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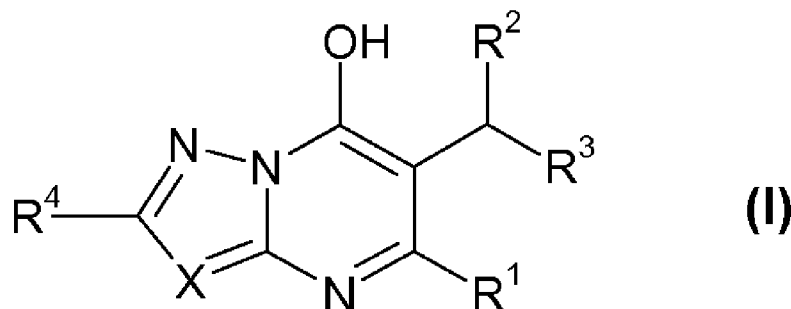
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(54) Title: HERBICIDAL AZOLOPYRIMIDINES



(57) Abstract: The present invention relates to azolopyrimidines of formula (I) wherein the variables are defined according to the description, compositions comprising them and their use as herbicides, i.e. for controlling harmful plants and a method for controlling unwanted vegetation which comprises allowing a herbicidal effective amount of at least one azolopyrimidine of the formula (I) to act on plants, their seed and/or their habitat.

Herbicidal azolopyrimidines

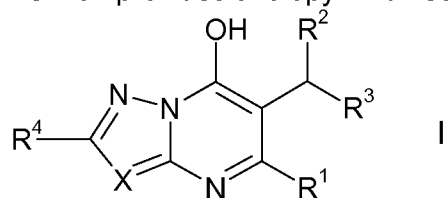
The present invention relates to azolopyrimidines of the general formula I defined below and to their use as herbicides. Moreover, the invention relates to compositions
 5 for crop protection and to a method for controlling unwanted vegetation.

The herbicidal properties of known herbicidal compounds with regard to the harmful plants are not always entirely satisfactory.

10 It is therefore an object of the present invention to provide novel compounds having improved herbicidal action. To be provided are in particular azolopyrimidines which have high herbicidal activity, in particular even at low application rates, and which are sufficiently compatible with crop plants for commercial utilization.

15 These and further objects are achieved by azolopyrimidines of the formula I, defined below, and by their agriculturally suitable salts.

Accordingly, the present invention provides azolopyrimidines of formula I



20 wherein

R¹ is CH₃, F, Cl or Br;

R² is hydrogen or C₁-C₄ alkyl;

R³ is phenyl or thienyl,

25 wherein the phenyl or thienyl ring is unsubstituted or substituted with halogen, cyano, nitro, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-alkylthio;

R⁴ is hydrogen or C₁-C₄-alkyl; and

X is nitrogen or CR⁵,

30 wherein R⁵ is hydrogen, cyano, C₁-C₄ alkyl, hydroxycarbonyl, C₁-C₆-alkoxycarbonyl, C₂-C₆-alkenyloxycarbonyl, C₂-C₆-alkynyloxycarbonyl, benzyloxycarbonyl, halobenzyloxycarbonyl, aminocarbonyl, C₁-C₆-alkylaminocarbonyl, di(C₁-C₆)-alkylaminocarbonyl, C₂-C₆-alkenylamino-carbonyl, C₂-C₆-alkynylaminocarbonyl,
 35 amino(thiocarbonyl);

including their agriculturally acceptable salts.

The present invention also provides the use of azolopyrimidines of the general formula
 40 I as herbicides, i.e. for controlling harmful plants.

The present invention also provides compositions comprising at least one azolopyrimidines of the formula I and auxiliaries customary for formulating crop protection agents.

5

The present invention furthermore provides a method for controlling unwanted vegetation where a herbicidal effective amount of at least one azolopyrimidines of the formula I is allowed to act on plants, their seeds and/or their habitat. Application can be done before, during and/or after, preferably during and/or after, the emergence of the undesirable plants.

10

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

15

As used herein, the terms "controlling" and "combating" are synonyms.

As used herein, the terms "undesirable vegetation" and "harmful plants" are synonyms.

20

If the azolopyrimidines of formula I as described herein are capable of forming geometrical isomers, for example E/Z isomers, it is possible to use both, the pure isomers and mixtures thereof, in the compositions according to the invention.

25

If the azolopyrimidines of formula I as described herein have one or more centers of chirality and, as a consequence, are present as enantiomers or diastereomers, it is possible to use both, the pure enantiomers and diastereomers and their mixtures, in the compositions according to the invention.

30

If the azolopyrimidines of formula I as described herein have ionizable functional groups, they can also be employed in the form of their agriculturally acceptable salts. Suitable are, in general, the salts of those cations and the acid addition salts of those acids whose cations and anions, respectively, have no adverse effect on the activity of the active compounds.

35

Preferred cations are the ions of the alkali metals, preferably of lithium, sodium and potassium, of the alkaline earth metals, preferably of calcium and magnesium, and of the transition metals, preferably of manganese, copper, zinc and iron, further ammonium and substituted ammonium in which one to four hydrogen atoms are replaced by C₁-C₄-alkyl, hydroxy-C₁-C₄-alkyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, hydroxy-C₁-C₄-alkoxy-C₁-C₄-alkyl, phenyl or benzyl, preferably ammonium, methylammonium, isopropylammonium, dimethylammonium, diisopropylammonium, trimethylammonium, tetramethylammo-

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nium, tetraethylammonium, tetrabutylammonium, 2-hydroxyethylammonium, 2-(2-hydroxyeth-1-oxy)eth-1-ylammonium, di(2-hydroxyeth-1-yl)ammonium, benzyl-trimethylammonium, benzyltriethylammonium, furthermore phosphonium ions, sulfo-
 5 nium ions, preferably tri(C₁-C₄-alkyl)sulfonium, such as trimethylsulfonium, and sulfoxonium ions, preferably tri(C₁-C₄-alkyl)sulfoxonium.

Anions of useful acid addition salts are primarily chloride, bromide, fluoride, iodide, hy-
 drogensulfate, methylsulfate, sulfate, dihydrogenphosphate, hydrogenphosphate, ni-
 10 trate, bicarbonate, carbonate, hexafluorosilicate, hexafluorophosphate, benzoate and
 also the anions of C₁-C₄-alkanoic acids, preferably formate, acetate, propionate and
 butyrate.

The organic moieties mentioned in the definition of the variables R¹ to R⁵, are - like the
 term halogen - collective terms for individual enumerations of the individual group
 15 members. The term halogen denotes in each case fluorine, chlorine, bromine or iodine.
 All hydrocarbon chains, i.e. all alkyl, can be straight-chain or branched, the prefix C_n-C_m
 denoting in each case the possible number of carbon atoms in the group.

Examples of such meanings are:

- 20 - C₁-C₄-alkyl: for example CH₃, C₂H₅, n-propyl, and CH(CH₃)₂ n-butyl, CH(CH₃)-
 C₂H₅, CH₂-CH(CH₃)₂ and C(CH₃)₃;
- C₁-C₆-alkyl: C₁-C₄-alkyl as mentioned above, and also, for example, n-pentyl, 1-
 methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, n-hexyl,
 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl,
 25 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 or 1-ethyl-2-methylpropyl,
 preferably methyl, ethyl, n-propyl, 1-methylethyl, n-butyl, 1,1-dimethylethyl, n-pentyl
 or n-hexyl;
- 30 - C₁-C₄-haloalkyl: a C₁-C₄-alkyl radical as mentioned above which is partially or
 fully substituted by fluorine, chlorine, bromine and/or iodine, for example, chloromethyl,
 dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chloro-
 fluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, bromomethyl, iodomethyl, 2-
 fluoroethyl, 2-chloroethyl, 2-bromoethyl, 2-iodoethyl, 2,2-difluoroethyl, 2,2,2-trifluoro-
 35 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 a C₁-C₃-haloalkyl radical as mentioned above, and also, for example,
 40 1-(fluoromethyl)-2-fluoroethyl, 1-(chloromethyl)-2-chloroethyl, 1-(bromomethyl)-
 2-bromoethyl, 4-fluorobutyl, 4-chlorobutyl, 4-bromobutyl, nonafluorobutyl, 1,1,2,2,-
 tetrafluoroethyl and 1-trifluoromethyl-1,2,2,2-tetrafluoroethyl;

- C₂-C₄-alkenyl: for example 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;
- C₂-C₆-alkenyl and also the C₂-C₆-alkenyl moieties of C₂-C₆-alkenyloxycarbonyl and C₂-C₆-alkenylaminocarbonyl: C₂-C₄-alkenyl as mentioned above and also, for example 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, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;
- C₂-C₄-alkynyl: for example ethynyl, 1-propynyl, 2-propynyl, 1-butylnyl, 2-butylnyl, 3-butylnyl and 1-methyl-2-propynyl;
- C₂-C₆-alkynyl and also the C₂-C₆-alkynyl moieties of C₂-C₆-alkynyloxycarbonyl and C₂-C₆-alkynylaminocarbonyl: C₂-C₄-alkynyl as mentioned above and also, for example 1-pentynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 1-methyl-2-butylnyl, 1-methyl-3-butylnyl, 2-methyl-3-butylnyl, 3-methyl-1-butylnyl, 1,1-dimethyl-2-propynyl, 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-butylnyl, 1,1-dimethyl-3-butylnyl, 1,2-dimethyl-3-butylnyl, 2,2-dimethyl-3-butylnyl, 3,3-dimethyl-1-butylnyl, 1-ethyl-2-butylnyl, 1-ethyl-3-butylnyl, 2-ethyl-3-butylnyl and 1-ethyl-1-methyl-2-propynyl;
- C₁-C₄-alkoxy: for example methoxy, ethoxy, propoxy, 1-methylethoxy butoxy, 1-methylpropoxy, 2-methylpropoxy and 1,1-dimethylethoxy;
- C₁-C₆-alkoxy and also the C₁-C₆-alkoxy moieties of C₁-C₆-alkoxycarbonyl: C₁-C₄-alkoxy as mentioned above, and also, for example, pentoxy, 1-methylbutoxy, 2-methylbutoxy, 3-methoxybutoxy, 1,1-dimethylpropoxy, 1,2-dimethylpropoxy, 2,2-dimethylpropoxy, 1-ethylpropoxy, hexoxy, 1-methylpentoxy, 2-methylpentoxy, 3-methylpentoxy, 4-methylpentoxy, 1,1-dimethylbutoxy, 1,2-dimethylbutoxy, 1,3-dimethylbutoxy, 2,2-dimethylbutoxy, 2,3-dimethylbutoxy, 3,3-dimethylbutoxy, 1-ethylbutoxy, 2-ethylbutoxy, 1,1,2-trimethylpropoxy, 1,2,2-trimethylpropoxy, 1-ethyl-1-methylpropoxy and 1-ethyl-2-

methylpropoxy.

- C₁-C₄-alkylthio: for example methylthio, ethylthio, propylthio, 1-methylethylthio, butylthio, 1-methylpropylthio, 2-methylpropylthio and 1,1-dimethylethylthio;
- C₁-C₆-alkylamino and the C₁-C₆-alkylamino moieties of C₁-C₆-alkylamino-carbonyl: for example methylamino, ethylamino, propylamino, 1-methylethylamino, butylamino, 1-methylpropylamino, 2-methylpropylamino, 1,1-dimethylethylamino, pentylamino, 1-methylbutylamino, 2-methylbutylamino, 3-methylbutylamino, 2,2-dimethylpropylamino, 1-ethylpropylamino, hexylamino, 1,1-dimethylpropylamino, 1,2-dimethylpropylamino, 1-methylpentylamino, 2-methylpentylamino, 3-methylpentylamino, 4-methylpentylamino, 1,1-dimethylbutylamino, 1,2-dimethylbutylamino, 1,3-dimethylbutylamino, 2,2-dimethylbutylamino, 2,3-dimethylbutylamino, 3,3-dimethylbutylamino, 1-ethylbutylamino, 2-ethylbutylamino, 1,1,2-trimethylpropylamino, 1,2,2-trimethylpropylamino, 1-ethyl-1-methylpropylamino or 1-ethyl-2-methylpropylamino;
- di(C₁-C₄-alkyl)amino: and the di(C₁-C₄-alkyl)amino moieties of di(C₁-C₄-alkyl)-aminocarbonyl: for example N,N-dimethylamino, N,N-diethylamino, N,N-dipropylamino, N,N-di(1-methylethyl)amino, N,N-dibutylamino, N,N-di(1-methylpropyl)amino, N,N-di(2-methylpropyl)amino, N,N-di(1,1-dimethylethyl)amino, N-ethyl-N-methylamino, N-methyl-N-propylamino, N-methyl-N-(1-methylethyl)amino, N-butyl-N-methylamino, N-methyl-N-(1-methylpropyl)amino, N-methyl-N-(2-methylpropyl)amino, N-(1,1-dimethylethyl)-N-methylamino, N-ethyl-N-propylamino, N-ethyl-N-(1-methylethyl)amino, N-butyl-N-ethylamino, N-ethyl-N-(1-methylpropyl)amino, N-ethyl-N-(2-methylpropyl)amino, N-ethyl-N-(1,1-dimethylethyl)amino, N-(1-methylethyl)-N-propylamino, N-butyl-N-propylamino, N-(1-methylpropyl)-N-propylamino, N-(2-methylpropyl)-N-propylamino, N-(1,1-dimethylethyl)-N-propylamino, N-butyl-N-(1-methylethyl)amino, N-(1-methylethyl)-N-(1-methylpropyl)amino, N-(1-methylethyl)-N-(2-methylpropyl)amino, N-(1,1-dimethylethyl)-N-(1-methylethyl)amino, N-butyl-N-(1-methylpropyl)amino, N-butyl-N-(2-methylpropyl)amino, N-butyl-N-(1,1-dimethylethyl)amino, N-(1-methylpropyl)-N-(2-methylpropyl)amino, N-(1,1-dimethylethyl)-N-(1-methylpropyl)amino and N-(1,1-dimethylethyl)-N-(2-methylpropyl)amino;
- di(C₁-C₆-alkyl)amino and the di(C₁-C₆-alkyl)amino moieties of di(C₁-C₆-alkyl)-aminocarbonyl: di(C₁-C₄-alkyl)amino as mentioned above, and also, for example, N,N-dipentylamino, N,N-dihexylamino, N-methyl-N-pentylamino, N-ethyl-N-pentylamino, N-methyl-N-hexylamino and N-ethyl-N-hexylamino;
- halobenzyloxycarbonyl: a benzyloxycarbonyl group [C₆H₅-CH₂-O-C(=O)-], wherein the phenyl ring is substituted by one to five halogen atoms.

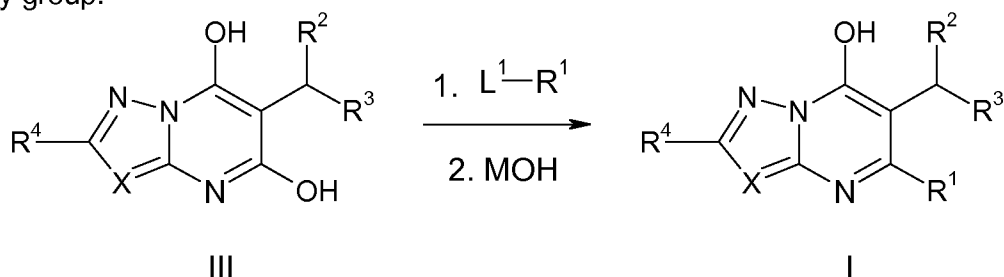
According to a preferred embodiment of the invention preference is also given to those azolopyrimidines of formula I, wherein the variables, either independently of one another or in combination with one another, have the following meanings:

- 40 R¹ is CH₃ or Cl;
 particularly preferred CH₃,
 also particularly preferred Cl;

- R^2 hydrogen;
 R^3 is phenyl, which is unsubstituted or substituted with halogen,
 preferably phenyl which is unsubstituted or substituted with one to three halogen
 atoms,
 5 particularly preferred phenyl which is unsubstituted,
 also particularly preferred phenyl which is substituted with one to three halogen
 atoms;
 R^4 is hydrogen;
 R^5 is cyano;
 10 X is preferably nitrogen,
 is also preferably CR⁵.

15 The azolopyrimidines of formula I according to the invention can be prepared by
 standard processes of organic chemistry, for example by the following process:

20 The azolopyrimidines of formula I wherein R^1 is halogen can be prepared by substitu-
 tion of the respective hydroxy groups in the hydroxyazolopyrimidine III by halogen and
 subsequent replacing in the resulting dihaloazolopyrimidine II one halogen with an hy-
 droxy group:



25 L^1R^1 is an halogenating agent like SOCl_2 , POCl_3 , PCl_5 , POBr_3 , PBr_5 , SOBr_2 .

MOH is an alkali metal and/or alkaline earth metal hydroxide such as lithium hydroxide,
 sodium hydroxide, potassium hydroxide and calcium hydroxide.

30 The substitution of hydroxyazolopyrimidine III is usually carried out at from 0°C to the
 boiling point of the reaction mixture, preferably at from 10°C to 150°C, particularly pref-
 erably at from 50°C to 100°C, in an inert organic solvent.

Suitable solvents are aliphatic hydrocarbons such as pentane, hexane, cyclohexane
 and mixtures of C₅-C₈-alkanes, aromatic hydrocarbons such as toluene, o-, m- and p-
 xylene, halogenated hydrocarbons such as dichloromethane, 1,2-dichloroethane, chlo-
 35 roform and chlorobenzene, ethers such as diethyl ether, diisopropyl ether, tert.-butyl
 methylether, dioxane, anisole and tetrahydrofuran, nitriles such as acetonitrile and
 propionitrile, ketones such as acetone, methyl ethyl ketone, diethyl ketone and tert-

butyl methyl ketone, as well as dimethylsulfoxide, dimethylformamide and N,N-dimethylacetamide or N-methylpyrrolidone. Particular preference is given to toluene. It is also possible to use mixtures of the solvents mentioned.

- 5 It is also possible to use a phase-transfer catalyst like triethylaminhydrochloride.

The substitution of the dihaloazolopyrimidine II is usually carried out at from 0°C to the boiling point of the reaction mixture, preferably at from 10°C to 150°C, particularly preferably at from 50°C to 100°C, in an inert organic solvent

Suitable solvents are dimethylsulfoxide, dimethylformamide and N,N-dimethylacetamide or N-methylpyrrolidone, alcohols like methanol, ethanol, isopropanol and water. Particular preference is given to water. It is also possible to use mixtures of the solvents mentioned.

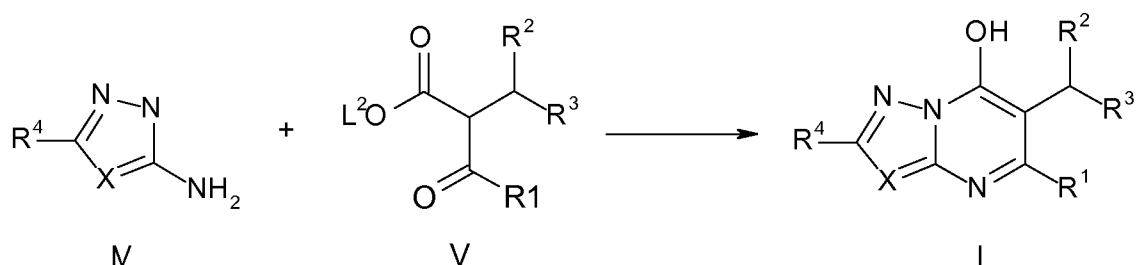
The reaction mixtures are worked up in a customary manner, for example by mixing with water, separation of the phases and, if appropriate, chromatographic purification of the crude product.

Some of the intermediates and end products are obtained in the form of viscous oils, which can be purified or freed from volatile components under reduced pressure and at moderately elevated temperature.

If the intermediates and the end products are obtained as solid, purification can also be carried out by recrystallisation or digestion.

The azolopyrimidines of formula I wherein R¹ is CH₃ or alkyl can be prepared by cyclisation of an acylacetate V with an aminoazol IV:

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L² stands for C₁-C₆-alkyl.

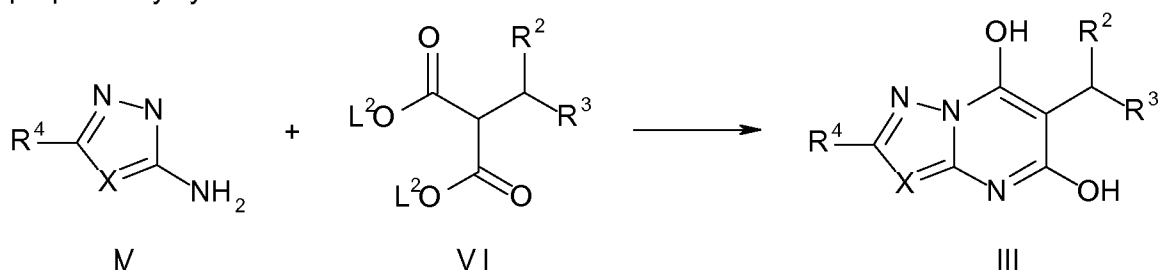
The reaction of the acylacetate V with the aminoazol IV is usually carried out at from 0°C to the boiling point of the reaction mixture, preferably at from 0°C to 150°C, particularly preferably at from 50°C to 100°C, in an inert organic solvent in the presence of a base (e.g. T. Russ, Synthesis, 1990, 8, 721-723).

Suitable solvents are aliphatic hydrocarbons such as pentane, hexane, cyclohexane and mixtures of C₅-C₈-alkanes, aromatic hydrocarbons such as toluene, o-, m- and p-xylene, halogenated hydrocarbons such as dichloromethane, 1,2-dichloroethane, chloroform and chlorobenzene, ethers such as diethyl ether, diisopropyl ether, tert.-butyl methylether, dioxane, anisole and tetrahydrofuran, nitriles such as acetonitrile and propionitrile, ketones such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol and tert.-butanol, as well as dimethylsulfoxide, dimethylformamide and N,N-dimethylacetamide or N-methylpyrrolidone. Particular preference is given to alcohols like methanol or ethanol. It is also possible to use mixtures of the solvents mentioned.

Work up can be carried out in a known manner.

15

The hydroxyazolopyrimidines II required for the preparation of the azolopyrimidines I are known from the literature (e.g. T. Russ, Synthesis, 1990, 8, 721-723) and can be prepared by cyclisation of a malonate VI with an aminoazol IV:



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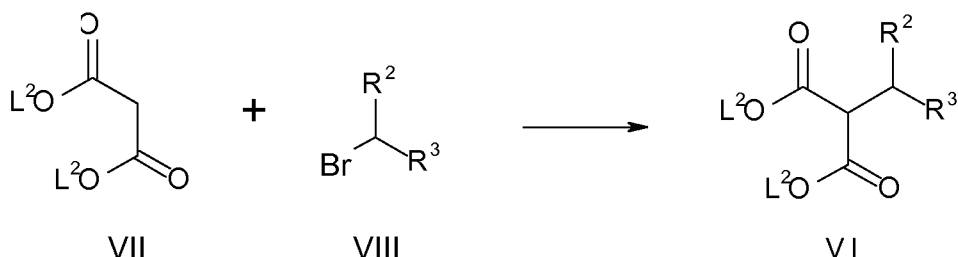
L² stands for C₁-C₆-alkyl.

The reaction of the malonate VI with the aminoazoles IV is usually carried out at from 0°C to the boiling point of the reaction mixture, preferably at from 0°C to 150°C, particularly preferably at from 50°C to 100°C, in an inert organic solvent in the presence of a base (e.g. T. Russ, Synthesis, 1990, 8, 721-723).

Suitable solvents are aliphatic hydrocarbons such as pentane, hexane, cyclohexane and mixtures of C₅-C₈-alkanes, aromatic hydrocarbons such as toluene, o-, m- and p-xylene, halogenated hydrocarbons such as dichloromethane, 1,2-dichloroethane, chloroform and chlorobenzene, ethers such as diethyl ether, diisopropyl ether, tert.-butyl methylether, dioxane, anisole and tetrahydrofuran, nitriles such as acetonitrile and propionitrile, ketones such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol and tert.-butanol, as well as dimethylsulfoxide, dimethylformamide and N,N-dimethylacetamide or N-methylpyrrolidone. Particular preference is given to alcohols like methanol or ethanol. It is also possible to use mixtures of the solvents mentioned.

Work up can be carried out in a known manner.

- 5 The malonates VI required for the preparation of the hydroxyazolopyrimidines III are known from the literature and can be prepared by the alkylation of an alkylmalonate VII with a bromide VIII:



- 10 L^2 stand for C_1 - C_6 -alkyl.

- The reaction of the alkylmalonate VII with the bromide VIII is usually carried out at from -80°C to the boiling point of the reaction mixture, preferably at from 0°C to 100°C, particularly preferably at from 0°C to 50°C, in an inert organic solvent in the presence of a
 15 base (e.g. T. Eisenaecher, Pharmazie, 1992, 47, 8, 580-581).

- Suitable solvents are aliphatic hydrocarbons such as pentane, hexane, cyclohexane and mixtures of C_5 - C_8 -alkanes, aromatic hydrocarbons such as toluene, o-, m- and p-xylene, halogenated hydrocarbons such as dichloromethane, 1,2-dichloroethane, chloroform and chlorobenzene, ethers such as diethyl ether, diisopropyl ether, tert.-butyl
 20 methylether, dioxane, anisole and tetrahydrofuran, nitriles such as acetonitrile and propionitrile, ketones such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, as well as dimethylsulfoxide, dimethylformamide and N,N-dimethylacetamide or N-methylpyrrolidone. Particular preference is given to tetrahydro-
 25 furane. 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 oxide such as lithium oxide, sodium oxide, calcium oxide and magnesium oxide, alkali metal and alkaline earth metal hydrides such as lithium hydride, sodium
 30 hydride, potassium hydride and calcium hydride, alkali metal and alkaline earth metal carbonates such as lithium carbonate, potassium carbonate and calcium carbonate, as well as alkali metal bicarbonates such as sodium bicarbonate, metal organic compounds, preferably alkali metal alkyls such as methyl lithium, butyl lithium and phenyl lithium, alkyl magnesium halides such as methyl magnesium chloride as well as and
 35 furthermore organic bases, such as tertiary amines such as trimethylamine, triethylamine, diisopropylethylamine and N-methylpiperidine, pyridine, substituted pyridines

such as collidine, lutidine, N-methylmorpholine and 4-dimethylaminopyridine and also bicyclic amines. Particular preference is given to sodiumhydride.

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

Work up can be carried out in a known manner.

10 The aminoazoles IV required for the preparation of the hydroxyazolopyrimidines III are known from the literature and can be prepared in accordance with the literature cited and/or are commercially available.

15 The alkylmalonates VII and the bromides VIII required for the preparation of the malonates VI are known from the literature and can be prepared in accordance with the literature cited and/or are commercially available.

20 The azolopyrimidines I are suitable as herbicides. They are suitable as such or as an appropriately formulated composition (herbicidal composition). As used in this application, the terms "formulated composition" and "herbicidal composition" are synonyms. The herbicidal compositions comprising the azolopyrimidines of formula I control vegetation on non-crop areas very efficiently, especially at high rates of application. They act against broad-leaved weeds and grass weeds in crops such as
25 wheat, rice, maize, soya 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 triazolopyrimidines of formula I or compositions comprising them can additionally be employed in a further number of
30 crop plants for eliminating undesirable plants. Examples of suitable crops are the following:

Allium cepa, Ananas comosus, Arachis hypogaea, Asparagus officinalis, Avena sativa, Beta vulgaris spec. altissima, Beta vulgaris spec. rapa, Brassica napus var. napus,
35 Brassica napus var. napobrassica, Brassica rapa var. silvestris, Brassica oleracea, Brassica nigra, Camellia sinensis, Carthamus tinctorius, Carya illinoensis, Citrus limon, Citrus sinensis, Coffea arabica (Coffea canephora, Coffea liberica), Cucumis sativus, Cynodon dactylon, Daucus carota, Elaeis guineensis, Fragaria vesca, Glycine max, Gossypium hirsutum, (Gossypium arboreum, Gossypium herbaceum, Gossypium
40 vitifolium), Helianthus annuus, Hevea brasiliensis, Hordeum vulgare, Humulus lupulus, Ipomoea batatas, Juglans regia, Lens culinaris, Linum usitatissimum, Lycopersicon lycopersicum, Malus spec., Manihot esculenta, Medicago sativa, Musa spec., Nicotiana

tabacum (*N.rustica*), *Olea europaea*, *Oryza sativa*, *Phaseolus lunatus*, *Phaseolus vulgaris*, *Picea abies*, *Pinus spec.*, *Pistacia vera*, *Pisum sativum*, *Prunus avium*, *Prunus persica*, *Pyrus communis*, *Prunus armeniaca*, *Prunus cerasus*, *Prunus dulcis* and *Prunus domestica*, *Ribes sylvestre*, *Ricinus communis*, *Saccharum officinarum*, *Secale cereale*, *Sinapis alba*, *Solanum tuberosum*, *Sorghum bicolor* (s. *vulgare*), *Theobroma cacao*, *Trifolium pratense*, *Triticum aestivum*, *Triticale*, *Triticum durum*, *Vicia faba*, *Vitis vinifera* and *Zea mays*.

Preferred crops are the following: *Arachis hypogaea*, *Beta vulgaris spec. altissima*, *Brassica napus var. napus*, *Brassica oleracea*, *Citrus limon*, *Citrus sinensis*, *Coffea arabica* (*Coffea canephora*, *Coffea liberica*), *Cynodon dactylon*, *Glycine max*, *Gossypium hirsutum*, (*Gossypium arboreum*, *Gossypium herbaceum*, *Gossypium vitifolium*), *Helianthus annuus*, *Hordeum vulgare*, *Juglans regia*, *Lens culinaris*, *Linum usitatissimum*, *Lycopersicon lycopersicum*, *Malus spec.*, *Medicago sativa*, *Nicotiana tabacum* (*N.rustica*), *Olea europaea*, *Oryza sativa*, *Phaseolus lunatus*, *Phaseolus vulgaris*, *Pistacia vera*, *Pisum sativum*, *Prunus dulcis*, *Saccharum officinarum*, *Secale cereale*, *Solanum tuberosum*, *Sorghum bicolor* (s. *vulgare*), *Triticale*, *Triticum aestivum*, *Triticum durum*, *Vicia faba*, *Vitis vinifera* and *Zea mays*.

The azolopyrimidines of formula I according to the invention can also be used in genetically modified plants. The term "genetically modified plants" is to be understood as plants, which genetic material has been modified by the use of recombinant DNA techniques in a way that under natural circumstances it cannot readily be obtained by cross breeding, mutations or natural recombination. Typically, one or more genes have been integrated into the genetic material of a genetically modified plant in order to improve certain properties of the plant. Such genetic modifications also include but are not limited to targeted post-translational modification of protein(s), oligo- or polypeptides e. g. by glycosylation or polymer additions such as prenylated, acetylated or farnesylated moieties or PEG moieties.

Plants that have been modified by breeding, mutagenesis or genetic engineering, e.g. have been rendered tolerant to applications of specific classes of herbicides, such as auxin herbicides such as dicamba or 2,4-D; bleacher herbicides such as hydroxyphenylpyruvate dioxygenase (HPPD) inhibitors or phytoene desaturase (PDS) inhibitors; acetolactate synthase (ALS) inhibitors such as sulfonyl ureas or imidazolinones; enolpyruvyl shikimate 3-phosphate synthase (EPSP) inhibitors such as glyphosate; glutamine synthetase (GS) inhibitors such as glufosinate; protoporphyrinogen-IX oxidase inhibitors; lipid biosynthesis inhibitors such as acetyl CoA carboxylase (ACCase) inhibitors; or oxynil (i. e. bromoxynil or ioxynil) herbicides as a result of conventional methods of breeding or genetic engineering; furthermore, plants have been made resistant to multiple classes of herbicides through multiple genetic modifications, such as

resistance to both glyphosate and glufosinate or to both glyphosate and a herbicide from another class such as ALS inhibitors, HPPD inhibitors, auxin herbicides, or AC-Case inhibitors. These herbicide resistance technologies are, for example, described in Pest Management Science 61, 2005, 246; 61, 2005, 258; 61, 2005, 277; 61, 2005, 269; 5 61, 2005, 286; 64, 2008, 326; 64, 2008, 332; Weed Science 57, 2009, 108; Australian Journal of Agricultural Research 58, 2007, 708; Science 316, 2007, 1185; and references quoted therein. Several cultivated plants have been rendered tolerant to herbicides by conventional methods of breeding (mutagenesis), e. g. Clearfield® summer rape (Canola, BASF SE, Germany) being tolerant to imidazolinones, e. g. imazamox, 10 or ExpressSun® sunflowers (DuPont, USA) being tolerant to sulfonyl ureas, e. g. tribenuron. Genetic engineering methods have been used to render cultivated plants such as soybean, cotton, corn, beets and rape, tolerant to herbicides such as glyphosate, imidazolinones and glufosinate, some of which are under development or commercially available under the brands or trade names RoundupReady® (glyphosate tolerant, Mon- 15 santo, USA), Cultivance® (imidazolinone tolerant, BASF SE, Germany) and LibertyLink® (glufosinate tolerant, Bayer CropScience, Germany).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more insecticidal proteins, especially those known 20 from the bacterial genus *Bacillus*, particularly from *Bacillus thuringiensis*, such as δ -endotoxins, e. g. CryIA(b), CryIA(c), CryIF, CryIF(a2), CryIIA(b), CryIIIA, CryIIIB(b1) or Cry9c; vegetative insecticidal proteins (VIP), e. g. VIP1, VIP2, VIP3 or VIP3A; insecticidal proteins of bacteria colonizing nematodes, e. g. *Photorhabdus* spp. or *Xenorhabdus* spp.; toxins produced by animals, such as scorpion toxins, arachnid toxins, wasp 25 toxins, or other insect-specific neurotoxins; toxins produced by fungi, such Streptomyces toxins, plant lectins, such as pea or barley lectins; agglutinins; proteinase inhibitors, such as trypsin inhibitors, serine protease inhibitors, patatin, cystatin or papain inhibitors; ribosome-inactivating proteins (RIP), such as ricin, maize-RIP, abrin, luffin, saporin or bryodin; steroid metabolism enzymes, such as 3-hydroxy-steroid oxidase, 30 ecdysteroid-IDP-glycosyl-transferase, cholesterol oxidases, ecdysone inhibitors or HMG-CoA-reductase; ion channel blockers, such as blockers of sodium or calcium channels; juvenile hormone esterase; diuretic hormone receptors (helicokinin receptors); stilben synthase, bibenzyl synthase, chitinases or glucanases. In the context of the present invention these insecticidal proteins or toxins are to be understood ex- 35 pressly also as pre-toxins, hybrid proteins, truncated or otherwise modified proteins. Hybrid proteins are characterized by a new combination of protein domains, (see, e. g. WO 02/015701). Further examples of such toxins or genetically modified plants capable of synthesizing such toxins are disclosed, e. g., in EP-A 374 753, WO 93/007278, WO 95/34656, EP-A 427 529, EP-A 451 878, WO 03/18810 und WO 03/52073. The 40 methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e. g. in the publications mentioned above. These insecticidal proteins contained in the genetically modified plants impart to the

plants producing these proteins tolerance to harmful pests from all taxonomic groups of arthropods, especially to beetles (Coleoptera), two-winged insects (Diptera), and moths (Lepidoptera) and to nematodes (Nematoda). Genetically modified plants capable to synthesize one or more insecticidal proteins are, e. g., described in the publications mentioned above, and some of which are commercially available such as YieldGard® (corn cultivars producing the Cry1Ab toxin), YieldGard® Plus (corn cultivars producing Cry1Ab and Cry3Bb1 toxins), Starlink® (corn cultivars producing the Cry9c toxin), Herculex® RW (corn cultivars producing Cry34Ab1, Cry35Ab1 and the enzyme Phosphinothricin-N-Acetyltransferase [PAT]); NuCOTN® 33B (cotton cultivars producing the Cry1Ac toxin), Bollgard® I (cotton cultivars producing the Cry1Ac toxin), Bollgard® II (cotton cultivars producing Cry1Ac and Cry2Ab2 toxins); VIPCOT® (cotton cultivars producing a VIP-toxin); NewLeaf® (potato cultivars producing the Cry3A toxin); Bt-Xtra®, NatureGard®, KnockOut®, BiteGard®, Protecta®, Bt11 (e. g. Agrisure® CB) and Bt176 from Syngenta Seeds SAS, France, (corn cultivars producing the Cry1Ab toxin and PAT enzyme), MIR604 from Syngenta Seeds SAS, France (corn cultivars producing a modified version of the Cry3A toxin, c.f. WO 03/018810), MON 863 from Monsanto Europe S.A., Belgium (corn cultivars producing the Cry3Bb1 toxin), IPC 531 from Monsanto Europe S.A., Belgium (cotton cultivars producing a modified version of the Cry1Ac toxin) and 1507 from Pioneer Overseas Corporation, Belgium (corn cultivars producing the Cry1F toxin and PAT enzyme).

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the resistance or tolerance of those plants to bacterial, viral or fungal pathogens. Examples of such proteins are the so-called "pathogenesis-related proteins" (PR proteins, see, e.g. EP-A 392 225), plant disease resistance genes (e. g. potato cultivars, which express resistance genes acting against *Phytophthora infestans* derived from the mexican wild potato *Solanum bulbocastanum*) or T4-lysozyme (e.g. potato cultivars capable of synthesizing these proteins with increased resistance against bacteria such as *Erwinia amylovora*). The methods for producing such genetically modified plants are generally known to the person skilled in the art and are described, e.g. in the publications mentioned above.

Furthermore, plants are also covered that are by the use of recombinant DNA techniques capable to synthesize one or more proteins to increase the productivity (e.g. bio mass production, grain yield, starch content, oil content or protein content), tolerance to drought, salinity or other growth-limiting environmental factors or tolerance to pests and fungal, bacterial or viral pathogens of those plants.

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve human or animal nutrition, e. g. oil crops that produce health-

promoting long-chain omega-3 fatty acids or unsaturated omega-9 fatty acids (e. g. Nexera® rape, DOW Agro Sciences, Canada).

Furthermore, plants are also covered that contain by the use of recombinant DNA techniques a modified amount of substances of content or new substances of content, specifically to improve raw material production, e.g. potatoes that produce increased amounts of amylopectin (e.g. Amflora® potato, BASF SE, Germany).

10 The azolopyrimidines I, or the herbicidal compositions comprising the azolopyrimidines 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 any case, they should ensure the finest possible distribution of the active ingredients according to the invention.

20 The herbicidal compositions comprise an herbicidal effective amount of at least one azolopyrimidine of the formula I and auxiliaries which are customary for the formulation of crop protection agents.

25 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, optionally colorants and, for seed formulations, adhesives.

30 The person skilled in the art is sufficiently familiar with the recipes for such formulations.

35 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 (Rhône Poulenc) or Veegum® (from R.T. Vanderbilt), and also organic and inorganic sheet minerals, such as Attaclay® (from Engelhardt).

40 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 formulations.

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).

5

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

10 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
15 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.

20

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
25 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.

Suitable carriers include liquid and solid carriers. Liquid carriers include e.g. non-aqueous solvents such as cyclic and aromatic hydrocarbons, e.g. paraffins, tetrahydronaphthalene, alkylated naphthalenes and their derivatives, alkylated benzenes and their derivatives, alcohols such as methanol, ethanol, propanol, butanol and cyclohexanol, ketones such as cyclohexanone, strongly polar solvents, e.g. amines such as N-methylpyrrolidone, and water as well as mixtures thereof. Solid carriers include e.g.

35 mineral earths such as silicas, silica gels, silicates, talc, kaolin, limestone, lime, chalk, bole, 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
40 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 dibutyl naphthalenesulfonic acid (Nekal types, BASF AG), and of fatty acids, alkyl- and alkylarylsulfonates, 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 naphthalenesulfonic acids with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctyl-, octyl- or nonylphenol, alkylphenyl or tributylphenyl polyglycol ether, alkylaryl polyether alcohols, isotridecyl alcohol, fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers or polyoxypropylene alkyl ethers, lauryl alcohol polyglycol ether acetate, sorbitol esters, lignosulfite waste liquors and proteins, denaturated proteins, polysaccharides (e.g. methylcellulose), hydrophobically modified starches, polyvinyl alcohol (Mowiol types Clariant), polycarboxylates (BASF AG, Sokalan types), polyalkoxylates, polyvinylamine (BASF AG, Lupamine types), polyethyleneimine (BASF AG, Lupasol types), polyvinylpyrrolidone and copolymers thereof.

Powders, materials for broadcasting and dusts can be prepared by mixing or concomitant 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 ... of the formula I, 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 compound, wetting agent, tackifier, dispersant or emulsifier and, if desired, solvent or oil, which are suitable for dilution with water.

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

In the formulation of the azolopyrimidines of formula I according to the present invention the active ingredients, e.g. the azolopyrimidines of formula I, are present in sus-

pended, emulsified or dissolved form. The formulation according to the invention can be in the form of aqueous solutions, powders, suspensions, also highly-concentrated aqueous, oily or other suspensions or dispersions, aqueous emulsions, aqueous microemulsions, aqueous suspo-emulsions, oil dispersions, pastes, dusts, materials for spreading or granules.

The azolopyrimidines of formula I according to the present 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 (eg. 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 (eg. 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 (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.
- 5 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.
- 10 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 mixed to give a fine suspension. Dilution with water gives a stable suspension with active compound content of 20% by weight.
- 15
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.
- 20
- 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.
- 25
- 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.
- 30

Aqueous use forms can be prepared from emulsion concentrates, suspensions, pastes, wettable powders or water-dispersible granules by adding water.

35

The azolopyrimidines of the formula I or the herbicidal compositions comprising them can be applied pre-, post-emergence or pre-plant, or together with the seed of a crop plant. It is also possible to apply the herbicidal composition or active compounds by applying seed, pretreated with the herbicidal compositions or active compounds, of a crop plant. If the active ingredients 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

40

not come into contact with the leaves of the sensitive crop plants, while the active ingredients reach the leaves of undesirable plants growing underneath, or the bare soil surface (post-directed, lay-by).

- 5 In a further embodiment, the azolopyrimidines of the formula I or the herbicidal compositions can be applied by treating seed. The treatment of seeds 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 azolopyrimidines of the
10 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, seedlings 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
15 the seed of transgenic plants or plants obtained by customary breeding methods.

The rates of application of the active azolopyrimidines of formula I according to the present invention (total amount of azolopyrimidines I) are from 0.1 g/ha to 3000 g/ha, preferably 10 g/ha to 1000 g/ha of active substance (a.s.), depending on the control
20 target, the season, the target plants and the growth stage.

In another preferred embodiment of the invention, the application rates of the azolopyrimidines of formula I are in the range from 0.1 g/ha to 5000 g/ha and preferably in the range from 1 g/ha to 2500 g/ha or from 5 g/ha to 2000 g/ha of active sub-
25 stance (a.s.).

In another preferred embodiment of the invention, the application rate of the azolopyrimidines of formula I is 0.1 to 1000 g/ha, preferably 1 to 750 g/ha, more preferably 5 to 500 g/ha, of active substance.
30

To treat the seed, the azolopyrimidines of formula I are generally employed in amounts of from 0.001 to 10 kg per 100 kg of seed.

- 35 To widen the spectrum of action and to achieve synergistic effects, the azolopyrimidines of the formula I may be mixed with a large number of representatives of other herbicidal or growth-regulating active ingredient groups and then applied concomitantly. Suitable components for mixtures are, for example, 1,2,4-thiadiazoles, 1,3,4-thiadiazoles, amides, aminophosphoric acid and its derivatives, aminotriazoles,
40 anilides, (het)aryloxyalkanoic acids and their derivatives, benzoic acid and its derivatives, benzothiadiazinones, 2-aryloxy-1,3-cyclohexanediones, 2-hetaryloxy-1,3-cyclohexanediones, hetaryl aryl ketones, benzylisoxazolidinones, meta-CF₃-phenyl

derivatives, carbamates, quinolinecarboxylic acid and its derivatives, chloroacetanilides, cyclohexenone oxime ether derivatives, diazines, dichloropropionic acid and its derivatives, dihydrobenzofurans, dihydrofuran-3-ones, dinitroanilines, dinitrophenols, diphenyl ethers, dipyridyls, halocarboxylic acids and their derivatives, ureas, 3-phenyl-
5 uracils, imidazoles, imidazolinones, N-phenyl-3,4,5,6-tetrahydrophthalimides, oxadiazoles, oxiranes, phenols, aryloxy- and hetaryloxyphenoxypropionic esters, phenylacetic 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,
10 uracils, phenyl pyrazolines and isoxazolines and derivatives thereof.

It may furthermore be beneficial to apply the azolopyrimidines of the formula I alone or in combination with other herbicides, or else in the form of a mixture with other crop protection agents, for example together with agents for controlling pests or
15 phytopathogenic fungi or bacteria. Also of interest is the miscibility with mineral salt solutions, which are employed for treating nutritional and trace element deficiencies. Other additives such as non-phytotoxic oils and oil concentrates may also be added.

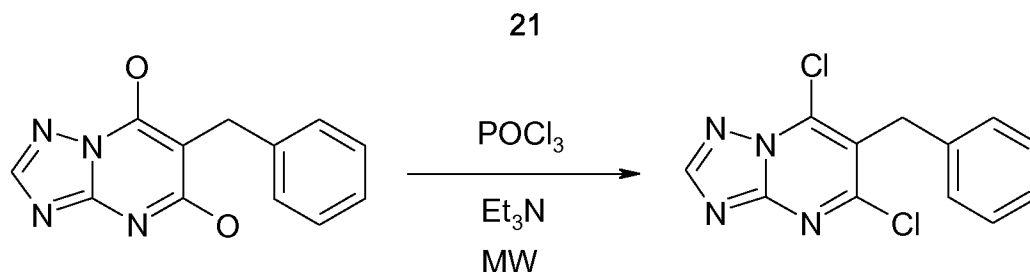
Moreover, it may be useful to apply the azolopyrimidines of the formula I in combination
20 with safeners. Safeners are chemical compounds which prevent or reduce damage on useful plants without having a major impact on the herbicidal action of the azolopyrimidines of the formula I towards unwanted plants. They can be applied either before sowings (e.g. on seed treatments, shoots or seedlings) or in the pre-emergence application or post-emergence application of the useful plant. The safeners and the
25 azolopyrimidines of the formula I can be applied simultaneously or in succession.

Suitable safeners are e.g. (quinolin-8-oxy)acetic acids, 1-phenyl-5-haloalkyl-1H-1,2,4-triazol-3-carboxylic acids, 1-phenyl-4,5-dihydro-5-alkyl-1H-pyrazol-3,5-dicarboxylic acids, 4,5-dihydro-5,5-diaryl-3-isoxazol carboxylic acids, dichloroacetamides, alpha-oximinophenylacetonitriles, acetophenonoximes, 4,6-dihalo-2-phenylpyrimidines, N-[[4-(aminocarbonyl)phenyl]sulfonyl]-2-benzoic amides, 1,8-naphthalic anhydride, 2-halo-4-(haloalkyl)-5-thiazol carboxylic acids, phosphorothiolates and N-alkyl-O-phenylcarbamates and their agriculturally acceptable salts and their agriculturally acceptable
30 derivatives such amides, esters, and thioesters, provided they have an acid group.

35 Hereinbelow, the preparation of the azolopyrimidines of the formula I is illustrated by examples; however, the subject matter of the present invention is not limited to the examples given.

40

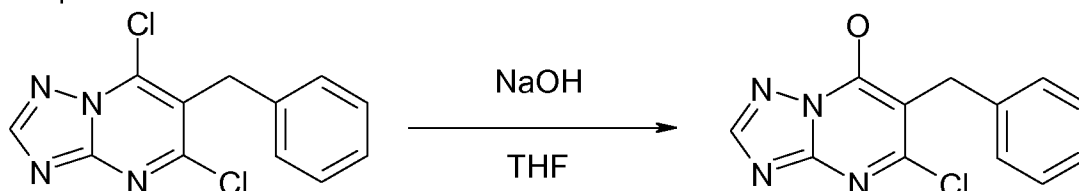
Example 1



A solution of 6-Benzyl-[1,2,4]triazolo[1,5-a]pyrimidine-5,7-diol (11.9mmol), triethyl-aminehydrochloride (29.8mmol) and POCl₃ (214mmol) was heated to 110°C for 20 min in the microwave (25 W). The suspension was added to icewater, neutralized with 2N NaOH-solution and extracted with ethylacetate. The organic phase was dried with sodiumsulfate and evaporated to yield crude 6-benzyl-5,7-dichloro-[1,2,4]triazolo[1,5-a]pyrimidine.

MS (m/z, M+H): 279

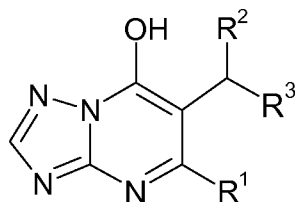
Example 2



To a solution of crude 6-benzyl-5,7-dichloro-[1,2,4]triazolo[1,5-a]pyrimidine (11.9 mmol) in THF was added 2N NaOH-solution at room temperature and the solution was stirred 14 hours. The solution was acidified with 2NHCl to pH1, extracted with ethylacetate and the organic phase dried with sodiumsulfate to yield 6-benzyl-5-chloro-[1,2,4]triazolo[1,5-a]pyrimidin-7-ol.

MS (m/z, M+H): 261

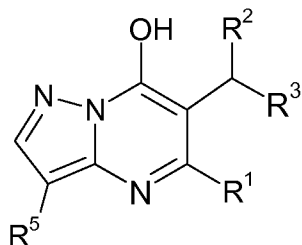
Further azolopyrimidines of formula I have been prepared in accordance to the processes described above, and are, in addition to the compounds mentioned above, listed in tables 1 to 3 below.



I wherein R⁴ is hydrogen and X is N

22

No.	R ¹	R ²	R ³	m/z (M+H)
1.1	CH ₃	H	C ₆ H ₅	241
1.2	CH ₃	H	(3,4-Cl ₂)C ₆ H ₃	309
1.3	Cl	H	C ₆ H ₅	262
1.4	Cl	H	(2-F)C ₆ H ₄	280
1.5	Cl	H	(3-F)C ₆ H ₄	280
1.6	Cl	H	(2,5-F ₂)C ₆ H ₃	298
1.7	Cl	H	(3,4-F ₂)C ₆ H ₃	298
1.8	Cl	H	(3,5-F ₂)C ₆ H ₃	298
1.9	Cl	H	(2,3,4-F ₃)C ₆ H ₂	316
1.10	Cl	H	(2-Cl)C ₆ H ₄	295
1.11	Cl	H	(3-Cl)C ₆ H ₄	295
1.12	Cl	H	(3,4-Cl ₂)C ₆ H ₃	331
1.13	Cl	H	(2-Cl-5-NO ₂)C ₆ H ₃	341
1.14	Cl	H	(2-CH ₃)C ₆ H ₄	276
1.15	Cl	H	(3-CH ₃)C ₆ H ₄	276
1.16	Cl	H	(4-CH ₃)C ₆ H ₄	276
1.17	Cl	H	[3,5(CH ₃) ₂]C ₆ H ₃	290
1.18	Cl	CH ₃	C ₆ H ₅	276
1.19	Cl	CH ₃	(4-F)C ₆ H ₄	294



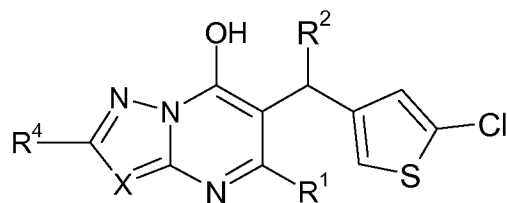
I wherein R⁴ is hydrogen
and X is CR⁵

5 Table 2

No.	R ¹	R ²	R ³	R ⁵	m/z (M+H)
2.1	CH ₃	H	C ₆ H ₅	CN	265
2.2	CH ₃	H	C ₆ H ₅	COOCH ₃	312
2.3	CH ₃	H	C ₆ H ₅	COOCH ₂ CH ₃	312
2.4	CH ₃	H	(2-F)C ₆ H ₄	COOCH ₃	316
2.5	CH ₃	H	(2-F)C ₆ H ₄	CONCH ₃	315
2.6	CH ₃	H	(2-Cl)C ₆ H ₄	COOCH ₃	333
2.7	CH ₃	H	(2-CH ₃)C ₆ H ₄	COOCH ₃	312
2.8	CH ₃	H	[2,5(CH ₃) ₂]C ₆ H ₃	COOH	312
2.9	Cl	H	C ₆ H ₅	CN	286

No.	R ¹	R ²	R ³	R ⁵	m/z (M+H)
2.10	Cl	H	C ₆ H ₅	CH ₃	275
2.11	Cl	H	C ₆ H ₅	COOH	305
2.12	Cl	H	C ₆ H ₅	COOCH ₂ CH ₃	333
2.13	Cl	H	C ₆ H ₅	COOC(CH ₃) ₃	361
2.14	Cl	H	C ₆ H ₅	COOCH ₂ CH(CH ₃) ₂	361
2.15	Cl	H	C ₆ H ₅	COOCH ₂ CH=CH ₂	345
2.16	Cl	H	C ₆ H ₅	COOCH ₂ C≡CH	343
2.17	Cl	H	C ₆ H ₅	COOCH ₂ C ₆ H ₅	395
2.18	Cl	H	C ₆ H ₅	COOCH ₂ (4-Cl-C ₆ H ₄)	429
2.19	Cl	H	C ₆ H ₅	CONH ₂	304
2.20	Cl	H	C ₆ H ₅	CONHCH ₂ CH(CH ₃) ₂	360
2.21	Cl	H	C ₆ H ₅	CONHCH ₂ CH ₂ CH ₂ CH ₂ CH ₃	374
2.22	Cl	H	C ₆ H ₅	CONHCH ₃ CH=CH ₂	344
2.23	Cl	H	C ₆ H ₅	CONHCH ₂ C≡CH	342
2.24	Cl	H	C ₆ H ₅	CSNH ₂	320
2.25	Cl	H	(2-F)C ₆ H ₄	CN	304
2.26	Cl	H	(2-F)C ₆ H ₄	COOH	323
2.27	Cl	H	(3-F)C ₆ H ₄	CN	304
2.28	Cl	H	(3-F)C ₆ H ₄	COOH	323
2.29	Cl	H	(4-F)C ₆ H ₄	COOCH ₃	316
2.30	Cl	H	(2,5-F ₂)C ₆ H ₃	CN	322
2.31	Cl	H	(2,5-F ₂)C ₆ H ₃	COOH	341
2.32	Cl	H	(3,4-F ₂)C ₆ H ₃	CN	322
2.33	Cl	H	(3,4-F ₂)C ₆ H ₃	COOH	341
2.34	Cl	H	(3,5-F ₂)C ₆ H ₃	CN	322
2.35	Cl	H	(3,5-F ₂)C ₆ H ₃	COOH	341
2.36	Cl	H	(2-Cl)C ₆ H ₄	CN	319
2.37	Cl	H	(2-Cl)C ₆ H ₄	COOH	338
2.38	Cl	H	(3-Cl)C ₆ H ₄	CN	319
2.39	Cl	H	(3-Cl)C ₆ H ₄	COOH	338
2.40	Cl	H	(3,4-Cl ₂)C ₆ H ₃	CN	354
2.41	Cl	H	(3,4-Cl ₂)C ₆ H ₃	COOH	373
2.42	Cl	H	(2-CH ₃)C ₆ H ₄	CN	300
2.43	Cl	H	(3-CH ₃)C ₆ H ₄	CN	300
2.44	Cl	H	(3-CH ₃)C ₆ H ₄	COOH	319
2.45	Cl	H	(4-CH ₃)C ₆ H ₄	COOH	319
2.46	Cl	H	[3,5(CH ₃) ₂]C ₆ H ₃	CN	314
2.47	Cl	H	[3,5(CH ₃) ₂]C ₆ H ₃	COOH	333
2.48	Cl	CH ₃	C ₆ H ₅	CN	300

No.	R ¹	R ²	R ³	R ⁵	m/z (M+H)
2.49	Cl	CH ₃	C ₆ H ₅	COOH	319



I where
R³ is 3(5-chloro)thienyl

5 Table 3

No.	R ¹	R ²	R ⁴	X	m/z (M+H)
3.1	Cl	H	H	C-CN	325
3.2	Cl	H	H	N	301

Use examples

10

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

15

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.

20

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.

25

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.

30

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.

- 5 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:

Bayer Code	Scientific name	Common name
ABUTH	Abutilon theophrasti	velvetleaf
ALOMY	Alopercurus myosuroides	blackgrass
AVEFA	Avena fatua	wild oat
SETFA	Setaria faberi	Faber's foxtail

10

Applied by the post-emergence method at an application rate of 3 kg/ha, the compounds 1.4, 1.6, 1.7 and 1.17 showed good herbicidal activity and compound 1.5 showed very good herbicidal activity against Abutilon theophrasti.

15

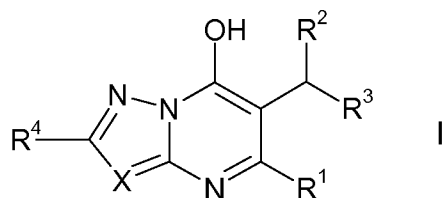
At an application rate of 3 kg/ha, the compounds 1.4, 1.5, 1.8 and 1.16 applied by the post-emergence method, showed good herbicidal activity against Alopercurus myosuroides.

- 20 At an application rate of 3 kg/ha, the compound 1.8 applied by the post-emergence method, showed good herbicidal activity against Avena fatua.

- 25 At an application rate of 3 kg/ha, the compounds 1.4, 1.5, 1.6, 1.7, 1.8, 1.16 and 1.17 applied by the post-emergence method, showed good herbicidal activity against Setaria faberi.

Claims

1. Azolopyrimidines of formula I



wherein

R¹ is CH₃, F, Cl or Br;

R² is hydrogen or C₁-C₄ alkyl;

R³ is phenyl or thienyl,

wherein the phenyl or thienyl ring is unsubstituted or substituted with halogen, cyano, nitro, C₁-C₄-alkyl, C₂-C₄-alkenyl, C₂-C₄-alkynyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-alkylthio;

R⁴ is hydrogen or C₁-C₄-alkyl; and

X is nitrogen or CR⁵,

wherein R⁵ is hydrogen, cyano, C₁-C₄ alkyl, hydroxycarbonyl, C₁-C₆-alkoxycarbonyl, C₂-C₆-alkenyloxycarbonyl, C₂-C₆-alkynyloxycarbonyl, benzyloxycarbonyl, halobenzyloxycarbonyl, aminocarbonyl, C₁-C₆-alkylaminocarbonyl, di(C₁-C₆)-alkylaminocarbonyl, C₂-C₆-alkenylaminocarbonyl, C₂-C₆-alkynylaminocarbonyl, amino(thiocarbonyl);

including their agriculturally acceptable salts.

2. The compound of formula I according to claim 1, wherein R¹ is CH₃ or Cl.
3. The compound of formula I according to claims 1 or 2, wherein R² is hydrogen.
4. The compound of formula I according to any of claims 1 to 3, wherein R³ is phenyl which is unsubstituted or substituted with one to three halogen atoms.
5. The compound of formula I according to any of claims 1 to 4 wherein R⁴ is hydrogen.
6. The compound of formula I according to any of claims 1 to 5 wherein R⁵ is cyano.
7. A herbicidal composition comprising a herbicidal active amount of at least one compound of formula I as claimed in claims 1 to 6 and at least one inert liquid

and/or solid carrier and, if appropriate, at least one surface-active substance.

- 5 8. A process for the preparation of herbicidal active compositions, which comprises mixing a herbicidal active amount of at least one compound of formula I as claimed in claims 1 to 6 and at least one inert liquid and/or solid carrier and, if desired, at least one surface-active substance.
- 10 9. A method of controlling undesired vegetation, which comprises allowing an herbicidal active amount of at least one compound of the formula I as claimed in claims 1 to 6 to act on plants, their environment or on seed.
- 10 10. The use of the compounds of formula I as claimed in claims 1 to 6 as herbicides.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/056339

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07D487/04 A01N43/54
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

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	WO 2008/116898 A1 (BIOVITRUM AB PUBL [SE]; BREMBERG ULF [SE]; LINDEN AURI [SE]; LUNDBAECK) 2 October 2008 (2008-10-02) Intermediate 20 on page 70 -----	1-5
A	EP 0 220 458 A1 (BAYER AG [DE]) 6 May 1987 (1987-05-06) claim 1 ----- -/-	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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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 docu-
ments, such combination being obvious to a person skilled
in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 May 2011

Date of mailing of the international search report

06/07/2011

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INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2011/056339

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2007/028434 A1 (BAYER CROPSCIENCE AG [DE]; SASAKI NORIO [JP]; HATAZAWA MAMORU [JP]; AR) 15 March 2007 (2007-03-15) claims 1,5 -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2011/056339

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