4.8 Hz, 2H), 3.46 (s, 3H).

Step 5: To a solution of compound 5 (2.0 g, 6.4 mmol) in acetonitrile (20 ml) was added potassium thioacetate (1.09 g, 9.6 mmol) in one portion. The resulting solution was stirred and refluxed for overnight. The mixture was filtered and the filtrate was concentrated in vacuum. The residue was purified by column (PE/ EtOAc: 50/ 1) to give compound 6 (1.74 g, 88.3%) as an orange syrup.

1H NMR: CDCl₃ 400 MHz 5 7.36 (t, J = 8.0 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 4.28 (s, 2H), 4.16 (t, J = 4.8 Hz, 2H), 3.77 (t, J = 4.8 Hz, 2H), 3.45 (s, 3H), 2.32 (s, H).

Step 6: To a solution of hydrochloric acid (2M, 0.5 ml) in acetonitrile (10 ml) was added NCS (1.07 g, 8 mmol) in portions. Then a solution of compound 6 (0.62 g, 2 mmol) in acetonitrile (1 ml) was added dropwise at 0°C. The resulting solution was stirred at 0°C for five minutes. The mixture was concentrated in vacuum. The residue was dissolved in Et2O and filtered. The filtrate was concentrated in vacuum to give compound 7 (0.66 g, 100%) as a yellow syrup used directly without further purification.

1H NMR: CDCl₃ 400 MHz 5 7.54 (t, J = 8.0 Hz, 1H), 7.20 (d, J = 8.4 Hz, 1H), 7.15 (d,
Step 7: To a solution of compound 8 (0.43 g, 2.0 mmol) in dry THF (15 ml) was added LiHMDS (4 mmol, 4 ml, 1.0 M) dropwise at -78°C under nitrogen. After stirred at -78°C for 1 hour, a solution of compound 7 (0.67 g, 2.0 mmol) in dry THF was added dropwise to the above mixture at -78°C. The resulting solution was stirred from -78°C to room temperature for overnight. The mixture was quenched with water. THF was removed by concentration and the residue was dissolved in water. The resulting aqueous phase was acidified to pH 3 and extracted with EtOAc. The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo to give the crude product compound 9 (1.03 g, 100%) as a yellow syrup used directly without further purification.

Step 8: To a solution of compound 9 (1.03 g, 2.0 mmol) in DMF (10 ml) was added potassium carbonate (0.55 g, 4.0 mmol) in one portion. The resulting solution was stirred at 110°C for 2 hours. The mixture was filtered and the filtrate was purified by prep. HPLC to give compound 10 (293 mg, 30.5%) as a yellow solid.

1H NMR: CDCls 400 MHz δ 8.54 (s, 1H), 8.41 (s, 1H), 7.58 (t, J = 8.0 Hz, 1H), 7.23-7.20 (m, 2H), 6.20 (t, J = 53.6 Hz, 1H), 4.90-4.79 (m, 1H), 4.55-4.43 (m, 1H), 4.24 (t, J = 4.4 Hz, 2H), 3.80 (t, J = 4.8 Hz, 2H), 3.46 (s, 3H).

Example 2: Preparation of 3-[5-chloro-3-morpholino-2-(trifluoromethyl)phenyl]-1-(2,2-difluoroethyl)-2,2-dioxo-pyrazino[2,3-c]thiazin-4-ol (hereinafter also referred to as compound 20 which corresponds to compound 1-12 in the Table I below)
Step 1: To a solution of compound 11 (80 g, 0.41 mol) in 800 ml AcOH was added Br2 (131 g, 0.82 mol) at room temperature. The mixture was stirred at 50 °C for 5 hrs. The mixture was diluted with CH2Cl2 and washed with water, aq. Na2C03 and brine, the organic layer was dried over Na2S04 and concentrated in vacuo, the crude product was purified by column chromatography to give compound 12 (80 g, yield: 55%).

1H NMR MeOD 400MHz δ 7.69 (s, 1H).

Step 2: To a solution of compound 12 (40 g, 0.11 mol) in H3PO4 (1.2 l) was added dropwise a solution of NaN02 (47 g, 0.68 mol) in 200 ml water at -4 °C, H3PO2 (480 ml) was added dropwise at -4 °C. The resulting mixture was stirred overnight at room temperature. The reaction mixture was diluted with CH2C12 and neutralized with sat. Na2C03, the organic layer was washed brine, dried over anhydrous Na2S04 and concentrated in vacuo, the crude product was purified by column chromatography to give compound 13 (30 g, yield: 78%).

1H NMR MeOD 400MHz δ 7.93 (s, 2H).

Step 3: A mixture of compound 13 (10 g, 29.6 mmol), morpholine (2.6 g, 29.6 mmol), t-BuONa (5.7 g, 59.1 mmol), dppf (1.0 g, 1.77 mmol) and Pd2(db)3 (0.81 g, 0.89 mmol) in toluene (150 ml) was heated to 90 °C under N2 atmosphere overnight. The reaction
mixture was filtered and concentrated in vacuo, the residue was purified by column chromatography to give compound 14 (2.8 g, yield: 25%).

\(^1\)H NMR MeOD 400MHz δ 7.56 (s, 1H), 7.33 (s, 1H), 3.77-3.79 (m, 4H), 2.95-2.97 (m, 4H).

Step 4: PdCp(dpff)\(2\) (1.6 g, 2.2 mmol) was added under N\(_2\) atmosphere to a mixture of compound 14 (7.5 g, 21.8 mmol) and TEA (4.4 g, 43.5 mmol) in MeOH (150 ml) and toluene (200ml) at room temperature. The mixture was heated to 75 °C at 50 psi under CO atmosphere for overnight. The mixture was filtrated and evaporated in vacuo, the residue was purified by column chromatography (PE:EtOAc=50:1) to give compound 15 (6.2 g, yield: 89%).

\(^1\)H NMR: CDCls 400 MHz δ 7.30 (s, 1H), 7.25 (s, 1H), 3.90 (s, 3H), 3.81-3.83 (m, 4H), 2.98-3.00 (m, 4H).

Step 5: To a mixture of compound 15 (6.2 g, 19.2 mmol) in 80 ml of THF was added portionwise LiBH\(_4\) (79 mg, 3.6 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 3 days. The mixture was quenched with water at ice-water and extracted with EtOAc. The organic layer was washed with brine and dried over anhydrous Na\(2\)SO\(_4\), the crude product was purified by column chromatograph (PE:EtOAc=200:1) to give compound 16 (3.8 g, yield: 67%).

\(^1\)H NMR: CDCls 400 MHz δ 7.48 (s, 1H), 7.12 (s, 1H), 4.78 (s, 2H), 3.74-3.76 (m, 4H), 2.82-2.84 (m, 4H).

Step 6: To a solution of compound 16 (3.8 g, 12.9 mmol) in dry CH\(_2\)Cl\(_2\) (50 ml) was added dropwise a solution of phosphorus tribromide (5.2 g, 19.3 mmol) in CH\(_2\)Cl\(_2\) (5 ml) at 0°C. The mixture was stirred at room temperature for 2 hours. The reaction mixture was poured into saturated aqueous sodium bicarbonate and adjusted to pH 8 by addition of more sodium bicarbonate. Then it was extracted with CH\(_2\)Cl\(_2\) and washed with brine. The organic phase was dried over anhydrous sodium sulfate and concentrated in vacuo, the residue was purified by column chromatograph (PE:EtOAc=300:1) to give compound 17 (2.9 g, 63%).

\(^1\)H NMR MeOD 400MHz δ 7.43 (s, 1H), 7.42 (s, 1H), 4.66 (s, 2H), 3.78-3.80 (m, 4H), 2.89-2.91 (m, 4H).

Step 7: To a stirred solution of compound 17 (1.0 g, 2.8 mmol) in acetone (10 ml) was added a solution of sodium sulfite (0.39 g, 3.1 mmol) in water (10 ml). A white precipitate formed. The reaction mixture was refluxed overnight, the reaction mixture was concentrated to approximately one-half of the original column and then filtered. After washing of the filter cake with water was obtained compound 18 (0.94 g, yield: 89%).

\(^1\)H NMR DMSO-d6 400MHz δ 7.49 (s, 1H), 7.40 (s, 1H), 3.92 (s, 2H), 3.66 (br, 4H), 2.81 (br, 4H).
Step 8: To a suspension of compound 18 (0.94 g, 2.5 mmol) in acetonitrile (10 ml) under nitrogen was added POCl₃ (2.3 g, 14.8 mmol) at room temperature. After refluxing for 6 hrs, the mixture was cooled to room temperature and dilute with EtOAc, then poured into a mixture of EtOAc and ice. The organic layer was washed cold water (twice) and brine (twice), and dried over MgSO₄ and concentrated to give compound 19 (0.7 g, yield: 75%).

¹H NMR DMSO-d6 400MHz δ 7.47 (s, 1H), 7.41 (s, 1H), 4.00 (s, 2H), 3.66 (br, 4H), 2.81 (br, 4H).

Step 9: LiHMDS (3.2 ml, 3.2 mmol, 1M) was added dropwise to a solution of compound 8 (0.35 g, 1.6 mmol) in THF at -78 °C under N₂ atmosphere, the mixture was continued to stir for 2 hrs at -78 °C, then compound 19 (0.38 g, 1.6 mmol) in THF was added dropwise to the above mixture, the resulting mixture was stirred for overnight at room temperature. The mixture was quenched with H₂O and acidified to pH 3 with aq. HCl, the reaction mixture was extracted with EtOAc and washed with brine. The organic layer was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified by prep. HPLC to give compound 20 (450 mg, yield: 54%)

¹H NMR: CDCl₃ 400 MHz δ 8.59 (d, 1H, J = 2.4 Hz), 8.46 (d, 1H, J = 2.4 Hz), 8.02 (br, 1H), 7.49 (s, 1H), 7.47 (s, 1H), 6.03-6.34 (m, 1H), 4.80-4.91 (m, 1H), 4.43-4.54 (m, 1H), 3.83-3.85 (m, 4H), 2.96-2.98 (m, 4H).

Table I: Compounds of the formula I.1A-1

<table>
<thead>
<tr>
<th>No.</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>R⁴</th>
<th>R⁵</th>
<th>MS m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-1</td>
<td>Me</td>
<td>3-Me-isoxazolin-5-yl</td>
<td>SO₂Me</td>
<td>H</td>
<td>CH₂CHF₂</td>
<td>514.5</td>
</tr>
<tr>
<td>I-2</td>
<td>Cl</td>
<td>OCF₃</td>
<td>H</td>
<td>H</td>
<td>CH₂CHF₂</td>
<td>457.8</td>
</tr>
<tr>
<td>I-3</td>
<td>Me</td>
<td>SO₂CH₂CH₂C(NOMe)</td>
<td>H</td>
<td>CH₂CHF₂</td>
<td>500.5</td>
<td></td>
</tr>
<tr>
<td>I-4</td>
<td>Me</td>
<td>OMe</td>
<td>SO₂Me</td>
<td>H</td>
<td>CH₂CHF₂</td>
<td>461.5</td>
</tr>
<tr>
<td>I-5</td>
<td>Cl</td>
<td>OEt</td>
<td>SO₂Et</td>
<td>H</td>
<td>CH₂CHF₂</td>
<td>509.9</td>
</tr>
<tr>
<td>I-6</td>
<td>CF₃</td>
<td>OCH₂CH₂OMe</td>
<td>H</td>
<td>CH₂CHF₂</td>
<td>481.8</td>
<td></td>
</tr>
<tr>
<td>I-7</td>
<td>Cl</td>
<td>SO₂CH₂CH₂CMe₂</td>
<td>H</td>
<td>CH₂CHF₂</td>
<td>505.9</td>
<td></td>
</tr>
</tbody>
</table>
Wherein Me denotes methyl, Et denotes ethyl, and Ph denotes phenyl

II. Use examples

The herbicidal activity of the compounds of the formula I was demonstrated by the following greenhouse experiments:

The culture containers used were plastic flowerpots containing loamy sand with approximately 3.0% of humus as the substrate. The seeds of the test plants were sown separately for each species.

For the pre-emergence treatment, the active ingredients, which had been suspended or emulsified in water, were applied directly after sowing by means of finely distributing nozzles. The containers were irrigated gently to promote germination and growth and subsequently covered with transparent plastic hoods until the plants had rooted. This cover caused uniform germination of the test plants, unless this has been impaired by the active ingredients.

For the post-emergence treatment, the test plants were first grown to a height of 3 to 15 cm, depending on the plant habit, and only then treated with the active ingredients which had been suspended or emulsified in water. For this purpose, the test plants were either sown directly and grown in the same containers, or they were first grown separately as seedlings and transplanted into the test containers a few days prior to treatment.

Depending on the species, the plants were kept at 10-25°C or 20-35°C. The test period extended over 2 to 4 weeks. During this time, the plants were tended, and their response to the individual treatments was evaluated.

Evaluation was carried out using a scale from 0 to 100. 100 means no emergence of
the plants, or complete destruction of at least the aerial moieties, and 0 means no
damage, or normal course of growth. A good herbicidal activity is given at values of at
least 70 and a very good herbicidal activity is given at values of at least 85.

The plants used in the greenhouse experiments belonged to the following species:

<table>
<thead>
<tr>
<th>Bayer Code</th>
<th>Scientific name</th>
<th>English name</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABUTH</td>
<td>Abutilon theophrasti</td>
<td>velvetleaf</td>
</tr>
<tr>
<td>AMARE</td>
<td>Amaranthus retroflexus</td>
<td>common amaranth</td>
</tr>
<tr>
<td>CHEAL</td>
<td>Chenopodium album</td>
<td>lampsquaters</td>
</tr>
<tr>
<td>ECHCG</td>
<td>Echinochloa crus-galli</td>
<td>comon barnyardgrass</td>
</tr>
<tr>
<td>GALAP</td>
<td>Galium aparine</td>
<td>goosegrass</td>
</tr>
<tr>
<td>SOLNI</td>
<td>Solanum nigrum</td>
<td>black nightshade</td>
</tr>
</tbody>
</table>

At an application rate of 0.25 kg/ha, the compound I-8, applied by the post-
emergence method, showed very good herbicidal activity against ABUTH.

At an application rate of 0.5 kg/ha, the compound I-1, applied by the post-emergence
method, showed very good herbicidal activity against AMARE.

At an application rate of 0.5 kg/ha, the compound I-4, applied by the post-emergence
method, showed good herbicidal activity against AMARE.

At an application rate of 0.4 kg/ha, the compound I-5, applied by the post-emergence
method, showed very good herbicidal activity against AMARE.

At an application rate of 0.25 kg/ha, the compounds I-1, I-2, I-3 and I-4, applied
by the post-emergence method, showed very good herbicidal activity against AMARE.

At an application rate of 0.5 kg/ha, the compounds I-1, I-4 and I-6, applied by the
post-emergence method, showed very good herbicidal activity against CHEAL.

At an application rate of 0.4 kg/ha, the compound I-5, applied by the post-emergence
method, showed very good herbicidal activity against CHEAL.

At an application rate of 0.25 kg/ha, the compound I-10, applied by the post-
emergence method, showed very good herbicidal activity against CHEAL.

At an application rate of 0.5 kg/ha, the compound I-1, applied by the post-emergence
method, showed very good herbicidal activity against ECHCG.

At an application rate of 0.4 kg/ha, the compound I-5, applied by the post-emergence
method, showed very good herbicidal activity against ECHCG.

At an application rate of 0.25 kg/ha, the compound I-14, applied by the post-
emergence method, showed very good herbicidal activity against ECHCG.

At an application rate of 0.5 kg/ha, the compound I-6, applied by the post-emergence
method, showed very good herbicidal activity against GALAP.

At an application rate of 0.25 kg/ha, the compounds I-1, I-2, I-3 and I-4, applied
by the post-emergence method, showed very good herbicidal activity against SOLNI.
Claims

1. A substituted pyridazine of the formula I

\[
\text{I}
\]

in which the variables have the following meaning:

\[R\] is 0-\(\text{R}^A\), S(0) \(\text{R}^a\) or 0-S(0) \(\text{R}^a\);

\[\text{R}^A\] is hydrogen, c \(\text{C}^4\)-alkyl, Z \(\text{C}^3\)-C\(6\)-cycloalkyl, c \(\text{C}^4\)-haloalkyl,
C\(2\)-C\(6\)-alkenyl, Z \(\text{C}^3\)-C\(6\)-cycloalkenyl, C\(2\)-C\(6\)-alkynyl,
Z-(tri-\(\text{C}^1\)-c\(4\)-alkyl)silyl, Z-c (\(=0\))-\(\text{R}^a\), Z-NR\(=\text{c}\) (0)-NR\(=\text{R}^a\), Z-P(\(=\text{R}^a\))(R \(^a\)) \(2\),
NR\(=\text{R}^a\), a 3- to 7-membered monocyclic or 9- or 10-membered bicyclic saturated, unsaturated or aromatic heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S, which may be partially or fully substituted by groups \(\text{R}^a\) and/or \(\text{R}^b\);

\[\text{R}^a\] is hydrogen, OH, \(\text{C}^1\)-\(\text{C}^6\)-alkyl, \(\text{C}^1\)-\(\text{C}^4\)-haloalkyl, Z \(\text{C}^3\)-c\(6\)-cycloalkyl, C\(2\)-c\(6\)-alkenyl, Z-c\(\text{c}^3\)-c\(6\)-cycloalkenyl, C\(2\)-c\(6\)-alkynyl,
Z-c\(\text{c}^1\)-c\(6\)-alkoxy, Z-c\(\text{c}^6\)-haloalkoxy, Z-c\(\text{c}^3\)-c\(6\)-alkenyloxy,
Z-c\(\text{c}^6\)-c\(6\)-alkynyl, NR\(=\text{R}^a\), c\(\text{c}^1\)-c\(6\)-alkylsulfonyl, Z-(tri-\(\text{C}^1\)-c\(4\)-alkyl)silyl, Z-phenyl, Z-phenoxy, Z-phenylamino or a 5- or 6-membered monocyclic or 9- or 10-membered bicyclic heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S, where the cyclic groups are unsubstituted or substituted by 1, 2, 3 or 4 groups \(\text{R}^b\);

\[\text{R}^b\] \(\text{R}^*\) independently of one another are hydrogen, c\(1\)-c\(8\)-alkyl, c\(1\)-c\(4\)-haloalkyl, c\(6\)-c\(8\)-alkenyl, c\(6\)-c\(8\)-alkynyl, Z-C\(3\)-C\(6\)-cycloalkyl, Z-c\(\text{c}1\)-c\(6\)-alkoxy, Z-c\(\text{c}1\)-c\(6\)-haloalkoxy, Z-c (\(=0\))-\(\text{R}^a\),
Z-phenyl, a 3- to 7-membered monocyclic or 9- or 10-membered bicyclic saturated, unsaturated or aromatic heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S and which is attached via Z;

\[\text{R}^*\] and \(\text{R}^*\) together with the nitrogen atom to which they are attached may also form a 5- or 6-membered monocyclic or 9- or 10-membered bicyclic heterocycle which contains 1, 2, 3 or
4 heteroatoms selected from the group consisting of O, N and S; 
Z is a covalent bond or c 1-C4 -alkylene;
n is 0, 1 or 2;
R^1 is cyano, halogen, nitro, c 1-C6 -alkyl, c 2-C6 -alkenyl, c 2-C6 -alkynyl, c 1-C6-
haloalkyl, Z-c1-C6 -alkoxy, Z-c1-C4 -alkoxy-c1-C4 -alkoxy, Z-c1-C4 -alkythio, 
Z-c1-C4 -alkythio-c1-C4 -alkoxy, c 2-C6 -alkenylxy, c 2-C6 -alkynloxy, c 1-C6-
haloalkoxy, c 1-C4 -haloalkoxy-c1-C4 -alkoxy, S(0) R^b, Z-phenoxy, Z-
heterocyclyloxy, where heterocyclyl is a 5- or 6-membered monocyclic or 9-
or 10-membered bicyclic saturated, partially unsaturated or aromatic 
heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the 
group consisting of O, N and S, where cyclic groups are unsubstituted or 
partially or fully substituted by R^b; 
R^bb is C1=C6-alkyl, C2-C6-alkenyl, C2-C6-alkynyl, C2-C6-haloalkenyl, C2-C6-
haloalkyl or c 1-C6 -haloalkyl and n is 0, 1 or 2; 
A is N or C-R^2; 
R^2 - is Z^1-heterocyclyl, where heterocyclyl is a 5- or 6-membered monocyclic or 
9- or 10-membered bicyclic saturated, partially unsaturated or aromatic 
heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the 
group consisting of O, N and S, where cyclic groups are unsubstituted or 
partially or fully substituted by R^b, 
- is phenyl which is attached via Z^1 or oxygen and is unsubstituted or 
substituted by c 1-C4 -alkyl, c 1-C4 -alkoxy, c 1-C4 -haloalkyl, c 1-C4 -alkoxy-
c 1-C4 -alkyl or c 1-C4 -alkoxy-c1-C4 -alkoxy; 
- is C1-C6 -alkenyl, c 2-C6 -haloalkyl, c 1-C4 -alkoxy-c1-C4 -alkyl, c2-C6 -alkenyl, 
c2-C6 -alkynyl, c 2-C8 -haloalkenylnyl, c 2-C8 -haloalkoxy, Z-c1-C4-
alkoxy-c1-C4 -alkoxy, Z-c1-C4 -haloalkenoxy-c1-C4 -alkoxy, Z-c1-C6 -haloalkoxy, 
c2-C8 -alkenylxy, c 2-C8 -alkynloxy, Z-c1-C4 -alkythio, Z-c1-C6 -haloalkythio, 
Z-C(=0)-R or S(0) R^b; 
Z^1 is a covalent bond, c 1-C4 -alkeneynoxy, c 1-C4 -oxyalkylene or c 1-C4-
alkeneynoxy-C1-C4 -alkylene; 
R^b independently of one another are Z-CN, Z-OH, Z-N=O, Z-halogen, 
oxo (=0), =N-R^b, C1-C6-alkenyl, c1-c4-haloalkenyl, C2-C6-alkenyl, C2-C6-
alkynyl, Z-c1-c6-alkenyl, Z-c1-c6-haloalkenyl, Z-C3-C10-cycloalkenyl, 
O-Z-c1-c10-cycloalkenyl, Z-C(=0)-R, NRR^*, Z-(tri-c1-c4-alkyl)silyl, 
Z-phenyl or S(0) R^b, where 
R^2 together with the group attached to the adjacent carbon atom may also 
form a five- to ten-membered saturated or partially or fully unsaturated 
mono- or bicyclic ring which, in addition to carbon atoms, may contain 1, 2 
or 3 heteroatoms selected from the group consisting of O, N and S and 
may be substituted by additional groups R^b;
R³ is hydrogen, cyano, halogen, nitro, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy, C₁-C₄-haloalkoxy, C₂-C₄-alkoxy, C₂-C₄-haloalkoxy, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₂-C₄-alkenyloxy, C₂-C₄-haloalkenyloxy, C₂-C₄-alkynyl, C₂-C₄-haloalkynyl, C₂-C₆-haloalkenyl, C₃-C₆-alkenyl, C₃-C₆-alkynyl, C₃-C₆-haloalkenyloxy, C₃-C₆-haloalkynyl or Z-phenyl which is unsubstituted or substituted by 1 to 5 groups R⁸b; where in the groups R⁸ and their substituents, the carbon chains and/or the cyclic groups may be partially or fully substituted by groups R⁸b, or a N-oxide or an agriculturally suitable salt thereof.

2. The compound of the formula I according to claim 1 in which A is CR².

5. The compound of the formula I according to claim 2 in which R² is an optionally substituted five- or six-membered saturated, partially unsaturated or aromatic heterocycle which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S.

4. The compound of the formula I according to claim 2 in which R² is phenyl in which # denotes the bond through which group R² is attached and:

R³ is H or OCH₃; and
R⁴ is H, CH₃, CF₃, OCH3, OCH₂OCH₃ or OCH₂CH₂OCH₃.

5. The compound of the formula I according to claim 3 in which R² is an optionally R⁸-substituted heterocycle selected from the group consisting of isoxazoline, tetrazolone, 1,2-dihydropyrimidone, 1,4-dihydropyrimidone, tetrahydrofuran, dioxolane, piperidine, morpholine, piperazine, isoxazole, pyrazole, thiazole, oxazole, furyl, pyridine and pyrazine.

6. The compound of the formula I according to claim 2 in which R² is an aliphatic group selected from the group consisting of C₁-C₆-alkyl, C₂-C₆-alkenyl, Z-C₁-C₄-alkenyl, Z-C₁-C₄-haloalkenyl, C₃-C₆-alkenyl, C₃-C₆-alkoxy, C₃-C₆-haloalkenyloxy, C₃-C₆-haloalkynyl, C₃-C₆-haloalkynyl, C₁-C₄-alkoxycarbonyl, S(O)n-C₁-C₈-alkyl and S(O)n-C₁-C₈-haloalkyl.

7. The compound of the formula I according to any of claims 1 to 6 in which
R is halogen, C_i-C_4-alkyl, C_i-C_4-haloalkyl, C_i-C_4-alkoxy-C_i-C_4-alkyl, C_1-C_4-alkoxy-C_1-C_4-alkyl, C_i-C_4-alkoxy, C_i-C_4-haloalkoxy, C_i-C_4-alkylthio, C_i-C_4-haloalkylthio and C_i-C_4-alkylsulfonyl; and

R is H, halogen, CN, N_0_2, C_i-C_4-alkyl, C_i-C_4-haloalkyl, C_i-C_4-alkoxy, C_1-C_4-haloalkoxy, C_i-C_4-alkylthio, C_i-C_4-haloalkylthio or C_i-C_4-alkylsulfonyl.

8. The compound of the formula I according to claim 2 in which R^2 together with R^1 or R^3 forms an optionally R^b-substituted five- to ten-membered mono- or bicyclic partially unsaturated ring which contains 1, 2, 3 or 4 heteroatoms selected from the group consisting of O, N and S.

9. The compound of the formula I according to claim 8 in which the ring substituted by groups R^1, R^2, R^3 and R^4 corresponds to one of groups A to L.

10. The compound of the formula I according to claim 1 in which A is nitrogen.

11. The compound of the formula I according to claim 10 in which

R is nitro, C_i-C_4-alkyl, C_i-C_4-haloalkyl, C_i-C_4-alkoxy-C_i-C_4-alkyl, C_i-C_4-alkoxy-, C_i-C_4-alkoxy-C_i-C_4-alkyl, C_i-C_4-alkoxy, C_i-C_4-haloalkoxy, C_i-C_4-alkylthio, C_i-C_4-haloalkylthio or C_i-C_4-alkylsulfonyl; and
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R^3 is H, CN, NO_2, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-alkythio or C_1-C_4-alkylsulfonyl.

12. The compound of the formula I according to any of the preceding claims in which the groups R^6 are selected from the group consisting of C_1-C_4-alkyl, C_i-C_4-haloalkyl, C_1-C_4-alkoxy, C_1-C_4-alkoxy-C_1-C_4-alkyl and C_1-C_4-alkythio-C_1-C_4-alkyl.

13. The compound of the formula I according to any of the preceding claims in which R^4 is H, C_5-C_6-alkenyl, C_5-C_6-haloalkenyl, C_5-C_6-alkynyl, C_5-C_6-haloalkynyl or C_1-C_6-alkylcarbonyl; R^5 is C_1-C_6-alkyl or C_1-C_4-haloalkyl; and R^4, R^5, R^6 are H.

14. A composition comprising a herbicidally effective amount of at least one compound of the formula I or an agriculturally suitable salt thereof according to any of claims 1 to 13 and auxiliaries customary for formulating crop protection agents.

15. A method for controlling unwanted vegetation which comprises allowing a herbicidally effective amount of at least one compound of the formula I or of an agriculturally suitable salt thereof according to any of claims 1 to 13 to act on plants, their seed and/or their habitat.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D513/04 A01N43/90

ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D A01N

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

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

EPO-Internal , CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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* Special categories of cited documents:

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

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

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

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

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

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

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

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

"Z" document member of the same patent family

Date of the actual completion of the international search

19 May 2011

Date of mailing of the international search report

25/05/2011

Name and mailing address of the ISA/
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Authorized officer

Johnson, Claire
# INTERNATIONAL SEARCH REPORT

**International application No.**  
PCT/EP2011/054128

## Box No. II  Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:  
   because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claims Nos.:  
   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. □ Claims Nos.:  
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III  Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

> see additional sheet

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ■ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:  

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:  

**Remark on Protest**

- □ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

- □ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

- ■ No protest accompanied the payment of additional search fees.
This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 2-6, 8, incompletely; 1, 7, 12-15 (partially)
   Compounds which differ from the exemplified compounds of D1 and D2 because of the nature of the R2 group
   ---

2. claims: 1, 7, 12-15 (all partially)
   Compounds which differ from the exemplified compounds of D1 and D2 because of the unsubstituted carbon atom adjacent to the CR4 group
   ---

3. claims: 10, 11 (completely); 1, 7, 12-15 (partially)
   Compounds which differ from the exemplified compounds of D1 and D2 because R3 and R4 cannot together form a fused ring
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

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