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**(71) Applicant** *(for all designated States except US)*: CIBA-GEIGY AG [CH/CH]; Klybeckstrasse 141, CH-4002 Basle (CH).

**(72) Inventors; and**
**(75) Inventors/Applicants** *(for US only)*: WALTER, Harald [DE/CH]; Chilchmattstrasse 12 B, CH-4118 Rodersdorf (CH). ZAMBACH, Werner [CH/CH]; Chlederenweg 35, CH-4112 Bättwil (CH).

**(74) Common Representative:** CIBA-GEIGY AG; Patentabteilung, Klybeckstrasse 141, CH-4002 Basle (CH).

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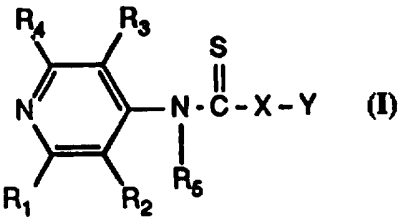
**(54) Title:** PESTICIDAL PYRIDINE THIOAMIDES

**(57) Abstract**



(I)

Compounds of formula (I), wherein, $R_1$ and $R_2$ are each independently of the other $C_1$-$C_6$alkyl, halo-$C_1$-$C_6$alkyl containing 1-5 halogen atoms, $C_1$-$C_2$alkoxy-$C_1$-$C_6$alkyl, nitro-$C_1$-$C_6$alkyl, cyano-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanoyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$akloxycarbonyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkylthio-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanesulfinyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanesulfonyl-$C_1$-$C_6$alkyl, $C_2$-$C_6$alkenyl, halo-$C_2$-$C_6$alkenyl containing 1-5 halogen atoms, $C_2$-$C_6$alkynyl, halo-$C_2$-$C_6$alkynyl containing 1-5 halogen atoms, $C_3$-$C_7$cycloalkyl or halogen; or $R_1$ and $R_2$, taken together, form a saturated or unsaturated 5- to 7-membered unsubstituted or substituted carbocyclic or heterocyclic ring which may contain one or two hetero atoms selected from O and S; $R_3$ and $R_4$ are each independently of the other hydrogen, $C_1$-$C_6$alkyl or halogen; $R_5$ is hydrogen, $C_1$-$C_6$alkyl which is unsubstituted or substituted by cyano, nitro, halogen, carboxyl, $C_1$-$C_2$alkoxycarbonyl, $C_1$-$C_2$alkanoyl, $C_1$-$C_2$alkanesulfonyl or phenylsulfonyl, $C_2$-$C_6$alkenyl, $C_2$-$C_6$alkynyl or benzyl; X is $(CH_2)_n$, CH=CH, or C≡C; Y is an unsubstituted or substituted 5-8-membered carbocyclic or heterocyclic ring which can be saturated or unsaturated, aromatic or nonaromatic and which may contain 1 or 2 hetero atoms selected from O, S and/or N and to which a further aromatic group can be fused; n is 1, 2, 3 or 4; or tautomers thereof, in the free form or in the form of a salt, are pesticidal compounds. Said compounds can be used for the control of pests, in particular as microbicides, insecticides and acaracides in agriculture, horticulture and in the hygiene sector.

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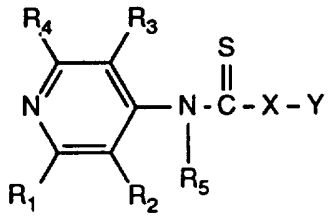
# PESTICIDAL PYRIDINE THIOAMIDES

The present invention relates to novel pesticidal compounds of formula I



I,

wherein:

$R_1$ and $R_2$ are each independently of the other $C_1$-$C_6$alkyl, halo-$C_1$-$C_6$alkyl containing 1-5 halogen atoms, $C_1$-$C_2$alkoxy-$C_1$-$C_6$alkyl, nitro-$C_1$-$C_6$alkyl, cyano-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanoyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkoxycarbonyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkylthio-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanesulfinyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanesulfonyl-$C_1$-$C_6$alkyl, $C_2$-$C_6$alkenyl, halo-$C_2$-$C_6$alkenyl containing 1-5 halogen atoms, $C_2$-$C_6$alkynyl, halo-$C_2$-$C_6$alkynyl containing 1-5 halogen atoms, $C_3$-$C_7$cycloalkyl or halogen; or
$R_1$ and $R_2$, taken together, form a saturated or unsaturated 5- to 7-membered unsubstituted or substituted carbocyclic or heterocyclic ring which may contain one or two hetero atoms selected from O and S;
$R_3$ and $R_4$ are each independently of the other hydrogen, $C_1$-$C_6$alkyl or halogen;
$R_5$ is hydrogen, $C_1$-$C_6$alkyl which is unsubstituted or substituted by cyano, nitro, halogen, carboxyl, $C_1$-$C_2$alkoxycarbonyl, $C_1$-$C_2$alkanoyl, $C_1$-$C_2$alkanesulfonyl or phenylsulfonyl, $C_2$-$C_6$alkenyl, $C_2$-$C_6$alkynyl or benzyl;
X is $(CH_2)_n$, CH=CH, or C≡C;
Y is an unsubstituted or substituted 5-8-membered carbocyclic or heterocyclic ring which can be saturated or unsaturated, aromatic or nonaromatic and which may contain 1 or 2 hetero atoms selected from O, S and/or N and to which a further aromatic group can be fused.
n is 1,2,3 or 4;
or tautomers thereof, in the free form or in the form of a salt.

The invention further relates to the preparation of these compounds, to agrochemical compositions comprising at least one of said compounds as active ingredient, and to the use of said compounds or compositions for pest control, preferably as microbicides,

insecticides and acaricides in agriculture, horticulture and in the hygiene sector.

The compounds of formula I and their possible tautomers may be obtained in salt form. As the compounds of formula I contain at least one basic centre, they may typically form acid addition salts. These salts may conveniently be formed with a mineral acid such as sulfuric acid, a phosphoric acid or a hydrohalic acid, with an organic carboxylic acid such as acetic acid, oxalic acid, malonic acid, maleic acid, fumaric acid or phthalic acid, with a hydroxycarboxylic acid such as ascorbic acid, lactic acid, malic acid, tartaric acid or citric acid, or with benzoic acid, or with an organic sulfonic acid such as methanesulfonic acid or p-toluenesulfonic acid.
Compounds of formula I having at least one acidic group can also form salts with bases. Suitable salts with bases are typically metal salts such as alkali metal salts or alkaline earth metal salts, e.g. sodium, potassium or magnesium salts, or salts with ammonia or an organic amine such as morpholine, piperidine, pyrrolidine, a mono-, di- or tri-lower alkylamine typically ethylamine, diethylamine, triethylamine or dimethylpropylamine, or a mono-, di- or trihydroxy-lower alkylamine, e.g. mono-, di- or triethanolamine. Corresponding inner salts may also be formed. Agrochemically acceptable salts are preferred within the scope of this invention.

If the compounds of formula I contain asymmetrical carbon atoms, then the compounds are obtained in optically active form. Owing to the presence of double bonds the compounds may be obtained in the [E] or [Z] form. Atropisomerism can also occur. The invention relates not only to the pure isomers, e.g. enantiomers and diastereoisomers, but also to all possible mixtures of isomers, e.g. mixtures of diastereoisomers, racemates or mixtures of racemates.

Unless otherwise indicated, the general terms used throughout this specification have the following meanings:

Alkyl groups are, in accordance with the number of carbon atoms, straight-chain or branched and will typically be methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, n-amyl, tert-amyl, 1-hexyl or 3-hexyl.

Alkenyl will be understood as meaning straight-chain or branched alkenyl such as allyl, methallyl, 1-methylvinyl or but-2-en-1-yl. Preferred alkenyl radials contain 3 to 4 carbon atoms in the chain.

Alkynyl can likewise, in accordance with the number of carbon atoms, be straight-chain or branched and is typically propargyl, but-1-yn-1-yl or but-1-yn-3-yl. The preferred meaning is propargyl.

Halogen and halo substituents will be understood generally as meaning fluoro, chloro, bromo or iodo. Fluoro, chloro or bromo are preferred meanings.

Haloalkyl can contain identical or different halogen atoms, typically fluoromethyl, difluoromethyl, difluorochloromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl, 3,3,3-trifluoropropyl.

Alkoxy is typically methoxy, ethoxy, propoxy, isopropoxy, n-butoxy, isobutoxy, sec-butoxy and tert-butoxy. Methoxy and ethoxy are preferred.

Haloalkoxy is typically difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy and 2,2-difluoroethoxy.

Cycloalkyl, depending on the size of the ring, is cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or cycloheptyl.

Depending on the number of carbon atoms comprised in the particular case, alkanoyl is straight-chain or branched and is typically formyl, acetyl, propionyl, butyryl or pivaloyl.

Carbocyclic and heterocyclic rings can be saturated or unsaturated, aromatic or nonaromatic.

Cyclic unsaturated hydrocarbon radicals can be aromatic, e.g. phenyl or naphthyl, or nonaromatic, e.g. cyclopentenyl, cyclohexenyl, cycloheptenyl and cyclooctadienyl, or partially aromatic, e.g. tetrahydronaphthyl and indanyl.

Typical examples of heterocyclyl groups are pyridyl, pyrimidinyl, imidazolyl, thiazolyl, 1,3,4-thiadiazolyl, triazolyl, thienyl, furanyl, pyrrolyl, morpholinyl, oxazolyl and the corresponding partially or completely hydrogenated rings.

Within the scope of this invention, preferred compounds are

(1) Compounds of formula I, wherein:
$R_1$ and $R_2$ are each independently of the other $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl, nitro-$C_1$-$C_4$alkyl, cyano-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkanoyl-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkoxycarbonyl-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkylthio-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkanesulfinyl-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkanesulfonyl-$C_1$-$C_4$alkyl, $C_2$-$C_4$alkenyl, halo-$C_2$-$C_4$alkenyl of 1, 2 or 3 haloatoms, $C_2$-$C_4$alkynyl, halo-$C_2$-$C_4$alkynyl of 1, 2 or 3 haloatoms, $C_3$-$C_7$cycloalkyl or halogen; or
$R_1$ and $R_2$, taken together, form a saturated or unsaturated 5-7-membered, unsubstituted or substituted carbocyclic or heterocyclic ring which may contain one or two hetero atoms selected from O and/or S;
$R_3$ and $R_4$ are each independently of the other hydrogen, $C_1$-$C_6$alkyl or halogen;
$R_5$ is hydrogen or $C_1$-$C_4$alkyl;
and wherein
X, Y and n have the given meanings;
among these compounds in particular those, wherein
$R_5$ is hydrogen, $C_1$-$C_6$alkyl or benzyl;

(2) Among the compounds described in (1), those compounds wherein:
$R_1$ is $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl or $C_3$-$C_7$cycloalkyl;
$R_2$ is halogen;
$R_3$ and $R_4$ are hydrogen;
$R_5$ is hydrogen or $C_1$-$C_4$alkyl;
and wherein
X, Y and n have the given meanings.

(3) Compounds of formula I, wherein:
Y is phenyl or pyridine, each of which is unsubstituted or substituted and to which a further aromatic group can be fused.

(4) Among the compounds described in (3), those compounds wherein:
Y is phenyl substitued by an unsubstituted or substituted aryloxy group.

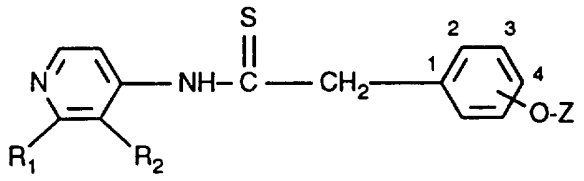
(5) Compounds of formula I, wherein:

Y is phenoxy-substituted phenyl, which phenoxy group is unsubstituted or substituted by $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy, halo-$C_1$-$C_2$alkyl containing 1-4 haloatoms, halo-$C_1$-$C_2$alkoxy containing 1-4 haloatoms, halogen or cyano.

(6) Compounds of formula I, wherein:
Y is naphthyl, tetrahydronaphthyl, indanyl, indenyl, quinolinyl, isoquinolinyl, quinoxalinyl, quinazolinyl, tetrahydroquinolinyl, indolyl, indolinyl, chromanyl, benzodioxyl, benzofuryl, benzodioxolyl, benzothienyl, benzodithianyl, benzothiophene, 2,3-dihydrobenzothiophenyl.

(7) Compounds of formula I, wherein:
X is $CH_2$, $CH_2$-$CH_2$ or CH=CH.

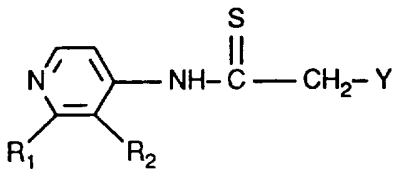
(8) Compounds of formula I.1



I.1,

wherein:
$R_1$ is $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl or $C_3$-$C_7$cycloalkyl;
$R_2$ is halogen;
Z is phenyl, naphthyl, pyridyl or quinolyl, which aromatic groups are unsubstituted or substituted by $C_1$-$C_4$alkyl, trifluoromethyl, halogen or cyano.

(9) Compounds of formula I.2

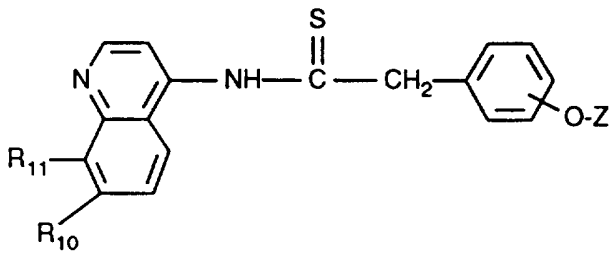


I.2,

wherein:
$R_1$ is $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl or

$C_3$-$C_7$cycloalkyl;
$R_2$ is halogen;
Y is naphthyl, tetrahydronaphthyl, indanyl, indenyl, quinolinyl, isoquinolinyl, quinoxalinyl, quinazolinyl, tetrahydroquinolinyl, indolyl, indolinyl, chromanyl, benzodioxyl, benzofuryl, benzodioxolyl, benzothienyl, benzodithianyl, benzothiophene, 2,3-dihydrobenzothiophenyl.

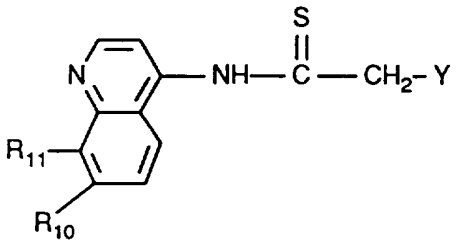
(10) Compounds of formula I.9



I.9,

wherein:
$R_{10}$ and $R_{11}$ are each independently of the other hydrogen or halogen;
Z is phenyl which is unsubstituted or substituted by $C_1$-$C_4$alkyl, trifluoromethyl, halogen or cyano.

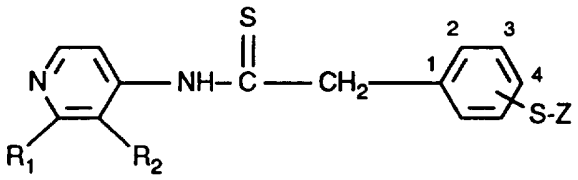
(11) Compounds of formula I.10



I.10,

wherein:
$R_{10}$ and $R_{11}$ are each independently of the other hydrogen or halogen;
Y is naphthyl, tetrahydronaphthyl, indanyl, indenyl, quinoliyl, isoquinolinyl, quinoxalinyl, quinazolinyl, tetrahydroquinolinyl, indolyl, indolynyl, chromanyl, benzodioxyl, benzofuryl, benzodioxolyl, benzothienyl, benzodithianyl, benzothiophene, 2,3-dihydrobenzothiophenyl.

(12) Compounds of formula I.11



I.11,

wherein:

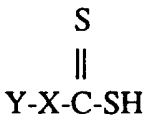
$R_1$ is methyl or ethyl;

$R_2$ is chloro;

Z is phenyl which is unsubstituted or substituted by one or two halogen atoms;

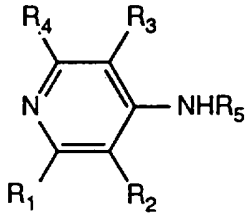
The compounds of formula I can be prepared as follows:

a) a dithiocarboxylic acid of formula II



II,

or the acid halide thereof, wherein X and Y are as defined for formula I, is reacted with a compound of formula III

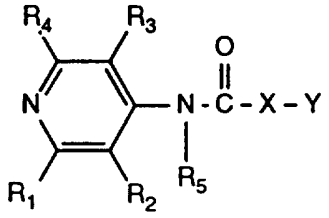


III,

wherein $R_1$ to $R_5$ have the meanings given for formula I, in the absence or in the presence of a suitable condensing agent and/or a base, to give a compound of formula I.

Illustrative examples of suitable condensing agents are N,N-dicyclohexylcarbodiimide, phosphorus pentachloride, phosgene, oxalyl chloride and thionyl chloride.

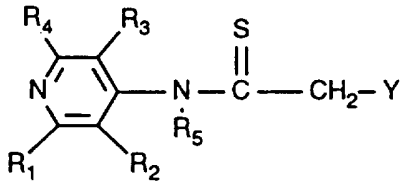
b) A compound of formula IV



IV,

wherein $R_1$ to $R_5$, X and Y have the meanings given for formula I, is reacted with a thionating agent, typically with phosphorus pentasulfide or 4-methoxyphenylthio-phosphoric acid cyclodithioanhydride ("Lawesson reagent").

Compounds of formula I.2a

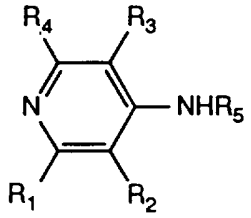


I.2a,

wherein $R_1$ to $R_5$ have the meanings given for formula I, and Y is an aromatic group, can be prepared by reacting a compound of formula V

$$Y\text{-}CO\text{-}CH_3 \qquad V,$$

wherein Y is an aromatic group, with a compound of formula III



III,

in the presence of sulfur or ammonium polysulfide solution (Willgerodt or Willgerodt-Kindler reaction).

The preparation of dithiocarboxylic acids of formula II is described, inter alia, in Chem. Ber. Vol.125, p.125 and 1023 (1992) and in J. Org.Chem. Vol.44, p. 44 and 569 (1979).

Compounds of formula III are known, e.g. from J. Med. Chem. 1989, 32, 1970-77, and can be prepared by the methods described therein.

The preparation of the compounds of formula IV is disclosed in Swiss patent specification CH 2783/94-4.

Compounds of formula V can be prepared by known methods, e.g. by Friedel-Crafts acylation.

The above described reactions are carried out in per se known manner, conveniently in the absence or in the presence of a suitable solvent or diluent or of a mixture thereof, and, as required, with cooling, at room temperature or with heating, suitably in the temperature range from c. -20°C to the boiling temperature of the reaction medium, preferably from c. -20°C to c. +150°C, and, if necessary, in a closed reactor under pressure, in an inert gas atmosphere and/or under anhydrous conditions. Illustrative examples of such solvents or diluents are: aromatic, aliphatic and alicyclic hydrocarbons and halogenated hydrocarbons such as benzene, toluene, xylene, chlorobenzene, bromobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, trichloromethane, dichloroethane or trichloroethane; ethers such as diethyl ether, tert-butylmethyl ether, tetrahydrofuran or dioxane; ketones such as acetone or methyl ethyl ketone; alcohols such as methanol, ethanol, propanol, butanol, ethylene glycol or glycerol; esters such as ethyl acetate or butyl acetate; amides such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone or hexamethylphosphoric triamide; nitriles such as acetonitrile; and sulfoxides such as dimethyl sulfoxide. Bases used in excess, for example triethylamine, pyridine, N-methylmorpholine or N,N-diethylaniline, may also be used as solvents or diluents. Illustrative examples of suitable bases are hydroxides, hydrides, amides, alkanolates, carbonates, dialkylamides or alkylsilylamides of alkali metals or alkaline earth metals, alkylamines, alkylenediamines, cycloalkylamines or N-alkylated and unsaturated or saturated cycloalkylamines, basic heterocycles, ammonium hydroxides and carbocyclic amines. Typical examples of such bases are sodium hydroxide, sodium hydride, sodium amide, sodium methanolate, sodium carbonate, potassium tert-butanolate and potassium carbonate, lithium diisopropylamide, potassium bis(trimethylsilyl)amide, calcium hydride, triethylamine, triethylenediamine, cyclohexylamine, N-cyclohexyl-N,N-dimethylamine, N,N-diethylaniline, pyridine, 4-(N,N-dimethylamino)pyridine, N-methylmorpholine, benzyl trimethylammonium hydroxide as well as 1,8-diazabicyclo[5.4.0]undec-5-ene

(DBU).
Alternatively, the reaction can be carried out under phase transfer catalysis in an organic solvent, e.g. methylene chloride or toluene, in the presence of an aqueous basic solution, e.g. sodium hydroxide solution, and of a phase transfer catalyst, e.g. tetrabutylammonium hydrogen sulfate.

It is already known to use N-(4-pyridyl)carboxamides as pesticides, inter alia from patent application WO 93/04580. The compounds of formula I of this invention differ structurally from these compounds in characteristic manner. The compounds of formula I can be used in agriculture and related fields as pest control agents for controlling plant pests. They are distinguished by their excellent activity at low concentrations, they are well tolerated by plants and are environmentally safe. They have very useful curative, preventive and, in particular, systemic properties, and can be used for protecting numerous cultivated plants. The compounds of formula I can be used to inhibit or destroy the pests which occur on plants or parts of plants (fruit, blossoms, leaves, stems, tubers, roots) in different crops of useful plants, while at the same time the parts of plants which also grow later are protected from infestation, for example by phytopathogenic microorganisms.

The compounds of formula I can also be used as seed dressing agents for protecting seeds (fruit, tubers, grains) and plant cuttings against fungal infections as well as against phytopathogenic fungi which occur in the soil.

The compounds of formula I are effective against the phytopathogenic fungi belonging to the following classes: Fungi imperfecti (e.g. Botrytis, Pyricularia, Helminthosporium, Fusarium, Septoria, Cercospora, and Alternaria); and Basidiomycetes (e.g. Rhizocotonia, Hemileia, Puccinia). They are also effective against the class of the Ascomycetes (e.g. Venturia and Erysiphe, Podosphaera, Monilinia and Uncinula), and especially against that of the Oomycetes (e.g. Phytophthora, Pythium and Plasmopara).

The compounds of formula I are also useful pest control agents for controlling insects and/or acarina in crop plants and ornamentals in agriculture, especially in cotton, vegetable and fruit crops, in forestry and in the storage and material protection sectors as well as in the hygiene sector, and for controlling pests of animals, especially on domestic animals and productive livestock. The compounds of formula I are effective against various stages of development and their activity may be observed in an immediate kill of the pests or sometime later, for example in moulting or in diminished oviposition and/or

hatching rate.

The animal pests typically include those of the order Lepidoptera, Coleoptera, Orthoptera, Isoptera, Acarina (e.g. Boophilus spp.).

Target crops suitable for the plant protective utility disclosed herein typically comprise within the scope of the present invention the following species of plants: cereals (wheat, barley, rye, oats, rice, maize, sorghum and related species), beet (sugar beet and fodder beet), pomes, drupes and soft fruit (apples, pears, plums, peaches, almonds, cherries, strawberries, raspberries and blackberries), leguminous plants (beans, lentils, peas, soybeans), oil plants (rape, mustard, poppy, olives, sunflowers, coconut, castor oil plants, cocoa beans, groundnuts), cucurbits (cucumbers, marrows, melons), fibre plants (cotton, flax, hemp, jute), citrus fruit (oranges, lemons, grapefruit, mandarins), vegetables (spinach, lettuce, asparagus, cabbages, carrots, onions, tomatoes, potatoes, sweet peppers), lauraceae (avocados, cinnamon, camphor), and plants such as tobacco, nuts, coffee, egg-plants, sugar cane, tea, pepper, vines, hops, bananas and natural rubber plants, as well as ornamentals.

The compounds of formula I are usually applied in the form of compositions and can be applied to the crop area or plant to be treated, simultaneously or in succession, with further compounds. These further compounds can be fertilisers or micronutrient donors as well as other preparations that influence plant growth. It is also possible in this connection to use selective herbicides, insecticides, fungicides, bactericides, nematicides, molluscicides or mixtures of several of these preparations, together with optional carriers, surfactants or application-promoting adjuvants commonly employed in the art of formulation.

Suitable carriers and adjuvants may be solid or liquid and correspond to the appropriate substances ordinarily employed in formulation technology, including natural or regenerated mineral substances, solvents, dispersants, wetting agents, tackifiers, thickeners, binders or fertilisers.

A preferred method of applying a compound of formula I, or an agrochemical composition which contains at least one of said compounds, is foliar application. The frequency of application and the rate of application will depend on the risk of infestation by the corresponding pathogen. However, the compound of formula I can also penetrate the plant through the roots via the soil (systemic action) by drenching the locus of the plant with a

liquid formulation, or by applying the compounds in solid form to the soil, e.g. in granular form (soil application). In crops of water rice such granular formulations can be applied to the flooded rice field. The compounds of formula I may also be applied to seeds (coating) by impregnating the seeds either with a liquid formulation of the fungicide or coating them with a solid formulation.

The compounds of formula I are used in unmodified form or, preferably, together with the adjuvants conventionally employed in the art of formulation. To this end they are conveniently formulated in known manner to emulsifiable concentrates, coatable pastes, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granulates, and also encapsulations in polymeric substances. As with the type of the compositions, the methods of application, such as spraying, atomising, dusting, scattering, coating or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

Advantageous rates of application are normally from 5 g to 2 kg of active ingredient (a.i.) per hectare, preferably from 10 g to 1 kg a.i./ha, most preferably from 20 g to 600 g a.i./ha. For use as seed dressing agents, advantageous rates of application are from 10 mg to 1 g of active ingredient per kg of seeds.

The formulations, i.e. the compositions, preparations or mixtures containing the compound of formula I and, where appropriate, a solid or liquid adjuvant, are prepared in known manner, conveniently by homogeneously mixing and/or grinding the active ingredient with extenders, as with a solvent (mixture), a solid carrier and, in some cases, surface-active compounds (surfactants).

Suitable solvents are: aromatic hydrocarbons, the fractions containing 8 to 12 carbon atoms, typically xylene mixtures or substituted naphthalenes, phthalates such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons such as cyclohexane or paraffins; also alcohols and glycols and their ethers and esters, such as ethanol, diethylene glycol, 2-methoxyethanol or 2-ethoxyethanol, ketones such as cyclohexanone, strongly polar solvents such as N-methyl-2-pyrrolidone, dimethyl sulfoxide or dimethyl formamide, as well as vegetable oils or epoxidised vegetable oils such as epoxidised coconut oil or soybean oil; or water.

The solid carriers typically used for dusts and dispersible powders are usually natural

mineral fillers such as calcite, talcum, kaolin, montmorillonite or attapulgite. To improve the physical properties it is also possible to add highly dispersed silica or highly dispersed absorbent polymers. Suitable granulated adsorptive carriers are porous types such as pumice, broken brick, sepiolite or bentonite; and suitable nonsorbent carriers are materials such as calcite or sand. In addition, a great number of pregranulated materials of inorganic or organic nature can be used, e.g. especially dolomite or pulverised plant residues.

Depending on the nature of the compound of formula I to be formulated, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants having good emulsifying, dispersing and wetting properties. The term "surfactants" will also be understood as comprising mixtures of surfactants.

Suitable anionic surfactants can be water-soluble soaps as well as water-soluble synthetic surface-active compounds.

Typical examples of nonionic surfactants are nonylphenolpolyethoxyethanols, polyethoxylated castor oil, polyadducts of polypropylene and polyethylene oxide, tributylphenoxypolyethoxyethanol, polyethylene glycol and octylphenoxypolyethoxyethanol. Fatty acid esters of polyoxyethylenesorbitane, e.g. polyoxyethylenesorbitane trioleate, are also suitable.

Cationic surfactants are preferably quaternary ammonium salts carrying, as N-substituents, at least one $C_8$-$C_{22}$alkyl radical and, as further substituents, optionally halogenated lower alkyl, benzyl or hydroxy-lower alkyl radicals.

Further surfactants customarily employed in formulation technology are familiar to those skilled in the art or may be found in the relevant literature.

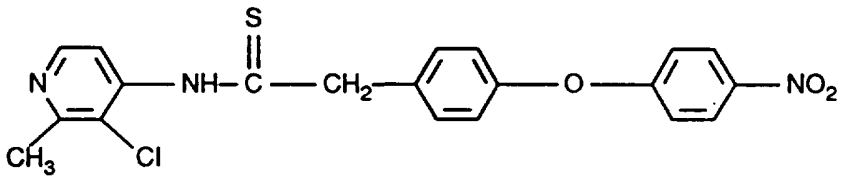
The agrochemical compositions usually contain 0.1 to 99 % by weight, preferably 0.1 to 95 % by weight, of a compound of formula I, 99.9 % to 1 % by weight, preferably 99.8 to 5 % by weight, of a solid or liquid adjuvant, and 0 to 25 % by weight, preferably 0.1 to 25 % by weight, of a surfactant.

Whereas commercial products will preferably be formulated as concentrates, the end user will normally use dilute formulations.

The compositions may also contain further ingredients such as stabilisers, antifoams, viscosity regulators, binders, tackifiers as well as fertilisers or other chemical agents to obtain special effects.

The invention is illustrated in more detail by the following non-limitative Examples. The following abbreviations are used: Ac = acetyl; Et = ethyl; i-Pr = isopropyl; Me = methyl; Ph = phenyl; Pr = n-propyl; Bu = n-butyl; m.p. = melting point. DS = diastereoisomer; Reg = regioisomer. "E" and "Z" relate to the configuration of the double bond. "NMR" stands for "nuclear magnetic resonance spectrum". MS = mass spectrum. "%" stands for "percent by weight", unless another concentration in another unit is indicated.

Example P-1: (Compound 1.1)

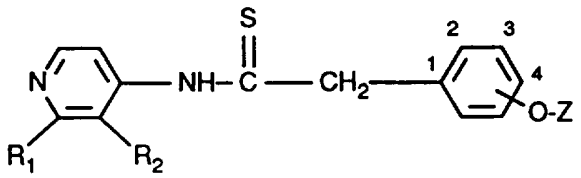


N-(3-chloro-2-methylpyridin-4-yl)-2-[4-(4-nitrophenoxy)phenyl]thioacetamide

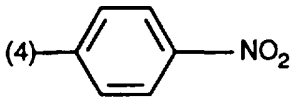
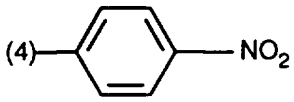
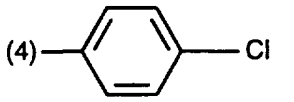
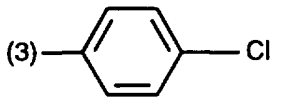
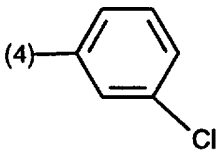
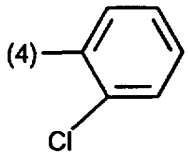
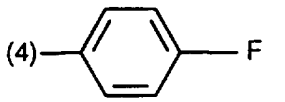
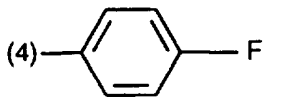
0.82 g (2.1 mmol) of N-(3-chloro-2-methylpyridin-4-yl)-2-[4-nitrophenoxy)phenyl]-acetamide and 0.46 g of phosphorus pentasulfide (2.1 mmol) are stirred vigorously in 15 ml of absolute dioxane at room temperature. The mixture is stirred for 6 h at 0-95°C in the vessel, and 2N of NaOH are then added at room temperature. The aqueous phase is then extracted 3 times with ethyl acetate. After drying over $Na_2SO_4$, the ethyl acetate is stripped off in a water-jet vacuum. The residue is purified by column chromatography over silica gel (eluant: ethyl acetate/hexane 1:1), affording 0.2 g of N-(3-chloro-2-methyl-pyridin-4-yl)-2-[4-(4-nitro-phenoxy)phenyl]thioacetamide in the form of a yellow oil ($^1$H-NMR).

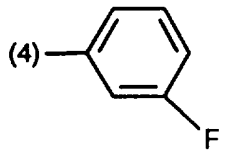
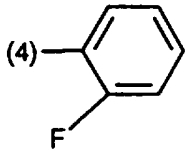
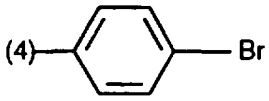
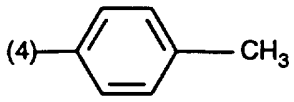
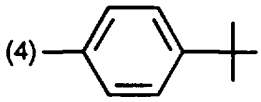
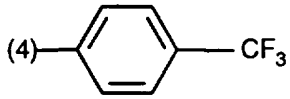
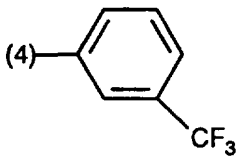
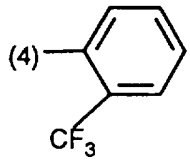
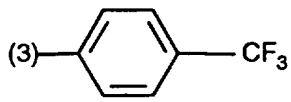
The compounds listed in the following Table can be prepared in analogous manner or by one of the processes given in the description.

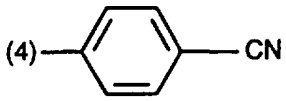
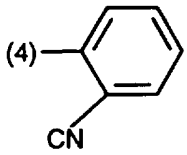
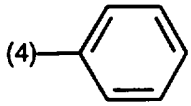
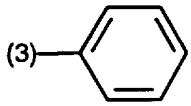
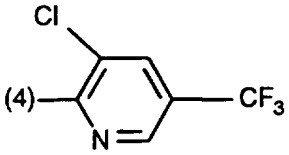
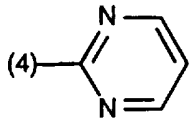
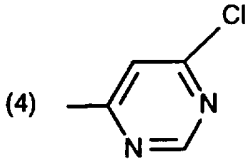
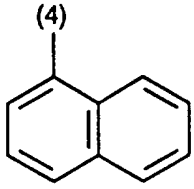
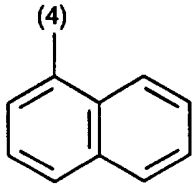
Table 1: Compounds of the general formula I.1

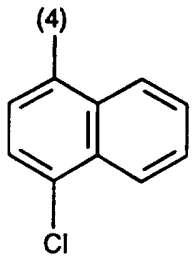
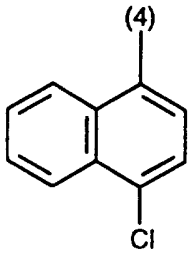
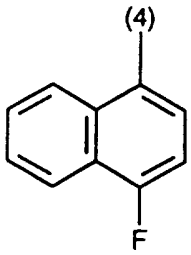
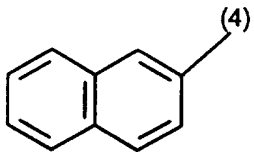
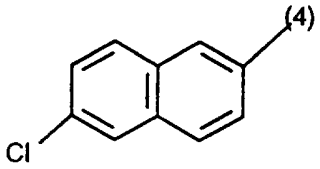
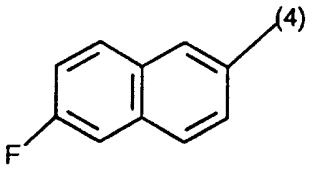


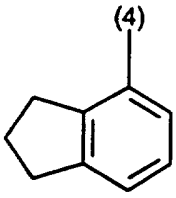
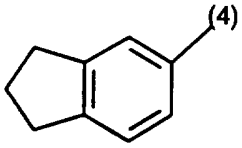
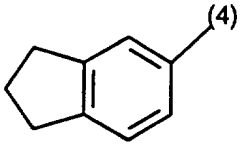
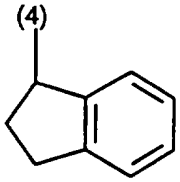
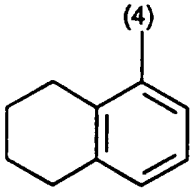
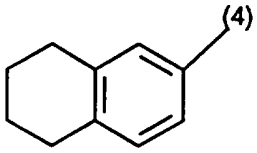
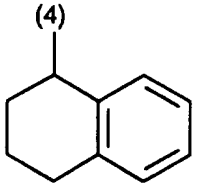
I.1

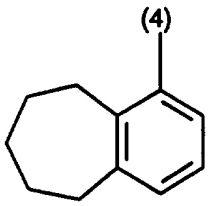
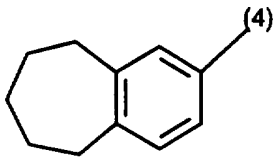
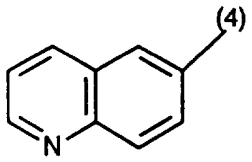
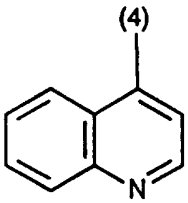
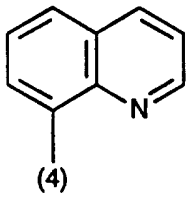
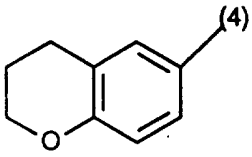
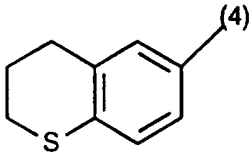
| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.1 | Me | Cl |  | oil; $^1$H-NMR |
| 1.2 | Et | Cl |  | |
| 1.3 | Me | Cl |  | oil; $^1$H-NMR |
| 1.4 | Me | Cl |  | oil; $^1$H-NMR |
| 1.5 | Me | Cl |  | oil; |
| 1.6 | Me | Cl |  | oil; |
| 1.7 | Me | Cl |  | m.p. 83-85°C |
| 1.8 | Et | Br |  | |

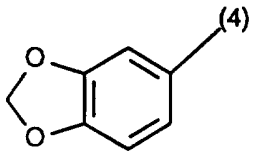
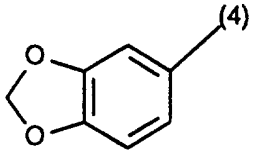
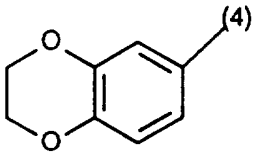
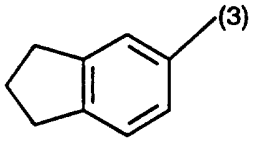
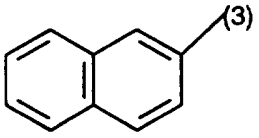
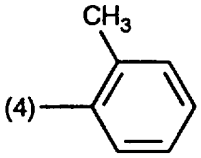
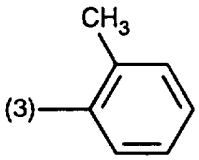
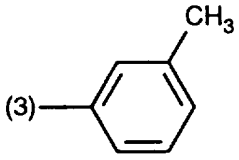
| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.9 | Me | Cl |  | oil; $^1$H-NMR |
| 1.10 | Me | Cl |  | resin; $^1$H-NMR |
| 1.11 | Me | Cl |  | oil; $^1$H-NMR |
| 1.12 | Me | Cl |  | |
| 1.13 | Me | Cl |  | |
| 1.14 | Me | Cl |  | resin; $^1$H-NMR |
| 1.15 | Me | Cl |  | |
| 1.16 | Me | Cl |  | oil; $^1$H-NMR |
| 1.17 | Me | Cl |  | |
| 1.18 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.19 | Me | Cl |  | |
| 1.20 | Me | Cl |  | |
| 1.21 | Me | Cl |  | resin; $^1$H-NMR |
| 1.22 | Me | Cl |  | |
| 1.23 | Me | Cl |  | |
| 1.24 | Me | Cl |  | oil; $^1$H-NMR |
| 1.25 | Me | Cl |  | |
| 1.26 | Me | Cl |  | |
| 1.27 | Et | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.28 | Me | Cl |  | m.p. 133-135°C |
| 1.29 | Me | Br |  | |
| 1.30 | Me | Cl |  | |
| 1.31 | Me | Cl |  | oil; $^1$H-NMR |
| 1.32 | Me | Cl |  | |
| 1.33 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.34 | Me | Cl |  | m.p. 83-85°C |
| 1.35 | Me | Cl |  | m.p. 100-104°C |
| 1.36 | Et | Cl |  | |
| 1.37 | Me | Cl |  | |
| 1.38 | Me | Cl |  | |
| 1.39 | Me | Cl |  | |
| 1.40 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.41 | Me | Cl |  | |
| 1.42 | Me | Cl |  | oil; $^1$H-NMR |
| 1.43 | Me | Cl |  | |
| 1.44 | Me | Cl |  | |
| 1.45 | Me | Cl |  | |
| 1.46 | Me | Cl |  | |
| 1.47 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.48 | Me | Cl |  | |
| 1.49 | Et | Br |  | |
| 1.50 | Me | Cl |  | |
| 1.51 | Me | Cl |  | |
| 1.52 | Me | Cl |  | resin; $^1$H-NMR |
| 1.53 | Me | Cl |  | m.p. 117-120°C |
| 1.54 | Me | Cl |  | oil; $^1$H-NMR |
| 1.55 | Me | Cl |  | oil; $^1$H-NMR |

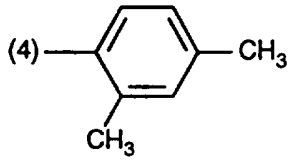
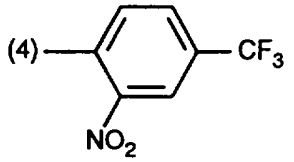
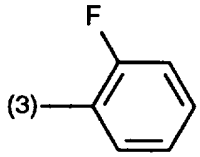
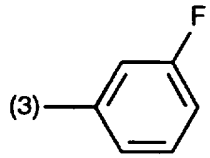
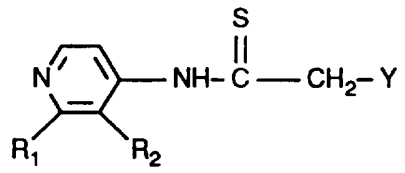
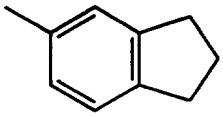
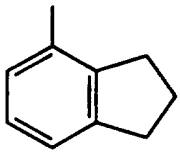
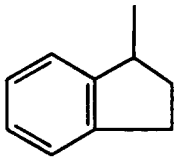
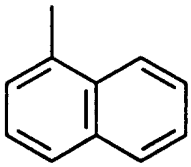
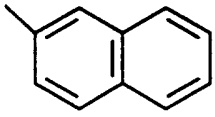
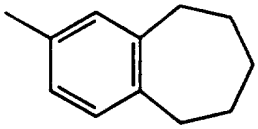
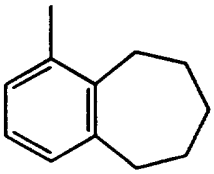
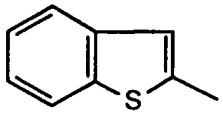
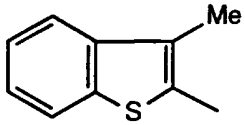
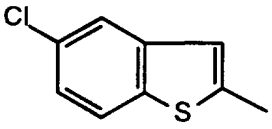
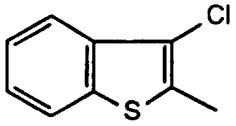
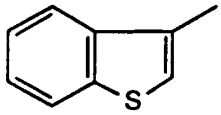
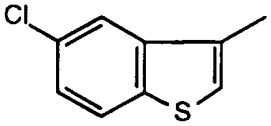
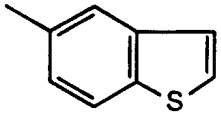
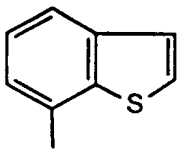
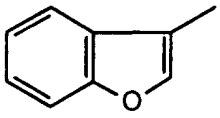
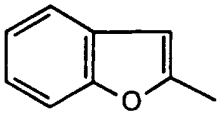
| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 1.56 | Me | Cl |  | oil; $^1$H-NMR |
| 1.57 | Me | Cl |  | resin; $^1$H-NMR |
| 1.58 | Me | Cl |  | resin; $^1$H-NMR$_1$ |
| 1.59 | Me | Cl |  | oil; $^1$H-NMR |

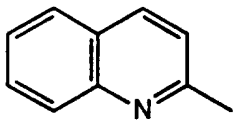
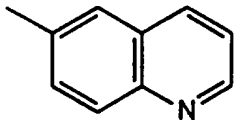
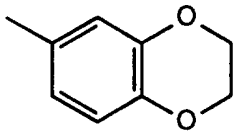
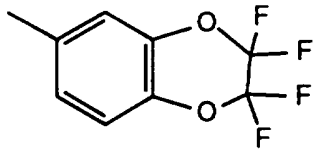
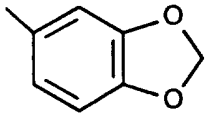
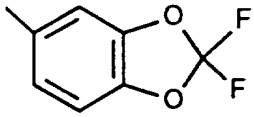
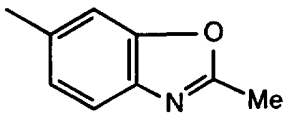
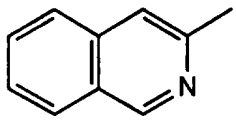
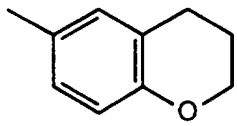
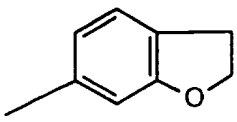
Table 2: Compounds of the general formula I.2

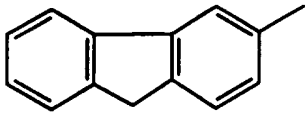
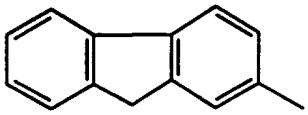
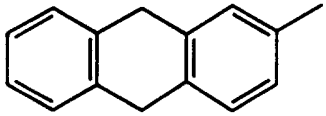
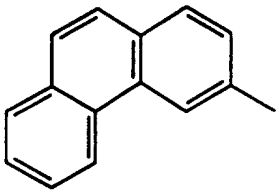
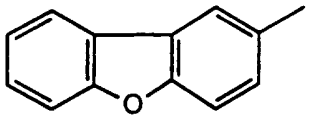
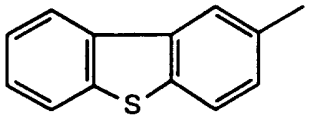
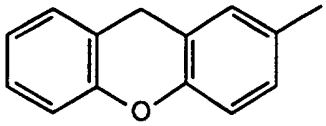
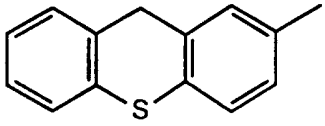
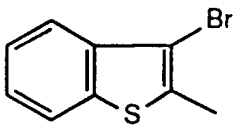


I.2

| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 2.1 | Me | Cl |  | |
| 2.2 | Me | Cl |  | |
| 2.3 | Me | Cl |  | |
| 2.4 | Me | Cl |  | |
| 2.5 | Me | Cl |  | m.p. 97-99°C |
| 2.6 | Me | Cl |  | oil; $^1$H-NMR |
| 2.7 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 2.8 | Me | Cl |  | m.p. 142-146°C |
| 2.9 | Me | Cl |  | m.p. 121-123°C |
| 2.10 | Me | Cl |  | |
| 2.11 | Me | Cl |  | m.p. 114-116°C |
| 2.12 | Me | Cl |  | |
| 2.13 | Me | Cl |  | |
| 2.14 | Me | Cl |  | |
| 2.15 | Me | Cl |  | |
| 2.16 | Me | Cl |  | |
| 2.17 | Me | Cl |  | oil; $^1$H-NMR |

| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 2.18 | Me | Cl |  | |
| 2.19 | Me | Cl |  | |
| 2.20 | Me | Cl |  | oil; $^1$H-NMR |
| 2.21 | Me | Cl |  | |
| 2.22 | Me | Cl |  | m.p. 107-109°C |
| 2.23 | Me | Cl |  | |
| 2.24 | Me | Cl |  | |
| 2.25 | Me | Cl |  | |
| 2.26 | Me | Cl |  | resin; $^1$H-NMR |
| 2.27 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 2.28 | Me | Cl |  | |
| 2.29 | Me | Cl |  | |
| 2.30 | Me | Cl |  | |
| 2.31 | Me | Cl |  | |
| 2.32 | Me | Cl |  | |
| 2.33 | Me | Cl |  | |
| 2.34 | Me | Cl |  | |
| 2.35 | Me | Cl |  | oil; $^1$H-NMR |
| 2.36 | Me | Cl |  | |

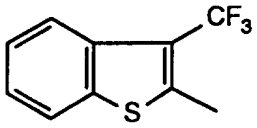
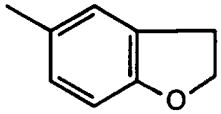
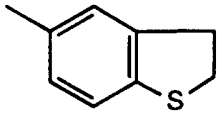
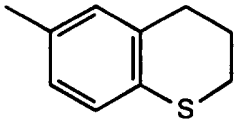
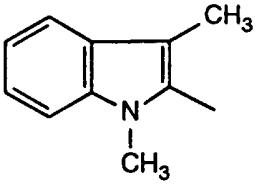
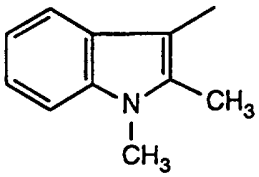
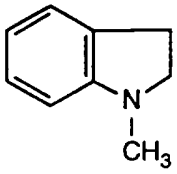
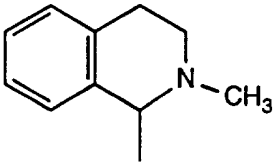
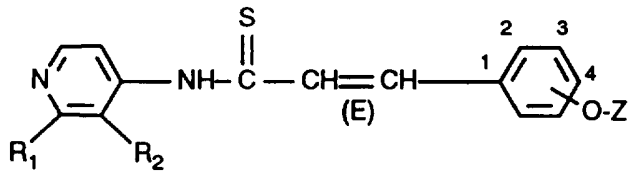
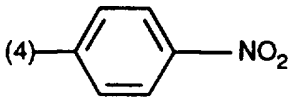
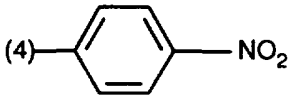
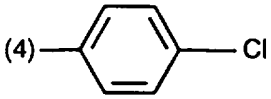
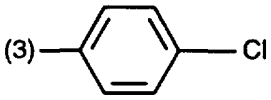
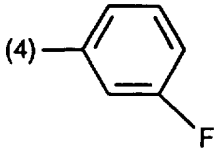
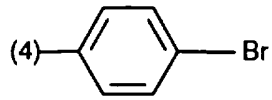
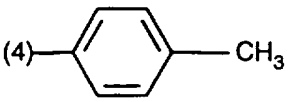
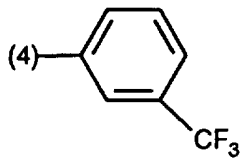
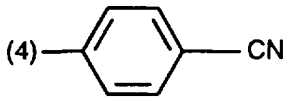
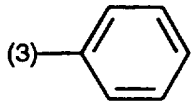
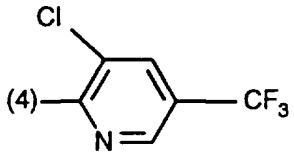
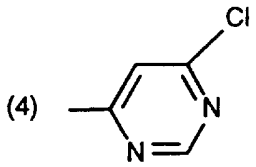
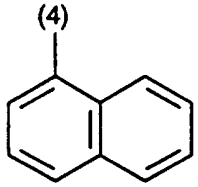
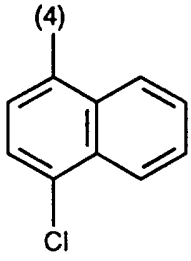
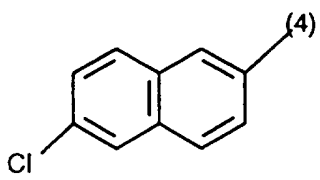
| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 2.37 | Me | Cl |  | |
| 2.38 | Me | Cl |  | |
| 2.39 | Me | Cl |  | |
| 2.40 | Me | Cl |  | resin; $^1$H-NMR |
| 2.41 | Me | Cl |  | |
| 2.42 | Me | Cl |  | |
| 2.43 | Me | Cl |  | |
| 2.44 | Me | Cl |  | |
| 2.45 | Me | Cl |  | |

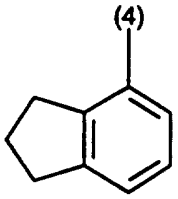
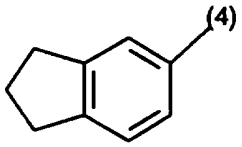
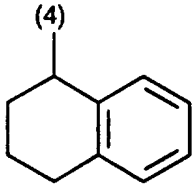
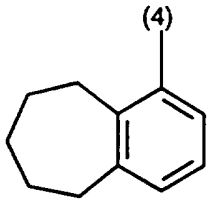
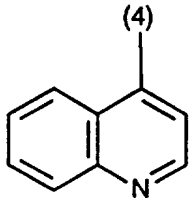
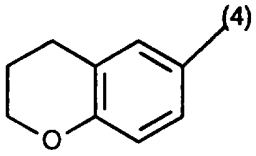
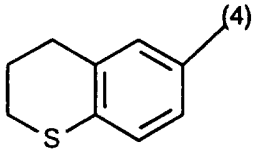
Table 3: Compounds of the general formula I.3




I.3

| Ex. No. | $R_1$ | $R_2$ | Z Phys. data |
|---|---|---|---|
| 3.1 | Me | Cl |  |
| 3.2 | Et | Cl |  |
| 3.3 | Me | Cl |  |
| 3.4 | Me | Cl |  |
| 3.5 | Me | Cl |  |
| 3.6 | Me | Cl |  |
| 3.7 | Me | Cl |  |
| 3.8 | Me | Cl |  |
| 3.9 | Me | Cl |  |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 3.10 | Me | Cl |  | |
| 3.11 | Me | Cl |  | |
| 3.12 | Me | Cl |  | |
| 3.13 | Me | Cl |  | |
| 3.14 | Me | Cl |  | |
| 3.15 | Me | Cl |  | |
| 3.16 | Me | Cl |  | |
| 3.17 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z Phys. data |
|---|---|---|---|
| 3.18 | Me | Cl |  |
| 3.19 | Et | Cl |  |
| 3.20 | Me | Cl |  |
| 3.21 | Me | Cl |  |
| 3.22 | Me | Cl |  |
| 3.23 | Me | Cl |  |
| 3.24 | Me | Cl |  |

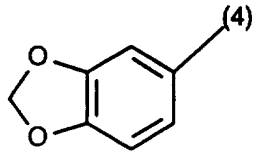
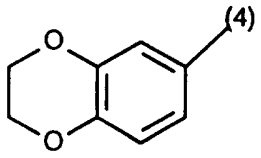
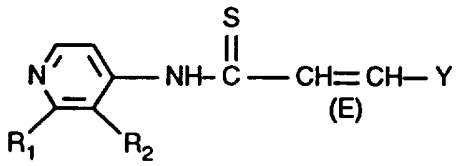
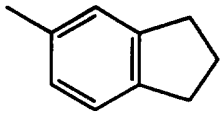
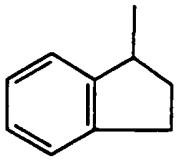
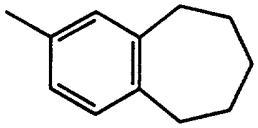
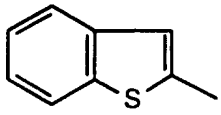
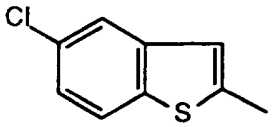
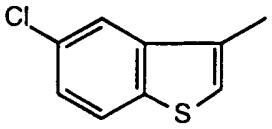
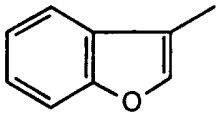
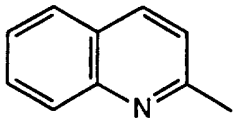
| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 3.25 | Et | Br |  | |
| 3.26 | Me | Cl |  | |

Table 4: Compounds of the general formula I.4




I.4

| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 4.1 | Me | Cl |  | |
| 4.2 | Me | Cl |  | |
| 4.3 | Me | Cl |  | |
| 4.4 | Me | Cl |  | |
| 4.5 | Me | Cl |  | |
| 4.6 | Me | Cl |  | |
| 4.7 | Me | Cl |  | |
| 4.8 | Me | Cl |  | |

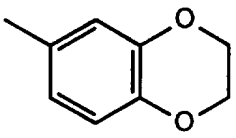
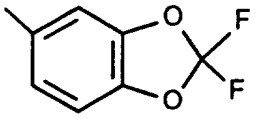
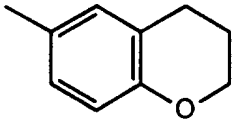
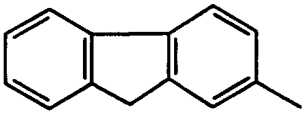
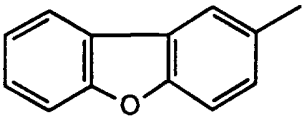
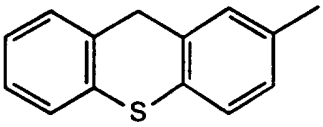
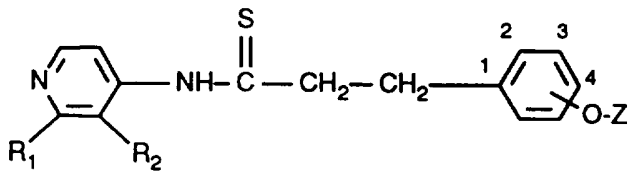
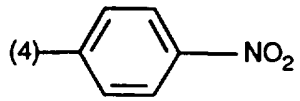
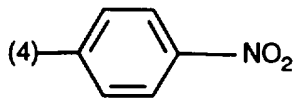
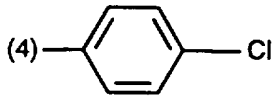
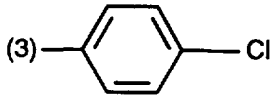
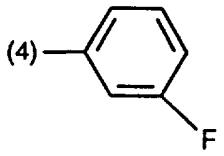
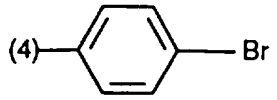
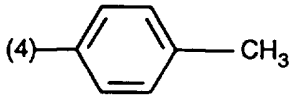
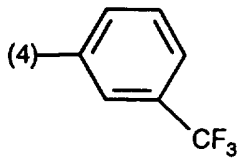
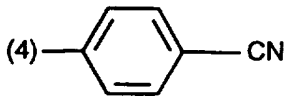
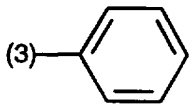
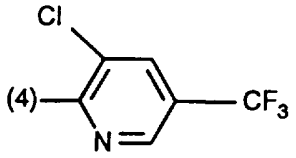
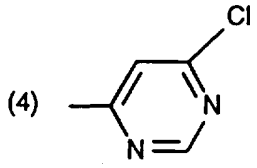
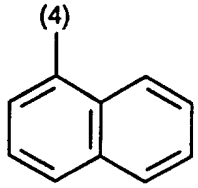
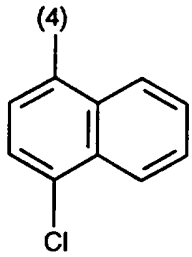
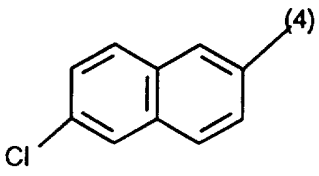
| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 4.9 | Me | Cl |  | |
| 4.10 | Me | Cl |  | |
| 4.11 | Me | Cl |  | |
| 4.12 | Me | Cl |  | |
| 4.13 | Me | Cl |  | |
| 4.14 | Me | Cl |  | |

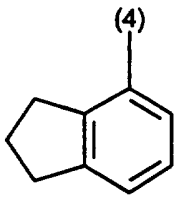
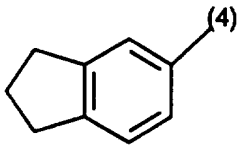
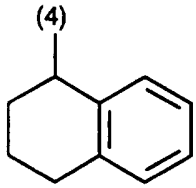
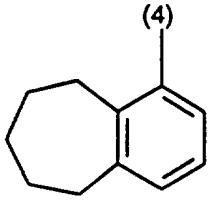
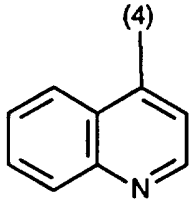
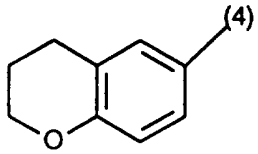
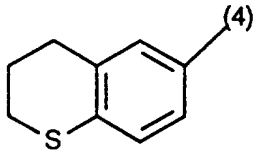
Table 5: Compounds of the general formula I.5



I.5

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 5.1 | Me | Cl |  | |
| 5.2 | Et | Cl |  | |
| 5.3 | Me | Cl |  | |
| 5.4 | Me | Cl |  | |
| 5.5 | Me | Cl |  | m.p. 135-137°C |
| 5.6 | Me | Cl |  | |
| 5.7 | Me | Cl |  | |
| 5.8 | Me | Cl |  | |
| 5.9 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 5.10 | Me | Cl |  | |
| 5.11 | Me | Cl |  | |
| 5.12 | Me | Cl |  | |
| 5.13 | Me | Cl |  | |
| 5.14 | Me | Cl |  | |
| 5.15 | Me | Cl |  | |
| 5.16 | Me | Cl |  | |
| 5.17 | Me | Cl |  | |

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 5.18 | Me | Cl |  | |
| 5.19 | Et | Cl |  | |
| 5.20 | Me | Cl |  | |
| 5.21 | Me | Cl |  | |
| 5.22 | Me | Cl |  | |
| 5.23 | Me | Cl |  | |
| 5.24 | Me | Cl |  | |

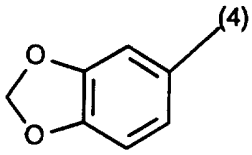
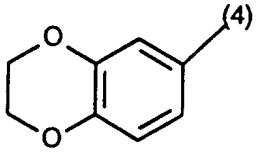
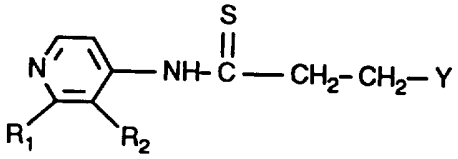
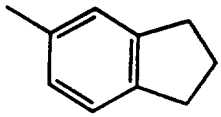
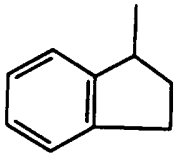
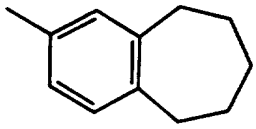
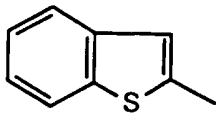
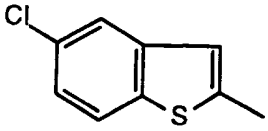
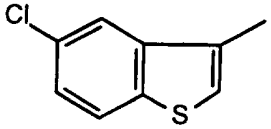
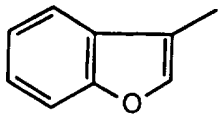
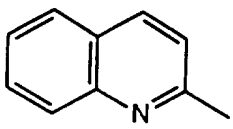
| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 5.25 | Et | Br |  | |
| 5.26 | Me | Cl |  | |

Table 6: Compounds of the general formula I.6



I.6

| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 6.1 | Me | Cl |  | |
| 6.2 | Me | Cl |  | |
| 6.3 | Me | Cl |  | |
| 6.4 | Me | Cl |  | |
| 6.5 | Me | Cl |  | |
| 6.6 | Me | Cl |  | |
| 6.7 | Me | Cl |  | |
| 6.8 | Me | Cl |  | |

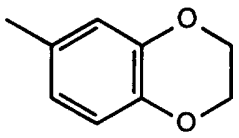
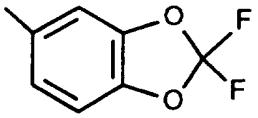
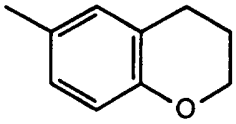
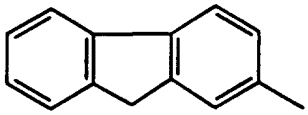
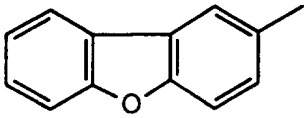
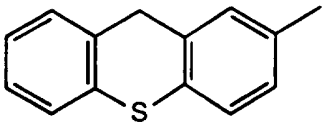
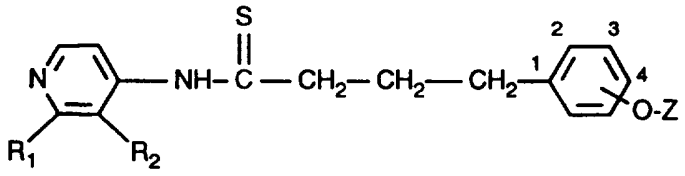
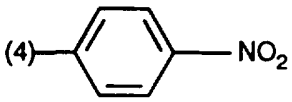
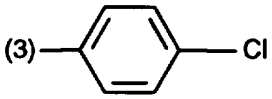
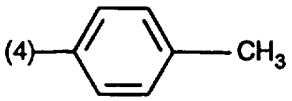
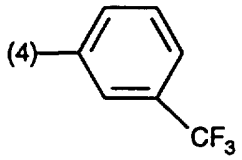
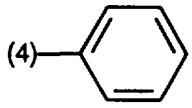
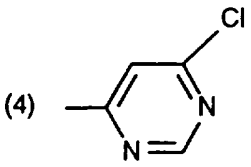
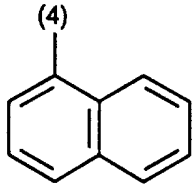
| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 6.9 | Me | Cl |  | |
| 6.10 | Me | Cl |  | |
| 6.11 | Me | Cl |  | |
| 6.12 | Me | Cl |  | |
| 6.13 | Me | Cl |  | |
| 6.14 | Me | Cl |  | |

Table 7: Compounds of the general formula I.7



I.7

| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 7.1 | Me | Cl |  | |
| 7.2 | Me | Cl |  | |
| 7.3 | Me | Cl |  | |
| 7.4 | Me | Cl |  | |
| 7.5 | Me | Cl |  | |
| 7.6 | Me | Cl |  | |
| 7.7 | Me | Cl |  | |

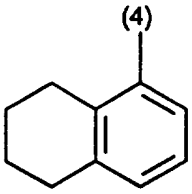
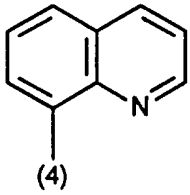
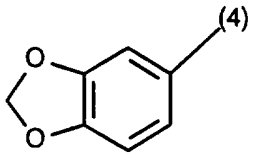
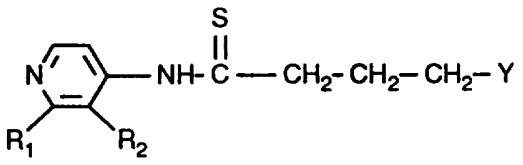
| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 7.8 | Me | Cl |  | |
| 7.9 | Me | Cl |  | |
| 7.10 | Me | Cl |  | |

Table 8: Compounds of the general formula I.8



I.8

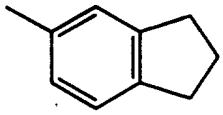
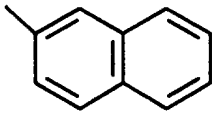
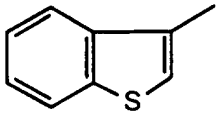
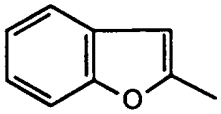
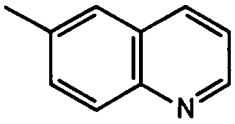
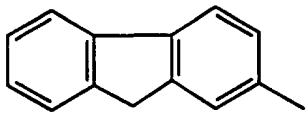
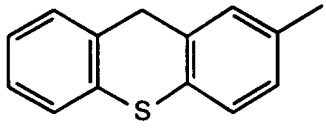
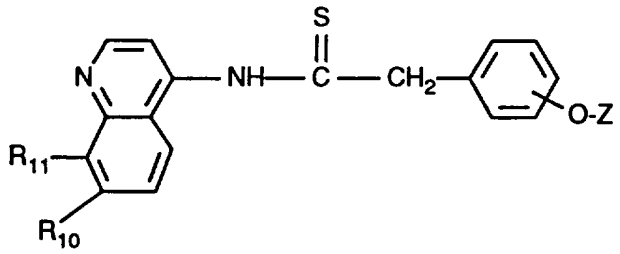
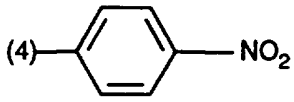
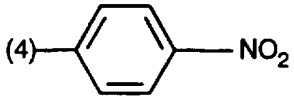
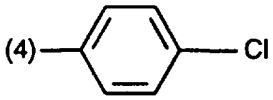
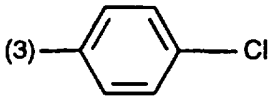
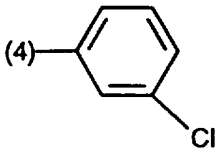
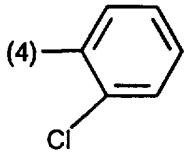
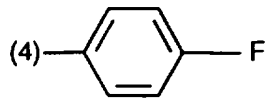
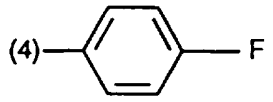
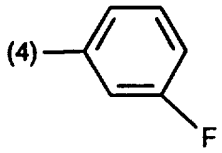
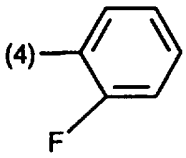
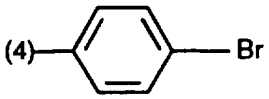
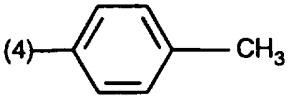
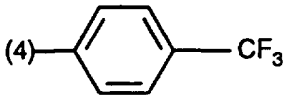
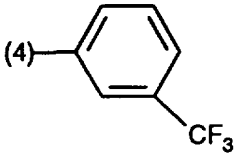
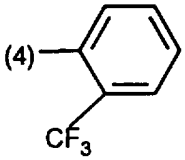
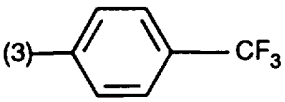
| Ex. No. | $R_1$ | $R_2$ | Y | Phys. data |
|---|---|---|---|---|
| 8.1 | Me | Cl |  | |
| 8.2 | Me | Cl |  | |
| 8.3 | Me | Cl |  | |
| 8.4 | Me | Cl |  | |
| 8.5 | Me | Cl |  | |
| 8.6 | Me | Cl |  | |
| 8.7 | Me | Cl |  | |

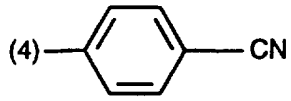
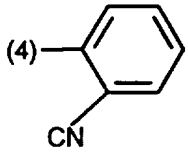
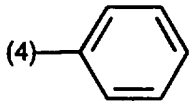
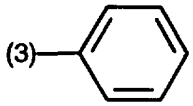
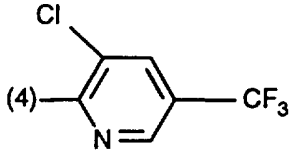
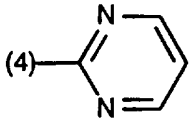
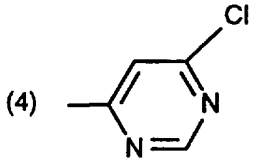
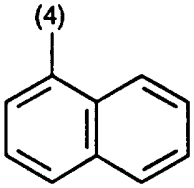
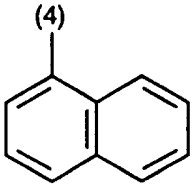
Table 9: Compounds of the general formula I.9

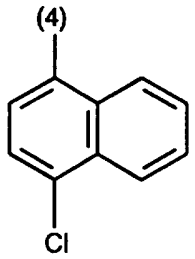
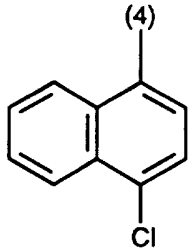
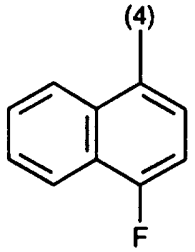
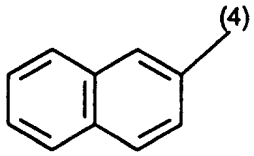
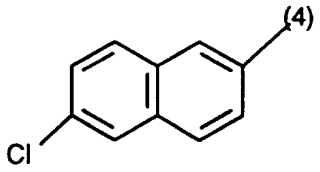
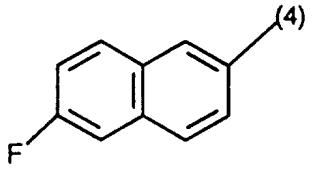


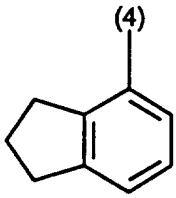
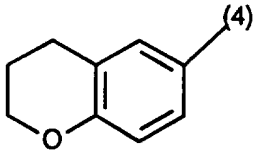
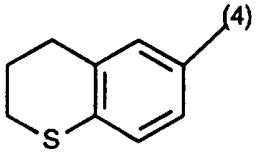
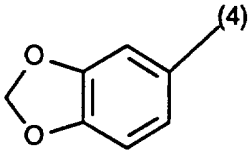
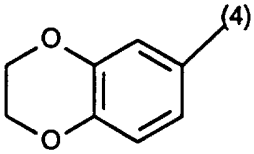
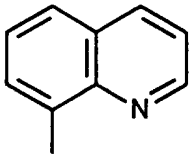
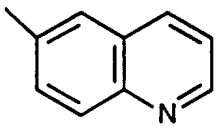
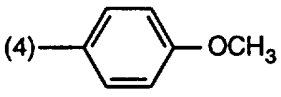
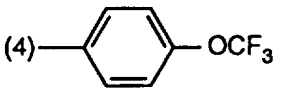
I.9

| Ex. No. | $R_{10}$ | $R_{11}$ | Z | Phys. data |
|---|---|---|---|---|
| 9.1 | H | H |  | m.p. 181-182°C |
| 9.2 | Cl | H |  | |
| 9.3 | H | F |  | m.p. 53-58°C |
| 9.4 | H | F |  | m.p. 168-171°C |
| 9.5 | H | F |  | |
| 9.6 | H | F |  | |
| 9.7 | Cl | H |  | |
| 9.8 | H | F |  | oil; $^1$H-NMR |

| Ex. No. | $R_{10}$ | $R_{11}$ | Z | Phys. data |
|---|---|---|---|---|
| 9.9 | Cl | H |  | |
| 9.10 | H | F |  | |
| 9.11 | H | F |  | |
| 9.12 | H | F |  | |
| 9.13 | H | F |  | |
| 9.14 | H | F |  | |
| 9.15 | H | F |  | |
| 9.16 | H | F |  | |
| 9.17 | H | F |  | |
| 9.18 | H | F |  | |

| Ex. No. | $R_{10}$ | $R_{11}$ | Z | Phys. data |
|---|---|---|---|---|
| 9.19 | H | F |  | |
| 9.20 | H | F |  | |
| 9.21 | H | F |  | resin |
| 9.22 | H | F |  | |
| 9.23 | H | F |  | |
| 9.24 | H | F |  | |
| 9.25 | H | F |  | |
| 9.26 | H | F |  | |
| 9.27 | Cl | H |  | |

| Ex. No. | $R_{10}$ | $R_{11}$ | Z | Phys. data |
|---|---|---|---|---|
| 9.28 | H | F |  | resin |
| 9.29 | F | F |  | |
| 9.30 | H | F |  | |
| 9.31 | H | F |  | |
| 9.32 | H | F |  | |
| 9.33 | H | F |  | |

| Ex. No. | $R_{10}$ | $R_{11}$ | Z | Phys. data |
|---|---|---|---|---|
| 9.34 | H | F |  | |
| 9.35 | H | F |  | |
| 9.36 | H | F |  | |
| 9.37 | H | F |  | |
| 9.38 | H | F |  | |
| 9.39 | H | F |  | |
| 9.40 | H | F |  | |
| 9.41 | H | F |  | m.p. 53-55°C |
| 9.42 | H | F |  | m.p. 132-135°C |

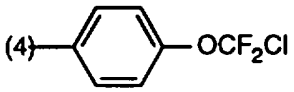
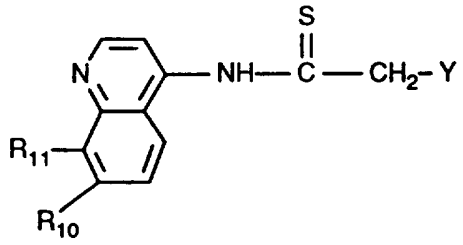
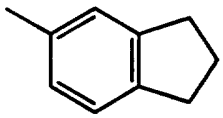
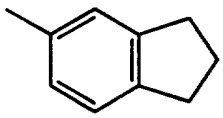
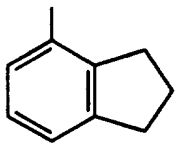
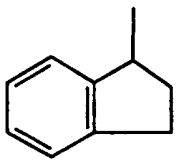
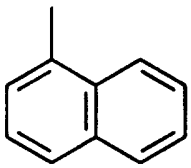
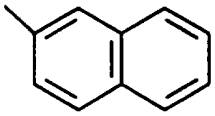
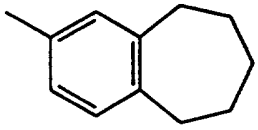
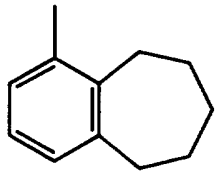
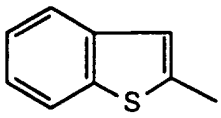
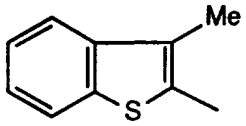
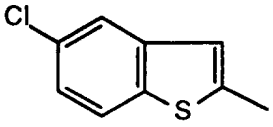
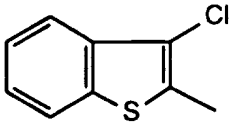
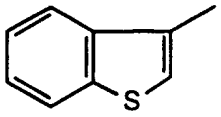
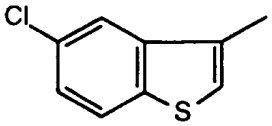
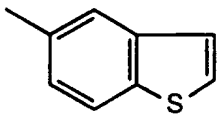
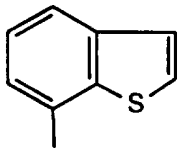
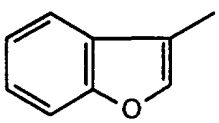
| | | | |
|---|---|---|---|
| 9.43 | H | F |  |

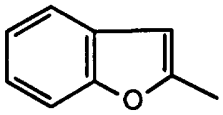
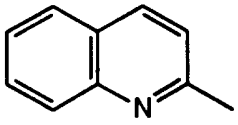
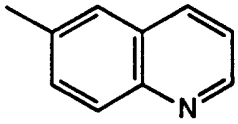
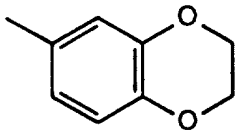
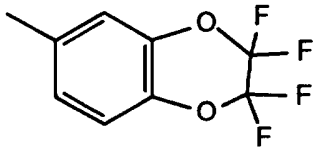
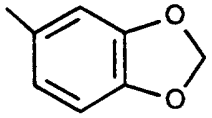
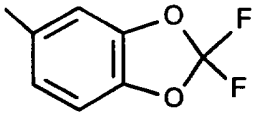
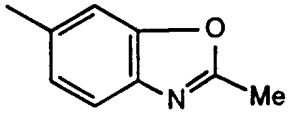
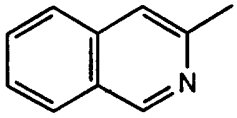
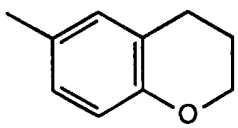
Table 10: Compounds of the general formula I.10.

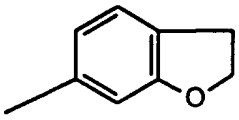
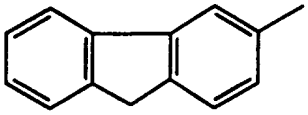
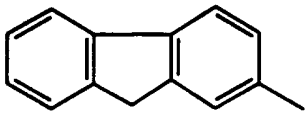
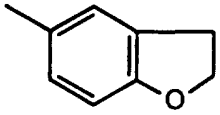
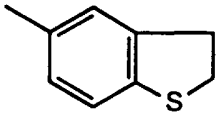
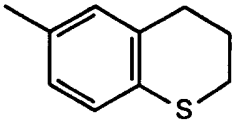
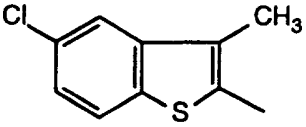
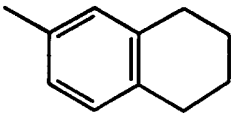
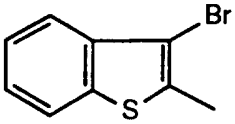
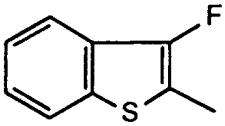


I.10

| Ex. No. | $R_{10}$ | $R_{11}$ | Y | Phys. data |
|---|---|---|---|---|
| 10.1 | Cl | H |  | |
| 10.2 | H | F |  | resin |
| 10.3 | H | F |  | |
| 10.4 | H | F |  | |
| 10.5 | H | F |  | |
| 10.6 | H | F |  | m.p. 77-80°C |
| 10.7 | H | F |  | m.p. 138-140°C |

| Ex. No. | $R_{10}$ | $R_{11}$ | Y | Phys. data |
|---|---|---|---|---|
| 10.8 | H | F |  | |
| 10.9 | H | F |  | |
| 10.10 | H | F |  | m.p. 160-165°C |
| 10.11 | H | F |  | |
| 10.12 | H | F |  | |
| 10.13 | H | F |  | |
| 10.14 | H | F |  | |
| 10.15 | H | F |  | |
| 10.16 | H | F |  | |
| 10.17 | H | F |  | |

| Ex. No. | $R_{10}$ | $R_{11}$ | Y | Phys. data |
|---|---|---|---|---|
| 10.18 | H | F |  | |
| 10.19 | H | F |  | |
| 10.20 | H | F |  | |
| 10.21 | H | F |  | |
| 10.22 | H | F |  | |
| 10.23 | H | F |  | |
| 10.24 | H | F |  | |
| 10.25 | H | F |  | |
| 10.26 | H | F |  | |
| 10.27 | H | F |  | resin |

| Ex. No. | $R_{10}$ | $R_{11}$ | Y | Phys. data |
|---|---|---|---|---|
| 10.28 | H | F |  | |
| 10.29 | H | F |  | |
| 10.30 | H | F |  | |
| 10.31 | H | F |  | m.p. 209-211°C |
| 10.32 | H | F |  | |
| 10.33 | H | F |  | |
| 10.34 | H | F |  | m.p. 93-95°C |
| 10.35 | H | F |  | m.p. 180-184°C |
| 10.36 | H | F |  | |
| 10.37 | H | F |  | |

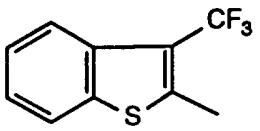
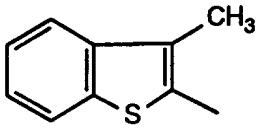
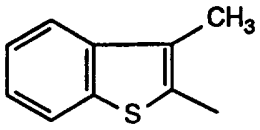
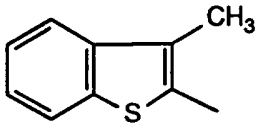
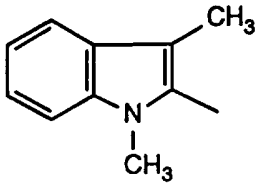
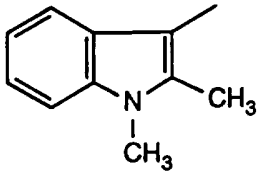
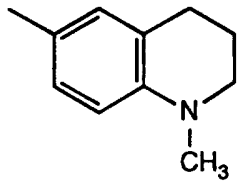
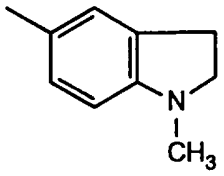
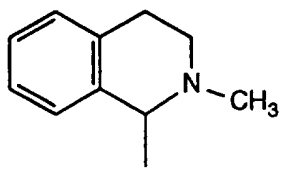
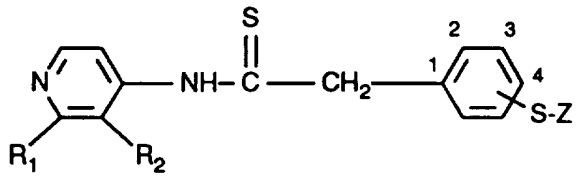
| Ex. No. | $R_{10}$ | $R_{11}$ | Y | Phys. data |
|---|---|---|---|---|
| 10.38 | H | F |  | |
| 10.39 | H | H |  | |
| 10.40 | Cl | H |  | |
| 10.41 | F | F |  | |
| 10.42 | H | F |  | |
| 10.43 | H | F |  | |
| 10.44 | H | F |  | |
| 10.45 | H | F |  | |
| 10.46 | H | F |  | |

Table 11: Compounds of the general formula I.11




I.11

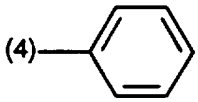
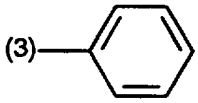
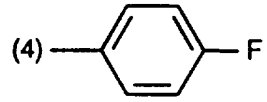
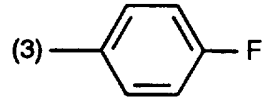
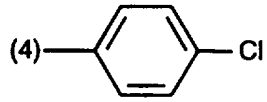
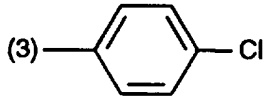
| Ex. No. | $R_1$ | $R_2$ | Z | Phys. data |
|---|---|---|---|---|
| 11.1 | Me | Cl |  | |
| 11.2 | Me | Cl |  | |
| 11.3 | Me | Cl |  | m.p. 117-119°C |
| 11.4 | Me | Cl |  | |
| 11.5 | Me | Cl |  | m.p. 114-116°C |
| 11.6 | Me | Cl |  | |

Table 12: $^1$H-NMR data of the oils or resins of Tables 1-11

| Example | $^1$H-NMR data (ppm/multiplicity/number of protones) solvent: $CDCl_3$ |
|---|---|
| 1.1 | 2.62/s/3H; 4.32/s/2H; 7.04/d/2H; 7.17/d/2H; 7.46/d/2H; 8.23/d/2H; 8.40/d/1H; 8.99/d/1H; 9.11/s/1H |
| 1.3 | 2.60/s/3H; 4.28/s/2H; 6.95/d/2H; 7.06/d/2H; 7.30-7.37/m/4H; 8.38/d/1H; 8.98/d/1H; 9.12/s/1H |
| 1.4 | 2.51/s/3H; 4.27/s/2H; 6.94-7.03/m/4H; 7.12/d/1H; 7.29-7.44/m/3H; 8.38/d/1H; 8.95/d/1H; 9.11/s/1H |
| 1.10 | 2.60/s/3H; 4.27/s/2H; 7.02-7.33/m/8H; 8.37/d/1H; 8.98/d/1H; 9.13/s/1H |
| 1.11 | 2.61/s/3H; 4.26/s/2H; 6.94-7.10/m/7H; 7.39/t/1H; 8.37/d/1H; 8.95/d/1H; 9.12/s/1H |
| 1.14 | 1.33/s/9H; 2.60/s/3H; 4.28/s/2H; 6.96/d/2H; 7.07/d/2H; 7.28-7.40/m/4H; 8.38/d/1H; 8.98/d/1H; 9.17/s/1H |
| 1.16 | 2.60/s/3H; 4.30/s/2H; 7.09-7.51/m/8H; 8.38/d/1H; 8.98/d/1H; 9.16/s/1H |
| 1.21 | 2.60/s/3H; 4.28/s/2H; 7.01-7.40/m/8H; 8.38/d/1H; 8.99/d/1H; 9.16/s/1H |
| 1.24 | 2.60/s/3H; 4.34/s/2H; 7.08/t/1H; 7.28-7.47/m/4H; 8.38/d/1H; 8.58/d/2H; 8.99/d/1H; 9.18/s/1H |
| 1.52 | 2.54/s/3H; 4.20/s/2H; 6.99-7.79/m/11H; 8.29/d/1H; 8.87/d/1H; 9.07/s/1H |

| | |
|---|---|
| 1.54 | 2.22/s/3H; 2.60/s/3H; 4.25/s/2H; 6.87-7.39/m/8H; 8.37/s/1H; 8.98/d/1H; 9.14/s/1H |
| 1.55 | 2.32/s/3H; 2.60/s/3H; 4.27/s/2H; 6.81-7.42/m/8H; 8.37/s/1H; 8.97/s/1H; 9.13/s/1H |
| 1.57 | 2.62/s/3H; 4.32/s/2H; 7.09-7.19/m/3H; 7.44-7.48/d/2H; 7.75/dd/1H; 8.25/d/1H; 8.39/d/1H; 8.94/d/1H; 9.13/s/1H |
| 1.58 | 2.60/s/3H; 4.27/s/2H; 6.95-7.42/m/8H; 8.37/d/1H; 8.93/d/1H; 9.12/s/1H |
| 1.59 | 2.60/s/3H; 4.30/s/2H; 6.69-6.86/m/3H; 7.10/d/2H; 7.28-7.38/m/3H; 8.38/d/1H; 8.98/d/1H; 9.14/s/1H |
| 2.17 | 2.60/s/3H; 4.46/s/2H; 6.79/s/1H; 7.24-7.35/m/2H; 7.49/d/1H; 7.59/d/1H; 8.38/d/1H; 8.96/d/1H; 9.78/s/1H |
| 2.20 | 2.59/s/3H; 5.19/s/2H; 4.28/s/4H; 6.81-6.95/m/3H; 8.36/d/1H; 8.97/d/1H; 9.20/s/1H |
| 2.35 | 2.55/s/2H; 3.88/s/2H; 4.28/s/2H; 7.18-7.52/m/7H; 8.38/m/1H; 8.93/d/1H; 9.13/s/1H |
| 9.8 | 4.37/s/2H; 6.95-7.15/m/7H; 7.35-7.49/m/5H; 8.55/s/1H; 8.98/d/2H |

Formulation Examples for compounds of formula I

Examples F-1.1 to F-1.3: Emulsifiable concentrates

| Components | F-1.1 | F-1.2 | F-1.3 |
|---|---|---|---|
| compound of the Tables | 25% | 40% | 50% |
| calcium dodecylbenzenesulfonate | 5% | 8% | 6% |
| polyethoxylated castor oil (36 mol EO units) | 5% | - | - |
| tributylphenoxy polyethoxy-ethanol (30 mol EO units) | - | 12% | 4% |
| cyclohexanone | - | 15% | 20% |
| xylene mixture | 65% | 25% | 20% |

Emulsions of any desired concentration can be prepared by diluting such concentrates with water.

Example F-2: Emulsifiable concentrate

| Components | F-2 |
|---|---|
| compound of the Tables | 10% |
| octylphenoxy polyethoxyethanol (4-5 mol EO units) | 3% |
| calcium dodecylbenzenesulfonate | 3% |
| polyethoxylated castor oil (36 mol EO units) | 4% |
| cyclohexanone | 30% |
| xylene mixture | 50% |

Emulsions of any desired concentration can be prepared by diluting such a concentrate with water.

Examples F-3.1 to F-3.4: Solutions

| Components | F-3.1 | F-3.2 | F-3.3 | F-3.4 |
|---|---|---|---|---|
| compound of the Tables | 80% | 10% | 5% | 95% |
| propylene glycol monomethyl ether | 20% | - | - | - |
| polyethylene glycol (relative molecular mass: 400 atomic mass units) | - | 70% | - | - |
| N-methylpyrrolid-2-one | - | 20% | - | - |
| epoxidised coconut oil | - | - | 1% | 5% |
| white spirit (boiling ranges: 160-190°) | | - | - | 94% - |

These solutions are suitable for application in the form of microdrops.

Examples F-4.1 to F-4.4: Granulates

| Components | F-4.1 | F-4.2 | F-4.3 | F-4.4 |
|---|---|---|---|---|
| compound of the Tables | 5% | 10% | 8% | 21% |
| kaolin | 94% | - | 79% | 54% |
| highly dispersed silica | 1% | - | 13% | 7% |
| attapulgite | - | 90% | - | 18% |

The compound is dissolved in dichloromethane, the solution is sprayed on to the carrier and the solvent is then evaporated under vacuum.

Examples F-5.1 and F-5.2: Dusts

| Components | F-5.1 | F-5.2 |
|---|---|---|
| compound of the Tables | 2% | 5% |
| highly dispersed silica | 1% | 5% |
| talcum | 97% | - |
| kaolin | - | 90% |

Ready-for-use dusts are obtained by intimately the carriers with the compound.

Examples F-6.1 to F-6.3: Wettable powders

| Components | F-6.1 | F-6.2 | F-6.3 |
|---|---|---|---|
| compound of the Tables | 25% | 50% | 75% |
| sodium ligninsulfonate | 5% | 5% | - |
| sodium lauryl sulfate | 3% | - | 5% |
| sodium diisobutylnaphthalene-sulfonate | - | 6% | 10% |
| octylphenoxy polyethoxyethanol (7-8 mol EO units) | - | 2% | - |
| highly dispersed silica | 5% | 10% | 10% |
| kaolin | 62% | 27% | - |

All components are mixed and the mixture is well ground in a suitable mill to give wettable powders which can be diluted with water to suspensions of any desired concentration.

Biological Examples: A. Microbicidal activity

B-1: Action against Puccinia graminis in wheat

a) Residual protective action

Wheat plants are sprayed to drip point 6 days after sowing with an aqueous spray mixture (0.02 % a.i.) prepared from a wettable powder formulation of the test compound and infected 24 hours later with a uredospore suspension of the fungus. After an incubation time of 48 hours (conditions: 95-100 % relative humidity at 20°C), the plants are stood at 22°C in a greenhouse. Evaluation of fungal infestation is made 12 days after infection.

b) Systemic action

Wheat plants are drenched 5 days after sowing with an aqueous spray mixture (0.006 % a.i., based on the volume of the soil) prepared from a wettable powder formulation of the test compound. Care is taken that the spray mixture does not come in contact with the growing parts of plants. After 48 hours, the plants are infected with a uredospore suspension of the fungus. After an incubation period of 48 hours (conditions: 95-100 % relative humidity at 20°C), the plants are stood at 22°C in a greenhouse. Evaluation of fungal infestation is made 12 days after infection

Example B-2: Action against Phytophthora infestans on tomatoes

a) Residual-protective action

After a growth period of 3 weeks, tomato plants are sprayed to drip point with a spray mixture (0.02 % a.i.) prepared from a wettable powder formulation of the test compound. The tomato plants are treated 24 hours later with a conidia suspension of the fungus. Evaluation of fungal infestation is made after the plants have been incubated for 5 days at 20°C and 90-100°C relative humidity.

b) Systemic action

After a growth period of 3 weeks, tomato plants are drenched with an aqueous spray mixture (0.006 % a.i., based on the volume of the soil) prepared from a wettable powder formulation of the test compound. Care is taken that the spray mixture does not come in contact with the growing parts of plants. After 48 hours, the plants are infected with a sporangia suspension of the fungus. Evaluation of fungal infestation is made after the plants have been incubated for 5 days at 20°C and 90-100°C relative humidity.

Compounds of the Tables show good activity.

Example B-3: Residual-protective action against Cercospora arachidicola on groundnut plants

Groundnut plants 10-15 cm in height are sprayed to drip point with an aqueous spray mixture (0.02 ppm a.i.) prepared from a wettable powder formulation of the test compound and infected 48 hours later with a conidia suspension of the fungus. The infected plants are incubated for 72 hours at c. 21°C and high humidity and then stood in a greenhouse until the typical leaf specks occur. Evaluation of the fungicidal action is made 12 days after infection and is based on the number and size of the specks.
Compounds of the Tables show good activity.

Example B-4: Action against Plasmopara viticola on vines

Vine seedlings in the 4- to 5-leaf stage are sprayed to drip point with an aqueous spray mixture (0.02 ppm a.i.) prepared from a wettable powder formulation of the test compound and infected 24 hours later with a sporangia suspension of the fungus. Evaluation of fungal infestation is made after the plants have been incubated for 6 days at 20°C and 95-100°C relative humidity.
Compounds of the Tables show good activity.

Example B-5: Action against Colletotrichum lagenarium on cucumbers

Cucumber plants are sprayed with an aqueous spray mixture (0.002 ppm a.i.) prepared from a wettable powder formulation of the test compound and infected 2 days later with a spore suspension ($1.5x10^5$ spores/ml) of the fungus and incubated for 36 hours at 23°C and high humidity Incubation is then continued at normal humidity and c. 22°C. Evaluation of fungal infestation is made 8 days after infection.
Compounds of the Tables show good activity.

Example B-6: Residual protective action against Venturia inaequalis on apple shoots

Apple cuttings with 10-20 cm long fresh shoots are sprayed to drip point with a spray mixture (0.02 % a.i.) prepared from a wettable powder formulation of the test compound. The plants are infected 24 hours later with a conidia suspension of the fungus. The plants are then incubated for 5 days at 90-100 % relative humidity and stood in a greenhouse for a further 10 days at 20-24°C. Scab infestation is evaluated 12 days after infection.
Compounds of the Tables show good activity.

Example B7: Action against Erysiphe graminis on barley

a) Residual protective action

Barley plants about 8 cm in height are sprayed to drip point with a spray mixture (0.02 % a.i.) prepared from a wettable powder formulation of the test compound and the treated plants are dusted with conidia of the fungus 3 to 4 hours later. The infected plants are stood in a greenhouse at c. 22°C and fungus infestation is evaluated 10 days after infection. Compounds of the Tables show good activity.

b) Systemic action

Barley plants about 8 cm in height are drenched with an aqueous spray mixture (0.002 % a.i., based on the volume of the soil) prepared from a wettable powder formulation of the test compound. Care is taken that the spray mixture does not come in contact with the growing parts of the plants. The treated plants are dusted 48 hours later with conidia of the fungus. The infected plants are then stood in a greenhouse at c. 22°C and evaluation of infestation is made 12 days after infection.

Compounds of the Tables show good activity.

Example B8: Action against Podosphaera leucotricha on apple shoots

Apple cuttings with c. 15 cm fresh shoots are sprayed with a spray mixture (0.06 % a.i.) of the test compound. The plants are infected 24 hours later with a conidia suspension of the fungus and then stood in a humidity chamber at 70 % relative humidity at 20°C. Fungus infestation is evaluated 12 days after infection.

Compounds of the Tables show good activity.

Biological Examples: B. Insecticidal activity

Example B-9: Action against Nilaparvata lugens

Rice plants are treated with an aqueous emulsion spray formulation containing the test compound in a concentration of 400 ppm. When the spray coating has dried, the rice plants are populated with cicada larvae in the 2nd and 3rd stage. Evaluation is made 21 days later. The percentage reduction in the population (percentage kill) is determined by comparing the number of surviving cicadas on the treated plants with those on the untreated plants.

The compounds of the Tables effect a more than 90 % kill.

Example B-10: Action against Plutella xylostella caterpillars

Young cabbage plants are sprayed with an aqueous emulsion spray formulation containing the test compound in a concentration of 400 ppm. When the spray coating has dried, the cabbage plants are populated with 10 caterpillars of Plutella xylostella in the 3rd stage and placed in a plastic container. Evaluation is made 3 days later. The percentage reduction of the population and of feeding damage (percentage kill) is determined by comparing the number of dead caterpillars and the feeding damage on the treated plants with those on the untreated plants.

Compounds of the Tables show good activity.

Example B-11: Action against Musca domestica

A sugar lump is moistened with a solution of the test compound such that, after drying overnight, the concentration of test compound in the sugar is 250 ppm. The treated sugar lump is placed in an aluminium dish together with a most cotton wool swab and 10 adult Musca domestica of an OP-resistent strain. The dish is then covered with a glass beaker and incubated at 25°C. The mortality rate is determined 24 hours later.

Compounds of the Tables show good activity.

Biological Examples C: Acaracidal activity

Example B-12: Action against Tetranychus urticae

Young bean plants are populated with a mixed population of Tetranychus urticae and sprayed 1 day later with an aqueous emulsion spray formulation containing 400 ppm of test compound. The plants are then incubated for 6 days at 25°C and afterwards evaluated. The percentage reduction in the population (percentage kill) is determined by comparing the number of dead eggs, larvae and adults on the treated plants with those on the untreated plants.

Compounds of the Tables show good activity.

Example B-13: Action against a mixed population of Tetranychus cinnabarinus

Dilution series

Dwarf beans in the 2-leaf stage are populated with a mixed population (eggs, larvae/nymphs, adults) of an OP-tolerant strain of Tetranychus cinnabarinus. The test compounds are sprayed on to the plants 24 hours after infection at rates of 200, 100, 50 mg a.i./litre in an automatic spray cabinet. The test compounds are formulated and diluted with water to the appropriate concentrations. The test is evaluated for the percentage kill

of
- eggs
- larvae/nymphs
- adults

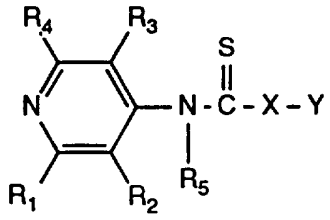
2 and 7 days after application.
Compounds of the Tables effect over 70 % kill in dilutions up to 50 mg a.i./litre.

Example B-14: Action against Boophilus microplus

Replete adult female ticks are fixed with adhesive tape to a PVC sheet and covered with a cotton wool swab. The test organisms are then treated by impregnating the cotton wool swab with 10 ml of an aqueous solution containing the test compound in a concentration of 125 ppm. The cotton wool swab is then removed and the ticks are incubated for 4 weeks for oviposition. The action is observed as kill or sterility of the females or takes the form of ovicidal action against the eggs.

What is claimed is

1. A compound of formula I



I,

wherein:

$R_1$ and $R_2$ are each independently of the other $C_1$-$C_6$alkyl, halo-$C_1$-$C_6$alkyl containing 1-5 halogen atoms, $C_1$-$C_2$alkoxy-$C_1$-$C_6$alkyl, nitro-$C_1$-$C_6$alkyl, cyano-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanoyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkoxycarbonyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkylthio-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanesulfinyl-$C_1$-$C_6$alkyl, $C_1$-$C_2$alkanesulfonyl-$C_1$-$C_6$alkyl, $C_2$-$C_6$alkenyl, halo-$C_2$-$C_6$alkenyl containing 1-5 halogen atoms, $C_2$-$C_6$alkynyl, halo-$C_2$-$C_6$alkynyl containing 1-5 halogen atoms, $C_3$-$C_7$cycloalkyl or halogen; or

$R_1$ and $R_2$, taken together, form a saturated or unsaturated 5- to 7-membered unsubstituted or substituted carbocyclic or heterocyclic ring which may contain one or two hetero atoms selected from O and S;

$R_3$ and $R_4$ are each independently of the other hydrogen, $C_1$-$C_6$alkyl or halogen;

$R_5$ is hydrogen, $C_1$-$C_6$alkyl which is unsubstituted or substituted by cyano, nitro, halogen, carboxyl, $C_1$-$C_2$alkoxycarbonyl, $C_1$-$C_2$alkanoyl, $C_1$-$C_2$alkanesulfonyl or phenylsulfonyl, $C_2$-$C_6$alkenyl, $C_2$-$C_6$alkynyl or benzyl;

X is $(CH_2)_n$, CH=CH, or C≡C;

Y is an unsubstituted or substituted 5-8-membered carbocyclic or heterocyclic ring which can be saturated or unsaturated, aromatic or nonaromatic and which may contain 1 or 2 hetero atoms selected from O, S and/or N and to which a further aromatic group can be fused;

n is 1,2,3 or 4;

or a tautomer thereof, in the free form or in the form of a salt.

2. A compound according to claim 1, wherein:

$R_1$ and $R_2$ are each independently of the other $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl, nitro-$C_1$-$C_4$alkyl, cyano-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkanoyl-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkoxycarbonyl-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkylthio-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkanesulfinyl-$C_1$-$C_4$alkyl, $C_1$-$C_2$alkanesulfonyl-$C_1$-$C_4$alkyl, $C_2$-$C_4$alkenyl, halo-$C_2$-$C_4$alkenyl of 1, 2 or 3 haloatoms, $C_2$-$C_4$alkynyl, halo-$C_2$-$C_4$alkynyl of 1, 2 or 3 haloatoms, $C_3$-$C_7$cycloalkyl or halogen; or
$R_1$ and $R_2$, taken together, form a saturated or unsaturated 5-7-membered unsubstituted or substituted carbocyclic or heterocyclic ring which may contain one or two hetero atoms selected from O and/or S;
$R_3$ and $R_4$ are each independently of the other hydrogen, $C_1$-$C_6$alkyl or halogen;
$R_5$ is hydrogen or $C_1$-$C_4$alkyl;
and wherein
X, Y and n have the given meanings.

3. A compound according to claim 1, wherein:
$R_5$ is hydrogen, $C_1$-$C_6$alkyl or benzyl.

4. A compound according to claim 2, wherein:
$R_1$ is $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl or $C_3$-$C_7$cycloalkyl;
$R_2$ is halogen;
$R_3$ and $R_4$ are hydrogen;
$R_5$ is hydrogen or $C_1$-$C_4$alkyl;
and wherein
X, Y and n have the given meanings.

5. A compound according to claim 1, wherein:
Y is phenyl or pyridine, each of which is unsubstituted or substituted and to which a further aromatic group can be fused.

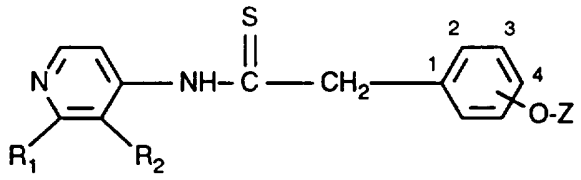
6. A compound according to claim 5, wherein:
Y is phenyl which is substituted by an unsubstituted or substituted aryloxy group.

7. A compound according to claim 6, wherein:
Y is phenoxy-substituted phenyl, which phenoxy group is unsubstituted or substituted by $C_1$-$C_4$alkyl, $C_1$-$C_4$alkoxy, halo-$C_1$-$C_2$alkyl containing 1-4 haloatom, halo-$C_1$-$C_2$alkoxy containing 1-4 haloatoms, halogen or cyano.

8. A compound according to claim 1, wherein:
Y is naphthyl, tetrahydronaphthyl, indanyl, indenyl, quinolinyl, isoquinolinyl, quinoxalinyl, quinazolinyl, tetrahydroquinolinyl, indolyl, indolinyl, chromanyl, benzodioxyl, benzofuryl, benzodioxolyl, benzothienyl, benzodithianyl, benzothiophene, 2,3-dihydrobenzothiophenyl.

9. A compound according to claim 1, wherein:
X is $CH_2$, $CH_2$-$CH_2$ or CH=CH.

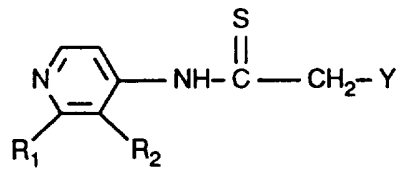
10. A compound according to claim 1, of formula I.1



I.1,

wherein:
$R_1$ is $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl or $C_3$-$C_7$cycloalkyl;
$R_2$ is halogen;
Z is phenyl, naphthyl, pyridyl or quinolyl, which aromatic groups are unsubstituted or substituted by $C_1$-$C_4$alkyl, trifluoromethyl, halogen or cyano.

11. A compound according to claim 1, of formula I.2

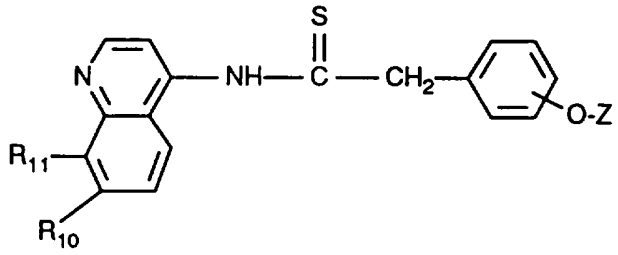


I.2,

wherein:
$R_1$ is $C_1$-$C_4$alkyl, halo-$C_1$-$C_4$alkyl containing 1-5 haloatoms, $C_1$-$C_2$alkoxy-$C_1$-$C_4$alkyl or $C_3$-$C_7$cycloalkyl;
$R_2$ is halogen;
Y is naphthyl, tetrahydronaphthyl, indanyl, indenyl, quinolinyl, isoquinolinyl,

quinoxalinyl, quinazolinyl, tetrahydroquinolinyl, indolyl, indolinyl, chromanyl, benzodioxyl, benzofuryl, benzodioxolyl, benzothienyl, benzodithianyl, benzothiophene, 2,3-dihydrobenzothiophenyl.

12. A compound according to claim 1 of formula I.9



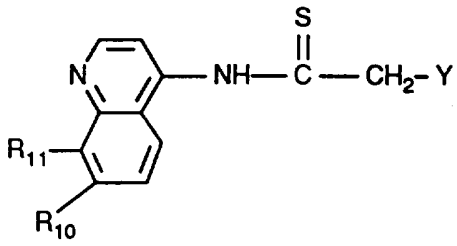
I.9,

wherein:

$R_{10}$ and $R_{11}$ are each independently of the other hydrogen or halogen;

Z is phenyl which is unsubstituted or substituted by $C_1$-$C_4$alkyl, trifluoromethyl, halogen or cyano.

13. A compound according to claim 1 of formula I.10



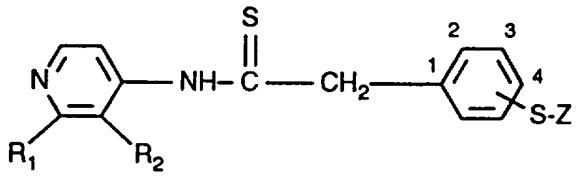
I.10,

wherein:

$R_{10}$ and $R_{11}$ are each independently of the other hydrogen or halogen;

Y is naphthyl, tetrahydronaphthyl, indanyl, indenyl, quinolinyl, isoquinolinyl, quinoxalinyl, quinazolinyl, tetrahydroquinolinyl, indolyl, indolinyl, chromanyl, benzodioxyl, benzofuryl, benzodioxolyl, benzothienyl, benzodithianyl, benzothiophene, 2,3-dihydrobenzothiophenyl.

14. A compound according to claim 1 of formula I.11



I.11,

wherein:

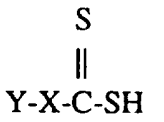
$R_1$ is methyl or ethyl;

$R_2$ is chloro;

Z is phenyl which is unsubstituted or substituted by one or two halogen atoms.

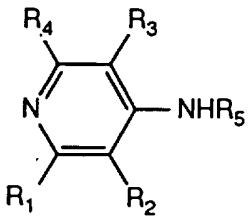
15. A process for the preparation of a compound of formula I according to claim 1, which comprises reacting

a) a dithiocarboxylic acid of formula II



II

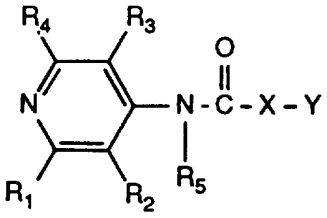
or the acid halide thereof, wherein X and Y are as defined for formula I, with a compound of formula III



III,

wherein $R_1$ to $R_5$ have the meanings given for formula I, in the absence or in the presence of a suitable condensing agent and/or a base, to give a compound of formula I; or

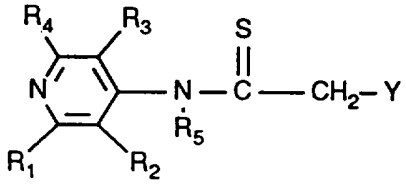
b) reacting a compound of formula IV



IV,

wherein $R_1$ to $R_5$, X and Y have the meanings given for formula I, with a thionating agent, typically with phosphorus pentasulfide or 4-methoxyphenylthiophosphoric acid cyclodithioanhydride ("Lawesson reagent").

16. A process for the preparation of a compound of formula I.2a

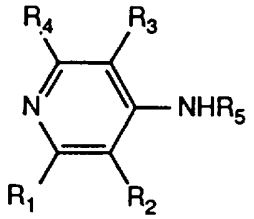


I.2a,

wherein $R_1$ to $R_5$ have the meanings given for formula I, and Y is an aromatic group, which comprises reacting a compound of formula V

$$Y\text{-}CO\text{-}CH_3 \qquad V,$$

wherein Y is an aromatic group, with a compound of formula III



III

in the presence of sulfur or ammonium polysulfide solution.

17. A composition for controlling and preventing pests, which comprises as active ingredient a compound as claimed in claim 1, together with a suitable carrier.

18. A method of controlling and preventing pests, which comprises applying a compound

as claimed in claim 1 to the pests or to the locus thereof.

19. A method according to claim 18, wherein the pests to be controlled and prevented are phytopathogenic microorganisms.

20. A method according to claim 19, wherein the microorganisms to be controlled and prevented are fungi.

21. A method according to claim 18, wherein the pests to be controlled and prevented are insects or acarina.

22. A method according to claim 18, wherein seeds are treated.

23. Seeds treated by the method as claimed in claim 22.

# INTERNATIONAL SEARCH REPORT

Inte. onal Application No
PCT/EP 95/04176

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D213/75 A61K31/44 C07D401/12 C07D409/12 C07D405/12 C07D413/12

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)
IPC 6 C07D A61K

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)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | WO-A-93 04580 (DOWELANCO) 18 March 1993 cited in the application see page 15 - page 18; claim 1 --- | 1-23 |
| P,A | WO-A-95 07891 (HOECHST SCHERING AGREVO) 23 March 1995 see claim 1 --- | 1-23 |
| P,A | WO-A-95 07890 (HOECHST SCHERING AGREVO) 23 March 1995 see claim 1 --- | 1-23 |
| A | EP-A-0 497 564 (RHONE-POULENC RORER LTD.) 5 August 1992 see page 2, line 30 - page 3, line 50; claim 1 ----- | 1-23 |

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 4 March 1996 | 14.03.96 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax (+ 31-70) 340-3016 | Gettins, M |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int onal Application No
PCT/EP 95/04176

| Patent document cited in search report | Publication date | Patent family member(s) | | Publication date |
|---|---|---|---|---|
| WO-A-9304580 | 18-03-93 | AU-B- | 662017 | 17-08-95 |
| | | AU-B- | 2641892 | 05-04-93 |
| | | AU-B- | 659498 | 18-05-95 |
| | | AU-B- | 2643092 | 05-04-93 |
| | | BR-A- | 9205385 | 08-03-94 |
| | | BR-A- | 9205386 | 08-03-94 |
| | | CA-A- | 2094907 | 04-03-93 |
| | | CA-A- | 2095332 | 04-03-93 |
| | | EP-A- | 0555469 | 18-08-93 |
| | | EP-A- | 0556381 | 25-08-93 |
| | | HU-A- | 68647 | 28-07-95 |
| | | JP-A- | 5221990 | 31-08-93 |
| | | JP-T- | 6501715 | 24-02-94 |
| | | PL-A- | 299184 | 05-04-94 |
| | | WO-A- | 9305050 | 18-03-93 |
| | | US-A- | 5399564 | 21-03-95 |
| WO-A-9507891 | 23-03-95 | DE-A- | 4331179 | 16-03-95 |
| | | AU-B- | 7615294 | 03-04-95 |
| WO-A-9507890 | 23-03-95 | DE-A- | 4331181 | 16-03-95 |
| | | AU-B- | 7615194 | 03-04-95 |
| EP-A-497564 | 05-08-92 | AT-T- | 132134 | 15-01-96 |
| | | AU-B- | 664694 | 30-11-95 |
| | | AU-B- | 1188192 | 27-08-92 |
| | | CA-A- | 2101423 | 29-07-92 |
| | | CZ-A- | 9301528 | 13-04-94 |
| | | DE-D- | 69207017 | 08-02-96 |
| | | EP-A- | 0569414 | 18-11-93 |
| | | EP-A- | 0669311 | 30-08-95 |
| | | WO-A- | 9212961 | 06-08-92 |
| | | HU-A- | 64942 | 28-03-94 |
| | | JP-T- | 6504782 | 02-06-94 |
| | | NZ-A- | 241427 | 26-08-94 |
| | | SK-A- | 80993 | 08-12-93 |
| | | ZA-A- | 9200547 | 03-05-93 |