

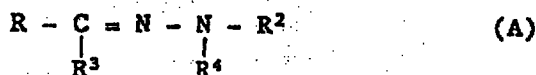
Description

The invention relates to novel substituted semicarbazones, thiosemicarbazones and isothiosemicarbazones, the synthesis thereof, the use of said compounds for the control of weeds, and compositions for weed control comprising such compounds.

EPA 0 034 010 discloses 2-formylbenzoic acid thiosemicarbazones and the use of such compounds as plant growth regulants.

US Patent 3,753,680 discloses phenyl-CR=NR₁-C(Z)-NR₂R₃ compounds, which may be substituted in the phenyl ring and wherein R is H or lower alkyl, that have herbicidal activity.

The compounds of the present invention are represented by the following formula (A) :



wherein R is phenyl or naphthyl, or is a heteroaromatic ring selected from

a) pyridyl which may be fused by its [b] or [c]-side with a benzene ring,

b) 2-pyridyl-N-oxide or 2-pyrazinyl-N'-oxide,

c) pyrimidinyl,

d) pyrazinyl,

e) 3- or 4-cinnolinyl or 2-quinoxaliny and

f) a five-membered heteroaromatic ring bound by one of its ring C-atoms to the CR³-group selected from thienyl, furanyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl or pyrazolyl ; whereby said five-membered heteroaromatic ring may be fused by its [b]-side with a benzene ring ;

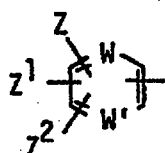
which group R is ortho-substituted by the group R' and additionally bears one further substituent Y, both R' and Y being attached to a ring carbon atom ;

R' is the carboxy group in free form, salt form or ester form or is the group CO-SR⁶ or CO-NR⁷R⁸,

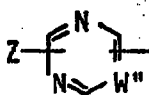
Y is H, C₁₋₈alkyl, C₁₋₈haloalkyl, C₁₋₈alkoxy, C₁₋₈haloalkoxy, C₂₋₈alkenyloxy, C₂₋₈haloalkenyloxy, C₂₋₈alkynioxy, phenyl, phenoxy, C₁₋₈alkylthio, OH, halogen, nitro or cyano ;

R² is the group -C(=NR¹⁰)-SR⁹ or -C(=X)-NHR¹⁰, each of R³, R⁴, R⁷ and R⁸ is independently hydrogen or C₁₋₈alkyl ; each of R⁶ and R⁹ is independently C₁₋₈alkyl,

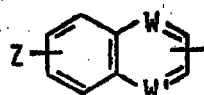
R¹⁰ is one of the groups



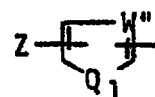
(G-1) ,



(G-2) ,



(G-3)



or (G-4)

each of W, W' and W'' is independently N or CH

Q₁ is oxygen, sulfur or NH

X is oxygen or sulfur

each of Z, Z¹ and Z² is independently one of the significances specified for - but independent of - Y, with the proviso that when R is phenyl mono-substituted in ortho by the carboxy group in free form or in salt form or by C₁₋₈alkoxy-carbonyl, then R³ is C₁₋₈alkyl.

Where R' is the carboxyl group in salt form, its cation is, for example, the cation of an alkali metal (e.g. the Li or Na cation) or of an earth alkali metal ; the ammonium cation ; a substituted ammonium cation (such as a C₁₋₈alkylammonium cation, a di-C₁₋₈alkylammonium cation, a tri-C₁₋₈alkylammonium cation, a tetra-C₁₋₈alkylammonium cation, a (C₁₋₈alkoxy-alkyl)ammonium cation, a (hydroxy-C₁₋₈alkoxy-C₁₋₈alkyl)ammonium cation, a (hydroxy-C₁₋₈alkyl)ammonium cation) ; a phosphonium cation ; a tri(C₁₋₈alkyl)sulfonium cation or a tri(C₁₋₈alkyl)sulfoxonium cation.

Where R' is a carboxyl ester group (hereinafter COOR⁵), then R⁵ is for example C₁₋₈alkyl, C₁₋₈haloalkyl, C₂₋₁₀alkoxyalkyl, or CH(R¹¹)O-C(=X')-R¹², wherein X' is O or S, and R¹¹ and R¹² are, independently, H or C₁₋₈alkyl.

Where any of R³, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², Y, Z, Z¹, Z² or the cation of the carboxyl group R' is or comprises C₁₋₈alkyl, such alkyl group or moiety comprises preferably C₁₋₆, more preferably C₁₋₄ e.g. 1 or 2

carbon atoms.

R¹² is preferably C₁₋₈alkyl.

The terms C₂₋₈alkenyl-O and C₂₋₈alkynyl-O when used herein refer to C₂₋₈hydrocarbyloxy groups having 1 or 2, preferably 1, ethylenic bonds or 1 or 2, preferably 1, acetylenic bonds resp.

The terms C₁₋₈haloalkyl, C₁₋₈haloalkoxy and C₂₋₈haloalkenyloxy refer to C₁₋₈alkyl, C₁₋₈alkoxy and C₁₋₈alkenyloxy resp. substituted by one to six, particularly 1 to 3 halogen; such halogen is preferably Cl or F.

It will be appreciated that heteroaromatic groups R which cannot be substituted at a ring carbon atom in ortho position relative to the bond by which R is tied to the CR³ group of formula (A) are excluded by the above definition of R.

It will further be appreciated that, also by definition, whenever R is a bicyclic ring system comprising a benzene ring and a heteroring, said group R is tied directly to the CR³ group of formula (A) through a carbon ring atom of the heteroring moiety (i.e. not of the benzene moiety).

Where R has one of the above defined heteroaromatic significances, the substituted heteroring is particularly selected from pyridyl, quinolyl, 2-pyridyl-N-oxide, pyrimidinyl, pyrazinyl, thienyl or furyl, more particularly from pyridyl (4-, 3- or 2-pyridyl, preferably the latter) or thienyl (2- or 3-thienyl).

Where R is substituted by Y, the substituent is particularly halogen, C₁₋₆alkyl, C₁₋₆alkoxy or phenyl.

R' is preferably the carboxy group in free form, salt form or ester form.

A preferred significance of R⁵ is CH(R¹¹)-O-CO-C₁₋₈alkyl.

R⁷ and R⁸ are preferably C₁₋₈alkyl.

R² is preferably C(X)-NHR¹⁰, more preferably CO-NHR¹⁰.

R³ is preferably C₁₋₈alkyl.

R¹⁰ is preferably phenyl or pyridyl, which groups are conveniently unsubstituted or mono- or disubstituted.

Each of Y and Z conveniently signify independently H, halogen (F, Cl, Br, I), C₁₋₆alkyl, C₁₋₆alkoxy, CF₃, phenoxy, phenyl, nitro, cyano or hydroxy

Z¹ signifies conveniently H, halogen or C₁₋₆alkoxy.

Z² is preferably H.

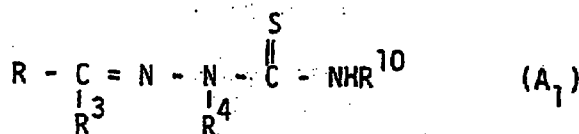
The compounds of formula (A) are obtained by
a) reacting a compound of formula I



wherein R and R³ are as defined above with a compound of formula II



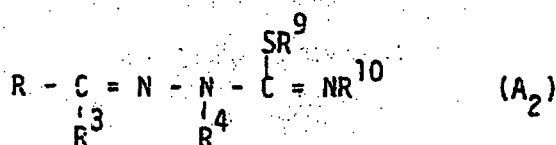
wherein R² and R⁴ are as defined above, followed, where desired, by esterifying compounds of formula (A) wherein R' is the carboxyl group to compounds (A) wherein R' is a carboxyl-ester group, or
b) S-alkylating a compound of formula A₁



wherein R, R³, R⁴ and R¹⁰ are as defined above, with an alkylhalogenide of formula III



wherein R⁹ is as defined above and Hal is halogen, or a reactive functional derivative of said compound of formula III to give a compound of formula (A₂)



wherein R, R³, R⁴, R⁹, and R¹⁰ are as defined above.

The reaction of compounds of formula (I) with compounds of formula (II) may be effected under the conditions known for the preparation of (thio)semicarbazones starting from the corresponding (thio)carbazides.

The reaction is conveniently carried out in a solvent which is inert under the reaction conditions, e.g. in an alcohol such as methanol or ethanol. An acid catalyst such as pyridyl tosylate may be added to promote the reaction. A suitable reaction temperature is room temperature or moderately enhanced temperature (e.g. between 10 and 40°C).

Compounds of formula (A) wherein R' is COOR⁵ may also be, and are in general preferably obtained by esterification of the corresponding compounds of formula (A) wherein R' is the carboxyl group, in free form or in salt form, e.g. alkali metal salt form, using the desired esterification agent. Suitable esterification agents are alkylating agents such as R⁵-halogenides, R⁵-mesylates and R⁵-tosylates or reactive functional derivatives thereof such as CH₂N₂.

The S-alkylation of thiosemicarbazones of formula (A₁) may be effected under the conditions known for the preparation of isothiosemicarbazones from thiosemicarbazones. In general, the reaction is carried out in a solvent which is inert under the reaction conditions, e.g. dimethylformamide. The compound of formula III is conveniently used as an iodide. It is in general advantageous to work in the presence of an acid binding agent, such as potassium carbonate. The R' group may partially or completely be esterified or its eventual R⁵ group interchanged, depending on the particular reaction conditions employed. Hydrolysis of such ester group followed, where desired, by treatment with an esterification (e.g. alkylation) agent for the introduction of the selected group R⁵, will then result in the desired compound of formula (A₂).

Compounds of formula (A) wherein R' is carboxyl may be converted to the corresponding salts in conventional manner and vice versa.

The compounds of formula (A) may be recovered from the reaction mixture in which they are formed by working up by established procedures.

The compounds of formula (A) may exist in either the syn or the anti form, although the anti form usually predominates.

The isothiosemicarbazones of the invention (see formula (A₂)) wherein R⁴ is hydrogen may also exist in the corresponding isomeric form



The starting materials and reagents employed in the process described herein are either known or, insofar as they are not known, may be produced in a manner analogous to the process described herein or to known processes.

The compounds of formula (A) have herbicidal activity as observed after their pre-emergent or post-emergent application to weeds or a weed locus.

The term "herbicide" (or "herbicidal") refers to an active ingredient (or an effect) which modifies the growth of plants because of plant growth regulating or phytotoxic properties so as to retard the growth of the plant or damage the plant sufficiently to kill it.

Application of a compound of formula (A) is made according to conventional procedure to the weeds or their locus using a herbicidally effective amount of the compound, usually from 100 g to 10 kg/ha.

The optimum usage of a compound of formula (A) is readily determined by one of ordinary skill in the art using routine testing such as green-house testing and small plot testing. It will depend on the compound employed, the desired effect (a phytotoxic effect requiring a higher rate than a plant growth regulating effect), the conditions of treatment and the like. In general satisfactory phytotoxic effects are obtained when the compound of formula (A) is applied at a rate in the range of from 0.2 to 5.0 kg, more preferably of from 0.25 to 2.5 kg per hectare.

While some of the compounds of formula (A), have activity on grass weeds, they demonstrate, in general, a higher level of herbicidal activity on broadleaf plants when applied post-emergence. Broadleaf plant (weed) species on which the compounds of the present invention show effective herbicidal activity include Brassica juncea, Amaranthus retroflexus, Abutilon theophrasti, Datura stramonium, Xanthium canadense, Cassia obtusifolia and Ipomoea purpurea.

When applied pre-emergence, the compounds of formula (A) demonstrate high levels of herbicidal activity on both broadleaf and grassy weeds.

The compounds of formula (A) may be advantageously combined with other herbicides for broadspectrum weed control. Examples of herbicides which can be combined with a compound of the present invention include those selected from the carbamates, thiocarbamates, chloroacetamides, dinitroanilines, benzoic acids, glycerol ethers, pyridazinones, uracils and ureas for controlling a broad spectrum of weeds.

The compounds of formula (A) are conveniently employed as herbicidal compositions in association with agriculturally acceptable diluents. Such compositions also form part of the present invention. They may contain, aside from a compound of formula (A) as active agent, other active agents, such as herbicides. They may be employed in either solid or liquid forms e.g. in the form of a wettable powder or an emulsifiable concentrate, incorporating conventional diluents. Such compositions may be produced in conventional manner, e.g. by mixing the active ingredient with a diluent and optionally other formulating ingredients such as surfactants.

The term diluents as used herein means any liquid or solid agriculturally acceptable material which may be added to the active constituent to bring it in an easier or improved applicable form, respectively to a usable or desirable strength of activity. It can for example be talc, kaolin, diatomaceous earth, xylene, or water.

Particularly formulations to be applied in spraying forms such as water dispersible concentrates or wettable powders may contain surfactants such as wetting and dispersing agents, e.g. the condensation product of formaldehyde with naphthalene sulphonate, an alkylarylsulphonate, a lignin sulphonate, a fatty alkyl sulphate, an ethoxylated alkylphenol and an ethoxylated fatty alcohol.

In general, the formulations include from 0.01 to 90% by weight of active agent and from 0 to 20% by weight of agriculturally acceptable surfactant, the active agent consisting either of at least one compound of formula (A) or mixtures thereof with other active agents. Concentrate forms of compositions generally contain between about 2 and 90%, preferably between about 5 and 70% by weight of active agent. Application forms of formulation may for example contain from 0.01 to 20% by weight of active agent.

The following examples are provided to illustrate the practice of the present invention. Temperature is given in degrees Centigrade. "RT" means room temperature. Parts and percentages are by weight. The symbols *, # and + when used in connection with melting points mean "gas", "softens" and "decomposes" resp.

COMPOSITION EXAMPLES

1. Water dispersible powder

The sodium salt or isopropylammonium salt of compound 4-A (hereinafter, Table A) are dissolved to the desired percentage concentration in water containing 0.5% surfactant (e.g. a 1 : 1 : 1 mixture of sorbitan mono-laurate : polyoxyethylene[20]sorbitane monolaurate : polyoxyethylene[20]sorbitan trioleate).

2. Suspension concentrate - 26%

26 Parts of the sodium salt of compound 30-A (Table A, hereinafter), 4 parts of propylene glycol and 1 part of octyl phenoxypoly[ethyleneoxy]ethanol are mixed and wet-milled to 5-10 micron particle size.

3. Wettable powder - 50%

50 Parts of the sodium salt of compound 30-A (Table A, hereinafter), 4 parts of sodium lignosulphonate, 1 part of sodium dialkyl-naphthalene sulphonate and 45 parts of kaolin are mixed and air-milled. The mixture is added to water for spraying.

EXAMPLE 1

To a solution of 2-acetylnicotinic acid (0.40 g, 2.4 mmol) in 7 ml of methanol is added a solution of 4-phenylsemicarbazide (0.37 g, 2.4 mmol) in 5 ml of methanol. The mixture is stirred at RT overnight, after which the solid precipitate is collected by filtration, washed with ethanol and dried to give 2-acetylnicotinic acid 4-phenylsemicarbazone, m.p. 174° (dec.) (compound 1, Table A).

EXAMPLE 2

2-Acetylbenzoic acid (0.50 g, 3.0 mmol) and 2-methyl-4-(3-trifluoromethyl)phenylsemicarbazide (0.67 g, 3.0 mmol) are dissolved together in 15 ml of ethanol. After 3 hours at RT, 50 mg of pyridyl tosylate is added. After 2 more hours, the precipitated solid is collected by filtration and dried to give 2-acetylbenzoic acid 2-methyl-4-(3-trifluoromethyl)phenylsemicarbazone, m.p. 172° (gas) (compound 2, Table A).

EXAMPLE 3

Following the procedure of either Example 1 or Example 2, each of the semicarbazone or thiosemicar-

bazone compounds 3-47 under Table A, 48-52 under Table B, 63-79 under Table C, 87-100 under Table D and 126-140 under Table E, is prepared from the corresponding semicarbazide or thiosemi- carbazide and acetyl compound.

5 **EXAMPLE 4**

To a solution of 2-acetylnicotinic acid 4-phenylsemicarbazone (0.32 g) in 5 ml of methanol is added 1 equivalent of sodium methoxide. The mixture is stirred at RT for 5 minutes, after which the solvent is removed by rotoevaporation to give the sodium salt of 2-acetylnicotinic acid 4-phenylsemicarbazone m.p. 203° (dec.).

10 Following the procedure of Example 4, each of the acids under Tables A, B, C, D and E is treated with 1 equivalent of sodium methoxide to give the corresponding sodium salt.

EXAMPLE 5

15 To 2-acetylnicotinic acid 4-phenylsemicarbazone (0.32 g) in 5 ml of methanol is added 1 equivalent of an aqueous solution of ammonium hydroxide. The mixture is stirred at RT for 5 minutes, after which the solvent is removed by rotoevaporation to give the ammonium salt of 2-acetylnicotinic acid 4-phenylsemicarbazone, m.p. 146-150° (softens) and 198-200° (gas).

20 Following the above procedure, each of the acids under Tables A, B, C, D and E is treated with 1 equivalent of aqueous ammonium hydroxide to give the corresponding ammonium salt.

EXAMPLE 6

25 Following the procedures of Example 5, using isopropylamine, 2-hydroxyethylamine or diisopropylamine, the following salts are obtained.

Of compound 1, the isopropylammonium salt, m.p. 94° (softens), 120°(gas)

Of compound 4, the isopropylammonium salt, m.p. 111-118°

Of compound 1, the 2-hydroxyethylammonium salt, m.p. 131° (gas)

Of compound 22, the 2-hydroxyethylammonium salt, m.p. 118° (gas)

30 Of compound 3, the diisopropylammonium salt, m.p. 208-210°

Of compound 4, the diisopropylammonium salt, m.p. 210-220°

(For the structure of compounds 1, 3, 4 and 22 see Table A, hereinafter).

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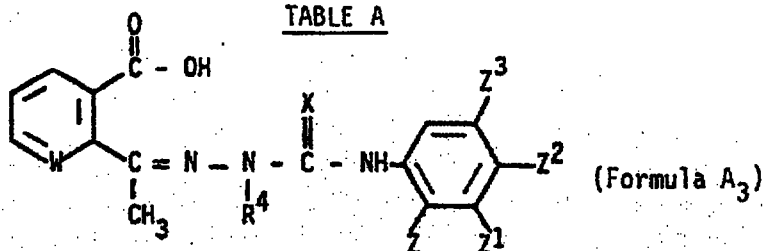
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TABLE A



Cpd. No.	W	R ⁴	X	Z	Z ¹	Z ²	Z ³	m.p. ^a		
								acid	Na salt	NH ₄ salt
1	N	H	O	H	H	H	H	174*	203	146# 200*
2	CH	CH ₃	O	H	CF ₃	H	H	172*	148*	
3	N	H	O	H	Cl	H	H	153*	205*	
4	N	H	O	H	F	H	H	159*	220# 232*	140# 200*
5	N	H	O	H	CF ₃	H	H	163-164	194*	
6	N	H	O	H	H	Cl	H	227*	213*	
7	N	H	O	Cl	H	H	H	300	131-132*	
8	N	H	O	H	Cl	Cl	H	163*	189# 201*	
9	N	H	O	H	CH ₃	H	H	166-167*	211*	192# 207*
10	N	H	O	H	H	F	H	146-149* 208-220	170# 205*	
11	N	H	O	H	OCH ₃	H	H	162-165*	197*	
12	N	H	O	F	H	H	H	162-165*	197*	
13	N	H	S	H	H	H	H	158-160		
14	N	H	S	H	Cl	H	H	114-115*	108 ⁺	
15	N	H	S	F	H	H	H	159-161*	128-130*	
16	N	H	S	H	H	F	H	173-174	159-163	
17	N	H	S	H	Cl	Cl	H	169-170	121-124*	
18	N	H	O	H	H	O-C ₆ H ₅	H	148 ⁺	211*	
19	N	CH ₃	O	H	H	H	H	98-100# 140*	147-56**	140-47
20	N	CH ₃	O	H	Cl	H	H	69# 140	118*	

TABLE A (Continued)

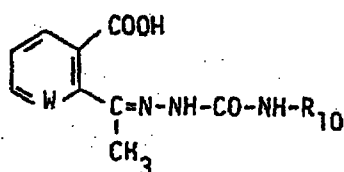
5	Cpd. No.	W	R ⁴	X	Z	Z ¹	Z ²	Z ³	m.p.*		
									acid	Na salt	NH ₄ salt
	21	N	CH ₃	O	H	F	H	H	120-130	120# 140*	
10	22	CH	H	O	H	H	H	H	174	184-86*	150**
	23	CH	H	O	H	CF ₃	H	H	164*	255	
	24	CH	H	O	H	Cl	H	H	158*	126*	87* 140-147
15	25	CH	H	O	H	F	H	H	169*	203*	
	26	CH	H	O	H	CF ₃	Cl	H	170*	173*	
	27	CH	H	S	H	H	H	H	129-131	115# 134*	
20	28	CH	CH ₃	O	H	H	H	H	177		
	29	CH	CH ₃	O	H	H	CH ₃	H	176-178*		
	30	N	H	O	H	Cl	H	Cl	193*	222*	
25	31	N	H	O	H	F	H	F	186*	240*	
	32	N	H	O	F	F	H	H	168# 202	220*	
30	33	N	H	O	Cl	Cl	H	H	168# 198	194*	
	34	N	H	O	F	H	H	F	154-157	234-235*	
	35	N	H	O	F	H	H	CH ₃	173# 203	226-227*	
35	36	N	H	O	H	OCH ₃	H	OCH ₃	185*	203	
	37	N	H	O	F	H	H	Cl	167-171*	204-206+	
	38	N	H	O	F	Cl	H	H	152-154*	200-202+	
40	39	N	H	O	H	Cl	Cl	H	163*	189#	
	40	N	H	O	H	NO ₂	H	H	190+	194-195+	
	41	N	H	S	H	CN	H	H	168-169	166#	
45	42	N	H	O	H	Br	H	H	175*	208-210*	
	43	N	H	O	H	I	H	H	174*	212*	
50	44	N	H	O	H	OH	H	H	204-210		

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TABLE A (Continued)

Cpd. No.	W	R ⁴	X	Z	Z ¹	Z ²	Z ³	m.p.	
								acid	Na salt
45	N	H	O	H	OC ₆ H ₅	H	H	164*	206*
46	N	H	O	H	C ₂ H ₅	H	H	178-80*	200* 218*
47	N	H	O	H	OnC ₄ H ₉	H	H	172-75*	207*

TABLE B

(Formula A₄)

Cpd.	W	R ₁₀	m.p.	
			acid	Na-salt
48	N	2-pyridyl	195-197°	183°
49	N	6-chloro-2-pyridyl	171-172°	190-194°
50	N	3-pyridyl	167° *	208°*
			206-208°	
51	CH	2-pyridyl	128-129°*	200°*
52	CH	3-pyridyl	152-153°	175°*

EXAMPLE 7

A suspension of 2-acetylnicotinic acid 4-phenylsemicarbazone (compound 1) (0.50 g) in 20 ml of methanol is treated with diazomethane until the yellow color of the solution persists. The solvent is removed in vacuo to give methyl 2-acetylnicotinate 4-phenylsemicarbazone, m.p. 177-178° (compound 53, Table C).

EXAMPLE 8

A mixture of the sodium salt of 2-acetylnicotinic acid 4-(3-fluorophenyl)semicarbazone (compound 4) (1.0 g, 3.0 mmol) and chloromethyl acetate (0.4 g, 3.5 mmol) in 18 ml of DMF is stirred at RT for 3 days. The reaction mixture is poured onto ice. The solid which precipitates is collected by filtration, is washed with water and is air-dried. It is stirred in 50 ml of chloroform for 2 hours and is filtered. The filtrate is evaporated to give glass

like material, which is triturated with ether to give the crude product. Purification by prep. TLC gives acetyloxymethyl 2-acetylnicotinate 4-(3-fluorophenyl)semicarbazone, m.p. 159-160° (compound 54, Table C).

EXAMPLE 9

Following the procedure of Example 8, chloromethyl butanoate, 1-chloroethyl propanat, 1-bromo-2-methyl-n-butyl acetate, methyl iodide, bromomethyl acetate, 1-chloroethyl propanate, chloromethyl butanoate and chloromethyl octanoate are reacted with the corresponding sodium salt to give compounds 55-62 and 80-86 in Table C.

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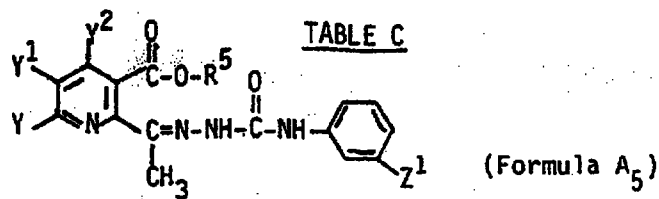
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TABLE C

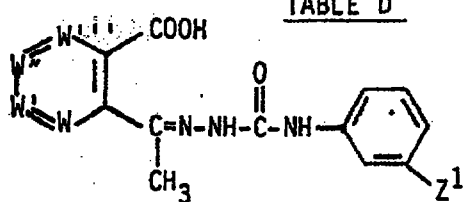


	Cpd	Y	Y ¹	Y ²	R ⁵	Z ¹	m.p.°	Na salt m.p.°
5	53	H	H	H	CH ³	H	177-178	-
10	54	H	H	H	CH ₂ -O-C(=O)-CH ₃	F	159-160	-
15	55	H	H	H	CH ₂ -O-C(=O)-CH ₂ CH ₂ CH ₃	F	108-124	-
20	56	H	H	H	CH ₃ -O-C(=O)-CH ₂ -CH ₃	F	158-164	-
25	57	H	H	H	CH ₃ CHCH ₂ CH ₃ -O-C(=O)-CH ₃	F	182-186	-
	58	H	H	H	CH ₃	F	206-214	-
30	59	H	H	H	CH ₂ -O-C(=O)-CH ₃	Cl	148-150	-
35	60	H	H	H	CH ₃ -O-C(=O)-CH ₂ CH ₃	Cl	168-170	-
40	61	H	H	H	CH ₂ -O-C(=O)-CH ₂ CH ₂ CH ₃	Cl	150-152	-
	62	H	H	H	CH ₂ -O-C(=O)-(CH ₂) ₆ CH ₃	Cl	46-47	-
45	63	OCH ₃	H	H	H	F	220-240	208*
	64	Cl	H	H	H	H	225	
	65	Cl	H	H	H	F	210-214*	200 ⁺
50	66	H	OCH ₂ CH ₃	H	H	H	141-142	
	67	H	OCH ₂ CH ₃	H	H	F	135-136	233-235

TABLE C (cont)

	Cpd	Y	Y ¹	Y ²	R ⁵	Z ¹	m.p.°	Na salt m.p.°
	68	H	Cl	H	H	Cl	163-164	>330
	69	H	Cl	H	H	F	157-159	>320
10	70	H	C ₆ H ₅	H	H	H	193-195	242-244 ⁺
	71	H	C ₆ H ₅	H	H	F	240-250	246-248 ⁺
15	72	H	H	Cl	H	H		
	73	H	H	Cl	H	F	214-215 ⁺	>320
	74	H	C ₂ H ₅	H	H	F	178*	190-193*
20	75	H	CH ₃	H	H	F	167-169*	228-230*
	76	CH ₃	H	H	H	F		
	77	C ₂ H ₅	H	H	H	F		
	78	H	H	CH ₃	H	F		
25	79	H	H	C ₂ H ₅	H	F		
	80	OCH ₃	H	H	CH ₂ -O-C(=O)-CH ₂ CH ₂ CH ₃	F		-
30	81	Cl	H	H	CH ₂ -O-C(=O)-CH ₂ CH ₂ CH ₃	F	118-120	-
	82	H	OCH ₂ CH ₃	H	CH ₂ -O-C(=O)-CH ₂ CH ₂ CH ₃	F	150-152	-
35	83	H	Cl	H	CH ₂ -O-C(=O)-CH ₂ CH ₃ CH ₃	F	160-163	-
40	84	H	C ₆ H ₅	H	CH ₂ -O-C(=O)-CH ₂ CH ₂ CH ₃	F	197-198	-
	85	H	H	H	CH ₂ -O-CO-C(CH ₃) ₃	F	173-175°	-
45	86	H	H	H	CH ₂ -O-CO-nC ₃ H ₇	C ₂ H ₅	103-105°	-
50								
55								

TABLE D

(Formula A₆)

10	Cpd. No.	W	W'	W''	W'''	Z ¹	m.p. °	
							acid	Na salt
	87	CH	CH	CH	N	H	160-162 ⁺	
15	88	CH	CH	CH	N	F	125-133*	198-199 ⁺
	89	CH	N	CH	CH	H	230-245	
	90	CH	N	CH	CH	F		
20	91	CH	CH	N	CH	H	180-182 ⁺	
	92	CH	CH	N	CH	F		
	93	CH	N	C-Cl	N	H	165-167	230-240*
25	94	CH	N	C-Cl	N	F		
	95	CH	N	CH	N	H	194-195*	214-216*
30	96	CH	N	CH	N	F		
	97	N	CH	N	CH	H	196-198*	207-208 ⁺
	98	N	CH	N	CH	F		
35	99	N	CH	CH	N	H	164-169 ⁺	
	100	N	CH	CH	N	F		

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EXAMPLE 10

Following the procedure of Example 2 an acetyl-quinoline carboxylic acid is reacted with a semicarbazide to give

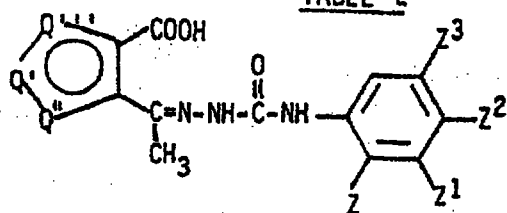
- 5 2-acetyl-3-quinolinecarboxylic acid 4-phenylsemicarbazone, m.p. 234-236° (compound 101), its Na-salt having a m.p. of 224-225° (gas)
3-acetyl-2-quinolinecarboxylic acid 4-phenylsemicarbazone, m.p. 243° (gas) (compound 102), its Na-salt having a m.p. of 300°;
10 3-acetyl-4-quinolinecarboxylic acid 4-phenylsemicarbazone, m.p. 251° (dec.) (compound 103), its Na-salt having a m.p. of 300°;
3-acetyl-4-quinolinecarboxylic acid 4-(3-chlorophenyl)semicarbazone, m.p. 229° (compound 104), both its Na-salt and isopropylammonium salt having a m.p. of 300°.

EXAMPLE 11

15 To a stirred solution of 2-acetyl-3-thiophenecarboxylic acid (1.70 g, 10.0 mmol) in 15 ml of dry methanol is added, all at once, 4-phenylsemicarbazide (1.51 g, 10.0 mmol) in 25 ml of dry methanol. Stirring is continued for 18 hours, after which the precipitate is filtered off, washed with diethyl ether and dried to give 2-acetyl-3-thiophenecarboxylic acid 4-phenylsemicarbazone, m.p. 238° (compound 105, Table E).

20 Compounds 106-125 (Table E) are obtained following the same procedure.

TABLE E

(Formula A₇)

	Cpd. No.	Q'	Q''	Q'''	Z	Z ¹	Z ²	Z ³	m.p. °	
									acid	Na salt
10	105	CH	S	CH	H	H	H	H	238	270
	106	CH	S	CH	Cl	H	H	H	235	>290
15	107	CH	S	CH	H	Cl	H	H	258	
	108	CH	S	CH	H	H	Cl	H	240	203
	109	CH	S	CH	H	Cl	H	Cl	210	240-244*
20	110	CH	S	CH	H	F	H	H	252	222
	111	CH	S	CH	H	H	F	H	260	>280
	112	CH	S	CH	H	OCH ₃	H	H	262	>280
25	113	CH	CH	S	H	H	H	H	258	223
	114	CH	CH	S	Cl	H	H	H	256	201-209*
30	115	CH	CH	S	H	Cl	H	H	249	192-203
	116	CH	CH	S	H	H	Cl	H	251	242
	117	CH	CH	S	H	Cl	H	Cl	216	242-246
35	118	CH	CH	S	H	F	H	H	255	239-242
	119	CH	CH	S	H	H	F	H	261	235-239
	120	CH	CH	S	H	OCH ₃	H	H	253	225
40	121	S	CH	CH	H	H	H	H	170-171	232-233
	122	S	CH	CH	H	Cl	H	H	174-175	223-224
	123	S	CH	CH	H	Cl	H	Cl	207-208	210 ⁺
45	124	S	CH	CH	H	F	H	H	174-176	218-220 ⁺
	125	S	CH	CH	H	F	H	F	194-195	227-229

50

55

TABLE E (cont.)

5	Cpd. No.	Q'	Q''	Q'''	Z	Z ¹	Z ²	Z ³	m.p. ^o	
									acid	Na salt
	126	CH	O	CH	H	H	H	H	240	210 ⁺
10	127	CH	O	CH	H	Cl	H	H	256	235 ⁺
	128	CH	O	CH	H	Cl	H	Cl		
15	129	CH	O	CH	H	F	H	H	253	225 ⁺
	130	CH	O	CH	H	F	H	F		
	131	CH	CH	O	H	H	H	H		
20	132	CH	CH	O	H	Cl	H	H		
	133	CH	CH	O	H	Cl	H	Cl		
	134	CH	CH	O	H	F	H	H		
25	135	CH	CH	O	H	F	H	F		
	136	O	CH	CH	H	H	H	H		
30	137	O	CH	CH	H	Cl	H	H		
	138	O	CH	CH	H	Cl	H	Cl		
	139	O	CH	CH	H	F	H	H		
35	140	O	CH	CH	H	F	H	F		

EXAMPLE 12

To a suspension of 2-acetyl-3-nicotinic acid N-oxide (2.5 g, 13.8 mmol) in 40 ml of ethanol is added 4-phenylsemicarbazide (2.1 g, 13.8 mmol). The mixture is stirred at 40° overnight, after which the solvent is removed and the product purified to give 2-acetyl-3-nicotinic acid N-oxide 4-phenylsemicarbazone, m.p. 218° (dec.) (compound 141); its Na-salt melts at 128-133°, its NH₄-salt softens at 137° and enters the gas phase at 155°.

EXAMPLE 13

Following the procedure of Example 12 2-acetyl-3-nicotinic acid N-oxide 2-methyl-4-phenylsemicarbazone, m.p. 55° (softens), 65° (melts) (compound 142) is obtained.

EXAMPLE 14

A mixture of N,N-diethyl 2-acetyl-3-nicotinamide (0.45 g, 2.0 mmol) and 4-phenylsemicarbazide (0.31 g, 2.0 mmol) in 10 ml of acetic acid is stirred at RT overnight. The solvent is then removed by rotoevaporation, and the residue is triturated with methanol. The solid is collected by filtration and is dried to give N,N-diethyl-2-acetyl-3-nicotinamide 4-phenylsemicarbazone, m.p. 241-243° (compound 143).

EXAMPLE 15

Following the procedures of Example 14, each of 4-(3-fluorophenyl)semicarbazide and 4-(3-chlorophenyl)semicarbazide is reacted with N,N-diethyl 2-acetyl-3-nicotinamide to give N,N-diethyl 2-acetyl-3-nicotinamide 4-(3-fluorophenyl)semicarbazone (compound 144) and N,N-diethyl 2-acetyl-3-nicotinamide 4-(3-chlorophenyl)semicarbazone (compound 145) resp.

EXAMPLE 16

A solution of ethyl 2-methylnicotinate (2.0 g, 12.12 mmol), selenium dioxide (20.0 g, 18.18 mmol) and dioxane (10 ml) is heated at 135° for 4 hours. The reaction mixture is filtered and the filtrate is concentrated and purified by prep. TLC to give ethyl 2-formylnicotinate.

Ethyl 2-formylnicotinate (1.0 g, 5.58 mmol) in 1 ml of ethanol is added to an aqueous solution of lithium hydroxide (0.28 g, 6.70 mmol) in 3 ml of water. The mixture is stirred at RT for 2 hours, then concentrated under vacuum at RT. The resulting lithium salt of 2-formylnicotinic acid is dissolved in 5 ml of methanol, and 4-methylsemicarbazide (0.77 g, 5.07 mmol) is added. The mixture is stirred at RT overnight. The resulting white precipitate is filtered and washed with methanol to give the lithium salt of 2-formylnicotinic acid 4-phenylsemicarbazone, m.p. 266° (compound 146).

EXAMPLE 17

To a mixture of 4-phenyl-3-thiosemicarbazone of 2-acetylnicotinic acid (1.0 g, 3.2 mmol) and potassium carbonate (0.88 g, 6.4 mmol) in 6 ml of dimethylformamide was added 0.4 ml (0.9 g, 6.4 mmol) of methyl iodide. The mixture was stirred overnight, and then poured into ether/CHCl₃ and water. The organic phase is separated and dried (Na₂SO₄). Removal of solvent gave the compound of formula A₁ wherein R is 3-methoxycarbonyl-2-pyridyl, R³ is CH₃, R² is C(=NC₆H₅)-SCH₃ and R⁴ is H (Compound 147) as a mixture of isomers (the isomer having the corresponding structure in which NR²R⁴ is N=C(SCH₃)-NH-C₆H₅), which mixture was crystallized from CH₃CN.

EXAMPLE 18

0.64 g (1.9 mmol) of the compound of Example 17 (compound 147) was hydrolysed by stirring with lithium hydroxide monohydrate (0.08 g, 1.9 mmol) in 10 ml of methanol and 2 ml of water at 80° for six hours. The methanol and water were removed by rotoevaporation to give the compound of formula A₁ wherein R is 3-CO-OLI-2-pyridyl, R³ is CH₃, R² is C(=NC₆H₅)-SCH₃ and R⁴ is H (compound 148).

EXAMPLE 19

0.6 g (1.9 mmol) of compound 148 was suspended in 5% HCl (8 ml), and the solution was separately extracted with CHCl_3 . The chloroform extracts were dried (Na_2SO_4), and the chloroform was removed to give the corresponding acid of formula A_1 , wherein R is 3-COOH-2-pyridyl, R^3 is CH_3 , R^2 is $\text{C}(=\text{NC}_6\text{H}_5)\text{-SCH}_3$ and R^4 is H (compound 149) ; m.p. 78° (softens), $132\text{-}35^\circ$ (gas).

EXAMPLE 20

Pre-emergent herbicidal activity of selected compounds of the present invention was determined as follows : Seeds of selected weeds were planted and the soil was drenched with a solution of water (17%), surfactant (0.17%) and the test compound at a rate equivalent to 10 lb/acre. Scoring was made two weeks after treatment. The grasses (GR) *Setaria viridis*, *Echinochloa crus-galli*, *Sorghum bicolor* and *Avena fatua* and the broadleaves (BL) *Ipomoea purpurea*, *Brassica juncea*, *Solanum nigrum* and *Abutilon theophrasti* were treated. The average pre-emergent activity of the compounds is presented in Table F below (10 lb/acre corresponds roughly to 11 kg/ha).

EXAMPLE 21

Post-emergence herbicidal activity of selected compounds of the present invention was tested as follows: Seedlings of selected weeds were sprayed with a solution of water/acetone (1 : 1), surfactant (0.5%) and the test compound at a rate equivalent to 10 lb/acre. Scoring was made two weeks after spraying. The grasses (GR) *Setaria viridis*, *Echinochloa crus-galli*, *Sorghum bicolor* and *Avena fatua* and the broadleaves (BL) *Ipomoea purpurea*, *Brassica juncea*, soybean and *Abutilon theophrasti* were treated. The average post-emergent activities of the compounds are presented in Table F below.

TABLE F

% Herbicidal Activity at 10 lb/Acre

5

10

Compound No.PrePost

GR

BL

GR

BL

1

91

86

48

61

Na salt of 1

88

93

47

62

15

3

96

90

58

75

Na salt of 3

93

89

63

81

20

4

91

91

72

85

Na salt of 4

94

89

81

85

NH₄ salt of 4

92

92

77

78

25

isoprop NH₃ salt of 4

77

80

61

77

diisoprop NH₂ salt of 4

82

80

63

80

30

22

58

58

30

71

Na salt of 22

53

73

20

56

23

75

63

53

70

35

Na salt of 23

68

80

66

73

24

92

86

55

76

Na salt of 24

85

82

63

75

40

25

90

68

68

81

Na salt of 25

79

90

66

85

45

30

96

87

78

86

Na salt of 30

100

89

83

90

50

55

TABLE F (continued)

5

	<u>Compound No.</u>	<u>Pre</u>		<u>Post</u>	
		<u>GR</u>	<u>BL</u>	<u>GR</u>	<u>BL</u>
	31	87	83	80	87
10	Na salt of 31	96	100	71	86
	32	92	95	90	95
15	Na salt of 32	96	94	86	90
	55	80	80	76	82
	57	85	90	63	85
20	60	85	80	71	78
	61	82	81	67	81
25	110	88	76	--	--
	Na salt of 110	81	80	60	80

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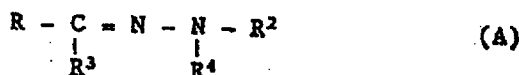


Claims

5 Claims for the Contracting States : BE CH DE FR GB IT LI LU NL SE

1. Compounds of formula (A) :

10



15

wherein R is phenyl or naphthyl, or is a heteroaromatic ring selected from

- a) pyridyl which may be fused by its [b] or [c]-side with a benzene ring,
- b) 2-pyridyl-N-oxide or 2-pyrazinyl-N¹-oxide,
- c) pyrimidinyl,
- d) pyrazinyl,

20

e) 3- or 4-cinnolinyl or 2-quinoxaliny and

f) a five-membered heteroaromatic ring bound by one of its ring C-atoms to the CR³-group selected from thienyl, furanyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl or pyrazolyl ; whereby said five-membered heteroaromatic ring may be fused by its [b]-side with a benzene ring ;

which group R is ortho-substituted by the group R' and additionally bears one further substituent Y, both R' and Y being attached to a ring carbon atom ;

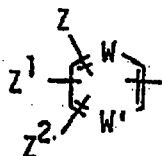
25

R' is the carboxy group in free form, salt form or ester form or is the group CO-SR⁶ or CO-NR⁷R⁸,

Y is H, C₁₋₈alkyl, C₁₋₈haloalkyl, C₁₋₈alkoxy, C₁₋₈haloalkoxy, C₂₋₈alkenyloxy, C₂₋₈haloalkenyloxy, C₂₋₈alkynyloxy, phenyl, phenoxy, C₁₋₈alkylthio, OH, halogen, nitro or cyano ;

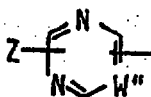
R² is the group -C(=NR¹⁰)-SR⁹ or -C(=X)-NHR¹⁰, each of R³, R⁴, R⁷ and R⁸ is independently hydrogen or C₁₋₈alkyl ; each of R⁶ and R⁹ is independently C₁₋₈alkyl, R¹⁰ is one of the groups

30

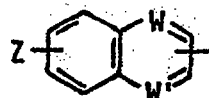


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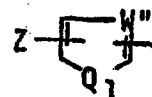
(G-1) ,



(G-2) ,



(G-3)



or (G-4)

each of W, W' and W'' is independently N or CH

40

Q₁ is oxygen, sulfur or NH

X is oxygen or sulfur each of Z, Z' and Z'' is independently one of the significances specified for - but independent of - Y,

with the proviso that when R is phenyl mono-substituted in ortho by the carboxy group in free form or in salt form or by C₁₋₄alkoxy-carbonyl, then R³ is C₁₋₈alkyl.

45

2. A compound of Claim 1, wherein R is 2-COOH-phenyl or 2-COOR⁵phenyl, which phenyl group is substituted by Y, R² is a group -C(=X)-NHR¹⁰, R³ is C₁₋₈alkyl R⁴ is H or C₁₋₈alkyl, R is C₁₋₈alkyl, C₁₋₈haloalkyl, C₂₋₁₀alkoxyalkyl or -CH(R¹¹)-O-C(=O)-C₁₋₈alkyl, R¹⁰ is phenyl or pyridyl, which groups are substituted by Z and Z', R¹¹ is H or C₁₋₈alkyl, X is O or S, each of Y and Z is independently H, halogen, C₁₋₈alkyl, C₁₋₈alkoxy, CF₃, phenyl, phenoxy, nitro, cyano or hydroxy, and Z' is H, halogen, C₁₋₈alkyl or C₁₋₈alkoxy, whereby any carboxy group in R is in free form or in salt form.

50

3. A compound of claim 1, wherein R is a heteroaromatic ring selected from

- a) pyridyl which may be fused by its [b] or [c]-side with a benzene ring,
- b) 2-pyridyl-N-oxide or 2-pyrazinyl-N¹-oxide,
- c) pyrimidinyl,
- d) pyrazinyl,

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e) 3- or 4-cinnolinyl or 2-quinoxaliny and

f) a five-membered heteroaromatic ring bound by one of its ring C-atoms to the CR³-group selected from thienyl, furanyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl or pyrazolyl ; whereby said



five-membered heteroaromatic ring may be fused by its [b]-side with a benzene ring ;
which group R is ortho-substituted by the group R' and additionally bears one further substituent Y, both R' and Y being attached to a ring carbon atom ;

R' is the carboxy group in free form or salt form, or is the group COOR⁵,

R³ is H or C₁₋₆alkyl and R², R⁴, R⁵, R¹⁰, R¹¹, X, Y, Z and Z¹ are as stated in Claim 2.

4. A compound of Claim 3, wherein the heteroaromatic ring R is selected from pyridyl, quinolyl, 2-pyridyl-N-oxide, pyrimidinyl, pyrazinyl, thienyl and furyl, substituted by R' and Y as stated in Claim 3.

5. A compound of Claim 4, wherein R is selected from pyridyl or thienyl, substituted by R' and Y as stated in Claim 3 and R⁴ is H.

6. A compound of Claim 5, wherein R³ is C₁₋₆alkyl, X is oxygen, R¹⁰ is Z, Z¹-substituted phenyl, Z is H, halogen, C₁₋₆alkyl, C₁₋₆alkoxy or CF₃ and Z¹ is H, chloro, fluoro, methyl or methoxy.

7. A compound of Claim 6, wherein R is 2-pyridyl ortho-substituted by R' as stated in Claim 3 and Y being H.

8. A compound of Claim 6, wherein R is thienyl ortho-substituted by R' as stated in Claim 3 and Y being H.

9. A compound of Claim 7, wherein R¹⁰ is phenyl, 3-chlorophenyl or 3-fluorophenyl.

10. A compound of any of Claims 1 to 9 wherein R' is the carboxy group in free form or salt form or is a group COO-CH(R¹¹)-O-C(=O)-C₁₋₆alkyl, wherein R¹¹ is as stated in Claim 2.

11. A compound of Claim 10 selected from

- a) 2-acetylnicotinic acid 4-phenylsemicarbazone in free acid form or salt form,
- b) 2-acetylnicotinic acid 4-(3-chlorophenyl)semicarbazone in free form or salt form,
- c) 2-acetylnicotinic acid 4-(3-fluorophenyl)-semicarbazone in free form or salt form,
- d) butyryloxymethyl 2-acetylnicotinate 4-(3-fluorophenyl)-semicarbazone,
- e) butyryloxymethyl 2-acetylnicotinate 4-(3-chlorophenyl)-semicarbazone.

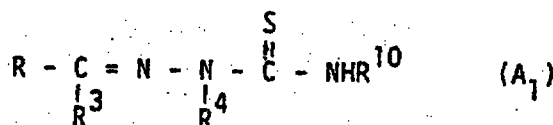
12. Process of preparing a compound of formula (A) stated in Claim 1, which comprises
a) reacting a compound of formula I



wherein R and R³ are as defined in Claim 1, with a compound of formula II



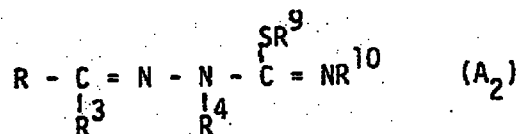
wherein R² and R⁴ are as defined in Claim 1, followed, where desired, by esterifying compounds of formula (A) wherein R' is the carboxyl group to compounds (A) wherein R' is a carboxyl-ester group, or
b) S-alkylating a compound of formula A₁



wherein R, R³, R⁴ and R¹⁰ are as defined in Claim 1, with an alkylhalogenide of formula III



wherein R⁹ is as defined in Claim 1 and Hal is halogen, or a reactive functional derivative of said compound of formula III to give a compound of formula (A₂)



wherein R, R³, R⁴, R⁹ and R¹⁰ are as defined in Claim 1.

13. A herbicidal composition comprising a compound of formula (A) according to any one of Claims 1 to

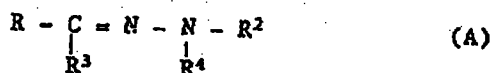


11' and an agriculturally acceptable diluent.

14. A method of combatting weeds which comprises applying to the locus thereof a herbicidally effective amount of a compound of formula (A) according to any one of Claims 1 to 11.

5 Claims for the Contracting State : AT

1. A herbicidal composition comprising a compound of formula (A) :



wherein R is phenyl or naphthyl, or is a heteroaromatic ring selected from

a) pyridyl which may be fused by its [b] or [c]-side with a benzene ring,

b) 2-pyridyl-N-oxide or 2-pyrazinyl-N¹-oxide,

c) pyrimidinyl,

d) pyrazinyl,

e) 3- or 4-cinnolinyl or 2-quinoxaliny and

f) a five-membered heteroaromatic ring bound by one of its ring C-atoms to the CR³-group selected from thienyl, furanyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl or pyrazolyl ; whereby said five-membered heteroaromatic ring may be fused by its [b]-side with a benzene ring ;

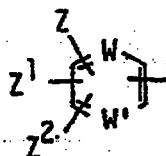
which group R is ortho-substituted by the group R' and additionally bears one further substituent Y, both R' and Y being attached to a ring carbon atom ;

R' is the carboxy group in free form, salt form or ester form or is the group CO-SR⁶ or CO-NR⁷R⁸,

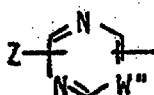
Y is H, C₁₋₅alkyl, C₁₋₅haloalkyl, C₁₋₅alkoxy, C₁₋₅haloalkoxy, C₂₋₅alkenyl, C₂₋₅haloalkenyl, C₂₋₅alkynyl, C₂₋₅haloalkynyl, phenyl, phenoxy, C₁₋₅alkylthio, OH, halogen, nitro or cyano ;

R² is the group -C(=NR¹⁰)-SR⁹ or -C(=X)-NHR¹⁰, each of R³, R⁴, R⁷ and R⁸ is independently hydrogen or C₁₋₅alkyl ; each of R⁶ and R⁹ is independently C₁₋₅alkyl,

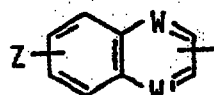
R¹⁰ is one of the groups



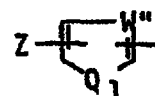
(G-1) ,



(G-2) ,



(G-3)



or (G-4)

each of W, W' and W'' is independently N or CH

Q₁ is oxygen, sulfur or NH

X is oxygen or sulfur each of Z, Z¹ and Z² is independently one of the significances specified for - but independent of - Y,

with the proviso that when R is phenyl mono-substituted in ortho by the carboxy group in free form or in salt form or by C₁₋₄alkoxy-carbonyl, then R³ is C₁₋₄alkyl.

2. A composition of Claim 1, wherein R is 2-COOH-phenyl, or 2-COOR⁵-phenyl which phenyl group is substituted by Y, R² is a group -C(=X)-NHR¹⁰, R³ is C₁₋₅alkyl R⁴ is H or C₁₋₅alkyl, R⁵ is C₁₋₅alkyl, C₁₋₅haloalkyl, C₂₋₁₀alkoxyalkyl or -CH(-R¹¹)-O-C(=O)-C₁₋₅alkyl, R¹⁰ is phenyl or pyridyl, which groups are substituted by Z and Z¹, R¹¹ is H or C₁₋₅alkyl, X is O or S, each of Y and Z is independently H, halogen, C₁₋₅alkyl, C₁₋₅alkoxy CF₃, phenyl, phenoxy, nitro, cyano or hydroxy, and Z¹ is H, halogen, C₁₋₅alkyl or C₁₋₅alkoxy, whereby any carboxy group in R is in free form or in salt form.

3. A composition of Claim 1, wherein R is a heteroaromatic ring selected from

a) pyridyl which may be fused by its [b] or [c]-side with a benzene ring,

b) 2-pyridyl-N-oxide or 2-pyrazinyl-N¹-oxide,

c) pyrimidinyl,

d) pyrazinyl,

e) 3- or 4-cinnolinyl or 2-quinoxaliny and

f) a five-membered heteroaromatic ring bound by one of its ring C-atoms to the CR³-group selected from thienyl, furanyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl or pyrazolyl ; whereby said



five-membered heteroaromatic ring may be fused by its [b]-side with a benzene ring ;
which group R is ortho-substituted by the group R' and additionally bears one further substituent Y, both R' and Y being attached to a ring carbon atom ;

R' is the carboxy group in free form or salt form, or is the group COOR⁵,

R³ is H or C₁₋₅alkyl and R², R⁴, R⁵, R¹⁰, R¹¹, X, Y, Z and Z¹ are as stated in Claim 2.

4. A composition of Claim 3, wherein the heteroaromatic ring R is selected from pyridyl, quinolyl, 2-pyridyl-N-oxide, pyrimidinyl, pyrazinyl, thienyl and furyl, substituted by R' and Y as stated in Claim 3.

5. A composition of Claim 4, wherein R is selected from pyridyl or thienyl, substituted by R' and Y as stated in Claim 3 and R⁴ is H.

6. A composition of Claim 5, wherein R³ is C₁₋₅alkyl, X is oxygen, R¹⁰ is Z,Z¹-substituted phenyl, Z is H, halogen, C₁₋₅alkyl, C₁₋₅alkoxy or CF₃ and Z¹ is H, chloro, fluoro, methyl or methoxy.

7. A composition of Claim 6, wherein R is 2-pyridyl ortho-substituted by R' as stated in Claim 3 and Y being H.

8. A composition of Claim 6, wherein R is thienyl ortho-substituted by R' as stated in Claim 3 and Y being H.

9. A composition of Claim 7, wherein R¹⁰ is phenyl, 3-chlorophenyl or 3-fluorophenyl.

10. A composition of any of Claims 1 to 9 wherein R' is the carboxy group in free form or salt form or is a group COO-CH(R¹¹)-O-C(=O)-C₁₋₅alkyl, wherein R¹¹ is as stated in Claim 2.

11. A composition of Claim 10 comprising a compound selected from

- a) 2-acetylnicotinic acid 4-phenylsemicarbazone in free acid form or salt form,
- b) 2-acetylnicotinic acid 4-(3-chlorophenyl)semicarbazone in free form or salt form,
- c) 2-acetylnicotinic acid 4-(3-fluorophenyl)-semicarbazone in free form or salt form,
- d) butyryloxymethyl 2-acetylnicotinate 4-(3-fluorophenyl)-semicarbazone,
- e) butyryloxymethyl 2-acetylnicotinate 4-(3-chlorophenyl)-semicarbazone.

12. Process of preparing a compound of formula (A) stated in Claim 1, which comprises

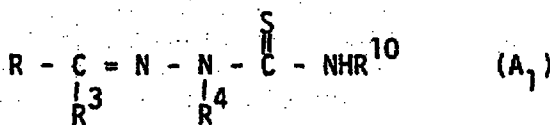
- a) reacting a compound of formula I



wherein R and R³ are as defined in Claim 1, with a compound of formula II



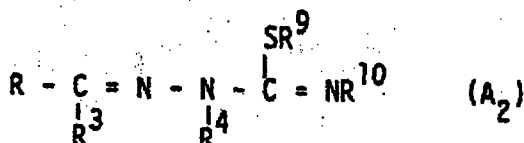
wherein R² and R⁴ are as defined in Claim 1, followed, where desired, by esterifying compounds of formula (A) wherein R' is the carboxyl group to compounds (A) wherein R' is a carboxyl-ester group, or
b) S-alkylating a compound of formula A₁



wherein R, R³, R⁴ and R¹⁰ are as defined in Claim 1, with an alkylhalogenide of formula III



wherein R⁹ is as defined in Claim 1 and Hal is halogen, or a reactive functional derivative of said compound of formula III to give a compound of formula (A₂)



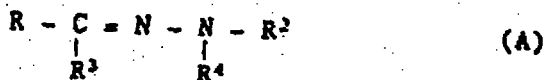
wherein R, R³, R⁴, R⁹ and R¹⁰ are as defined in Claim 1.



Ansprüche

Patentansprüche für die Vertragsstaaten : BE, CH/LI, DE, FR, GB, IT, LU, NL, SE

1. Verbindungen der Formel (A):



worin R eine Phenyl- oder Naphthylgruppe ist oder ein heteroaromatischer Ring, ausgewählt aus

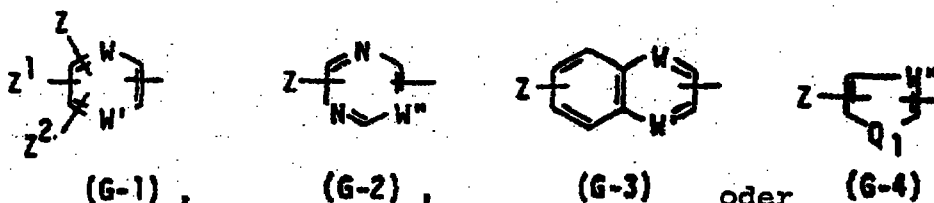
- einer Pyridylgruppe, die an ihrer [b]- oder [c]-Seite an einen Benzolring kondensiert sein kann,
- 2-Pyridyl-N-oxid oder 2-Pyrazinyl-N¹-oxid,
- einer Pyrimidinylgruppe,
- einer Pyrazinylgruppe,
- einer 3- oder 4-Cinnoliny- oder 2-Chinoxaliny-Gruppe und
- einem fünfgliedrigen heteroaromatischen Ring, der mit einem seiner Ring-C-Atome an die CR³-Gruppe, ausgewählt aus Thienyl, Furanyl, Pyrrolyl, Oxazolyl, Thiazolyl, Isoxazolyl, Isothiazolyl, Imidazolyl oder Pyrazolyl, gebunden ist; wobei dieser fünfgliedrige heteroaromatische Ring an seiner [b]-Seite an einen Benzolring kondensiert sein kann;

wobei die Gruppe R durch die Gruppe R' ortho-substituiert ist und zusätzlich einen weiteren Substituenten Y trägt, und sowohl R' als auch Y an ein Ringkohlenstoffatom gebunden sind;

R' die Carboxygruppe in freier Form, Salzform oder Esterform ist oder die Gruppe CO-SR⁶ oder CO-NR⁷R⁸ ist,

Y H, eine C₁₋₅-Alkyl-, C₁₋₅-Halogenalkyl-, C₁₋₅-Akoxy-, C₁₋₅-Halogenalkoxy-, C₂₋₅-Alkenyloxy-, C₂₋₅-Halogenalkenyloxy-, C₂₋₅-Alkynyloxy-, Phenyl-, Phenoxy-, C₁₋₅-Alkylthio-, OH-Gruppe, Halogen, eine Nitro- oder Cyanogruppe ist;

R² die Gruppe -C(=NR¹⁰)-SR⁹ oder -C(=X)-NHR¹⁰ ist, wobei R³, R⁴, R⁷ und R⁸ jeweils unabhängig Wasserstoff oder eine C₁₋₅-Alkylgruppe ist; R⁶ und R⁹ jeweils unabhängig eine C₁₋₅-Alkylgruppe ist, R¹⁰ eine der Gruppen



ist, W, W' und W'' jeweils unabhängig N oder CH ist, Q₁ Sauerstoff, Schwefel oder NH ist, X Sauerstoff oder Schwefel ist, Z, Z' und Z'' jeweils unabhängig eine der für Y angegebenen - aber unabhängig von Y - Bedeutungen hat, mit dem Vorbehalt, daß dann, wenn R eine in ortho-Stellung durch die Carboxygruppe in freier Form oder in Salzform oder mit der C₁₋₄-Alkoxy-carbonylgruppe monosubstituierte Phenylgruppe ist, daß dann R³ eine C₁₋₅-Alkylgruppe ist.

2. Verbindung nach Anspruch 1, worin R eine 2-COOH-Phenyl- oder 2-COOR⁵-Phenylgruppe ist, wobei die Phenylgruppe mit Y substituiert ist, R² eine Gruppe -C(=X)-NHR¹⁰ ist, R³ eine C₁₋₅-Alkylgruppe ist, R⁴ H oder eine C₁₋₅-Alkylgruppe ist, R⁵ eine C₁₋₅-Alkyl-, C₁₋₅-Halogenalkyl-, C₂₋₁₀-Alkoxyalkyl- oder -CH(-R¹¹)-O-C(=O)-C₁₋₅-Alkylgruppe ist, R¹⁰ eine Phenyl- oder Pyridylgruppe ist, wobei diese Gruppen mit Z und Z' substituiert sind, R¹¹ H oder eine C₁₋₅-Alkylgruppe ist, X O oder S ist, Y und Z jeweils unabhängig H, Halogen, eine C₁₋₅-Alkyl-, C₁₋₅-Akoxy-, CF₃-, Phenyl-, Phenoxy-, Nitro-, Cyano- oder Hydroxygruppe ist und Z' H, Halogen, eine C₁₋₅-Alkyl- oder C₁₋₅-Alkoxygruppe ist, wobei jede Carboxygruppe in R in freier oder in Salzform vorliegt.

3. Verbindung nach Anspruch 1, worin R ein heteroaromatischer Ring ist, ausgewählt aus

- einer Pyridylgruppe, die an ihrer [b]- oder [c]-Seite an einen Benzolring kondensiert sein kann,
- 2-Pyridyl-N-oxid oder 2-Pyrazinyl-N¹-oxid,

c) einer Pyrimidinylgruppe,

d) einer Pyrazinylgruppe,

e) einer 3- oder 4-Cinnoliny- oder 2-Chinoxaliny-Gruppe und

f) einem fünfgliedrigen heteroaromatischen Ring, der mit einem seiner Ring-C-Atome an die CR³-Gruppe,



ausgewählt aus Thienyl, Furanyl, Pyrrolyl, Oxazolyl, Thiazolyl, Isoxazolyl, Isothiazolyl, Imidazolyl oder Pyrazolyl, gebunden ist; wobei der fünfgliedrige heteroaromatische Ring an seiner[b]-Seite an einen Benzolring kondensiert sein kann;

wobei die Gruppe R ortho-substituiert ist mit der Gruppe R' und zusätzlich einen weiteren Substituenten Y trägt, und sowohl R' als auch Y an ein Ringkohlenstoffatom gebunden sind; R' die Carboxygruppe in freier Form oder Salzform ist oder die Gruppe COOR⁵ ist, R³ H oder eine C₁₋₅-Alkylgruppe ist und R², R⁴, R⁵, R¹⁰, R¹¹, X, Y, Z und Z' wie in Anspruch 2 angegeben sind.

4. Verbindung nach Anspruch 3, worin der heteroaromatische Ring R ausgewählt ist aus Pyridyl, Chinolyl, 2-Pyridyl-N-oxid, Pyrimidinyl, Pyrazinyl, Thienyl und Furyl, substituiert mit R' und Y, wie in Anspruch 3 angegeben.

5. Verbindung nach Anspruch 4, worin R ausgewählt ist aus Pyridyl oder Thienyl, substituiert mit R' und Y, wie in Anspruch 3 angegeben, und R⁴ H ist.

6. Verbindung nach Anspruch 5, worin R³ eine C₁₋₅-Alkylgruppe ist, X Sauerstoff ist, R¹⁰ eine Z, Z'-substituierte Phenylgruppe ist, Z H, Halogen, eine C₁₋₅-Alkyl-, C₁₋₅-Alkoxy- oder CF₃-Gruppe ist und Z H, Chlor, Fluor, eine Methyl- oder Methoxygruppe ist.

7. Verbindung nach Anspruch 6, worin R ein mit wie in Anspruch 3 definiertem R' ortho-substituierter 2-Pyridylrest ist und Y H ist.

8. Verbindung nach Anspruch 6, worin R ein mit wie in Anspruch 3 definiertem R' ortho-substituierter Thienylrest ist und Y H ist.

9. Verbindung nach Anspruch 7, worin R¹⁰ eine Phenyl-, 3-Chlorphenyl- oder 3-Fluorphenylgruppe ist.

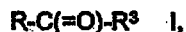
10. Verbindung nach einem der Ansprüche 1 bis 9, worin R' die Carboxygruppe in freier Form oder in Salzform ist oder eine Gruppe COO-CH(R¹¹)-O-C(=O)-C₁₋₅-Alkylgruppe, worin R¹¹ wie in Anspruch 2 definiert ist.

11. Verbindung nach Anspruch 10, ausgewählt aus

- a) 2-Acetylnicotinsäure-4-phenylsemicarbazon in freier Säure-form oder Salzform,
- b) 2-Acetylnicotinsäure-4-(3-chlorphenyl)semicarbazon in freier Form oder in Salzform,
- c) 2-Acetylnicotinsäure-4-(3-fluorphenyl)semicarbazon in freier Form oder in Salzform,
- d) Butyryloxymethyl-2-acetylnicotinat-4-(3-fluorphenyl)semicarbazon,
- e) Butyryloxymethyl-2-acetylnicotinat-4-(3-chlorphenyl)semicarbazon.

12. Verfahren zur Herstellung einer Verbindung der Formel (A), wie in Anspruch 1 definiert, das umfaßt, daß man

a) eine Verbindung der Formel I

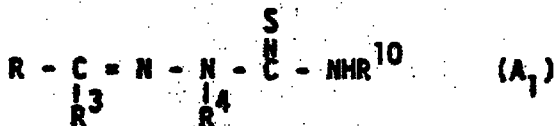


worin R und R³ wie in Anspruch 1 definiert sind, mit einer Verbindung der Formel II



worin R² und R⁴ wie in Anspruch 1 definiert sind, umgesetzt und anschließend, falls erwünscht, die Verbindungen der Formel (A), worin R' die Carboxylgruppe ist, zu Verbindungen (A) verestert, worin R' eine Carboxylestergruppe ist, oder

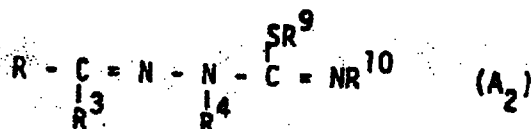
b) eine Verbindung der Formel A₁



worin R, R³, R⁴ und R¹⁰ wie in Anspruch 1 definiert sind, mit einem Alkylhalogenid der Formel III



worin R⁹ wie in Anspruch 1 definiert ist und Hal Halogen ist, oder einem reaktiven funktionellen Derivat der Verbindung der Formel III S-alkyliert, um eine Verbindung der Formel (A₂)



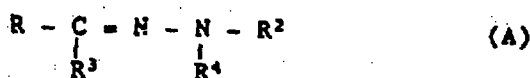
zu erhalten, worin R, R³, R⁴, R⁹ und R¹⁰ wie in Anspruch 1 definiert sind.

13. Herbizidzusammensetzung, umfassend eine Verbindung der Formel (A) gemäß einem der Ansprüche 1 bis 11 und ein landwirtschaftlich annehmbares Verdünnungsmittel.

14. Verfahren zur Bekämpfung von Unkraut, umfassend das Aufbringen einer herbizid wirksamen Menge einer Verbindung der Formel (A) gemäß einem der Ansprüche 1 bis 11 an seinem Standort.

Patentansprüche für den Vertragsstaat : AT

1. Herbizidzusammensetzung, umfassend eine Verbindung der Formel (A) :



worin R eine Phenyl- oder Naphthylgruppe oder ein heteroaromatischer Ring, ausgewählt aus

a) einer Pyridylgruppe, die an ihrer [b]- oder [c]-Seite an einen Benzolring kondensiert sein kann,

b) 2-Pyridyl-N-oxid oder 2-Pyrazinyl-N¹-oxid,

c) einer Pyrimidinylgruppe,

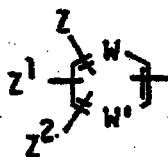
d) einer Pyrazinylgruppe,

e) einer 3- oder 4-Cinnolinyl- oder 2-Chinoxalinygruppe und

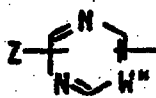
f) einem fünfgliedrigen heteroaromatischen Ring, der mit einem seiner Ring-C-Atome an die CR³-Gruppe, ausgewählt aus Thienyl, Furanyl, Pyrrolyl, Oxazolyl, Thiazolyl, Isoxazolyl, Isothiazolyl, Imidazolyl oder Pyrazolyl gebunden ist ; wobei der fünfgliedrige heteroaromatische Ring an seiner [b]-Seite an einen Benzolring kondensiert sein kann ;

wobei die Gruppe R mit der Gruppe R' in ortho-Stellung substituiert ist und zusätzlich einen weiteren Substituenten Y trägt und sowohl R' als auch Y an ein Ringkohlenstoffatom gebunden sind ; R' die Carboxygruppe in freier Form, Salzform oder Esterform oder die Gruppe CO-SR⁹ oder CO-NR⁷R⁸ ist, Y H, eine C₁₋₅-Alkyl-, C₁₋₅-Halogenalkyl-, C₁₋₅-Alkoxy-, C₁₋₅-Halogenalkoxy-, C₂₋₈-Alkenyloxy-, C₂₋₈-Halogenalkenyloxy-, C₂₋₈-Alkynyloxy-, Phenyl-, Phenoxy-, C₁₋₈-Alkylthio-, OH-Gruppe, Halogen, eine Nitro- oder Cyano-Gruppe ist ;

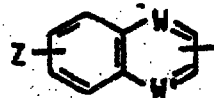
R² die Gruppe -C(=NR¹⁰)-SR⁹ oder -C(=X)-NHR¹⁰ ist, R³, R⁴, R⁷ und R⁸ jeweils unabhängig Wasserstoff oder eine C₁₋₈-Alkylgruppe ist ; R⁶ und R⁹ jeweils unabhängig eine C₁₋₈-Alkylgruppe ist, R¹⁰ eine der Gruppen



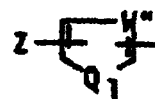
(G-1) ,



(G-2) ,



(G-3) oder



(G-4)

ist, W, W' und W'' jeweils unabhängig N oder CH ist, Q₁ Sauerstoff, Schwefel oder NH ist, X Sauerstoff oder Schwefel ist, Z, Z' und Z'' jeweils unabhängig eine der für Y angegebenen - aber unabhängig davon - Bedeutungen hat, mit dem Vorbehalt, daß dann, wenn R eine in ortho-Stellung mit der Carboxygruppe in freier Form oder in Salzform oder mit einer C₁₋₄-Alkoxy-carbonylgruppe monosubstituierte Phenylgruppe ist, daß dann R³ eine C₁₋₈-Alkylgruppe ist.

2. Zusammensetzung nach Anspruch 1, worin R eine 2-COOH-Phenyl- oder 2-COOR⁵-Phenylgruppe ist, wobei die Phenylgruppe mit Y substituiert ist, R² eine Gruppe -C(=X)-NHR¹⁰, R³ eine C₁₋₅-Alkylgruppe ist, R⁴ H oder eine C₁₋₅-Alkylgruppe ist, R⁵ eine C₁₋₅-Alkyl-, C₁₋₅-Halogenalkyl-, C₂₋₁₀-Alkoxyalkyl- oder -CH(-R¹¹)-O-C(=O)-C₁₋₈-Alkylgruppe ist, R¹⁰ eine Phenyl- oder Pyridylgruppe ist, wobei die Gruppen mit Z und Z' substituiert sind, R¹¹ H oder eine C₁₋₅-Alkylgruppe ist, X O oder S ist, Y und Z jeweils unabhängig H, Halogen, eine C₁₋₅-Alkyl-, C₁₋₅-Alkoxy-, CF₃-, Phenyl-, Phenoxy-, Nitro-, Cyano- oder Hydroxygruppe ist und Z' H, Halogen, eine



C_{1-5} -Alkyl- oder C_{1-5} -Alkoxygruppe ist, wobei jede Carboxygruppe in R in freier Form oder in Salzform vorliegt.

3. Zusammensetzung nach Anspruch 1, worin R ein heteroaromatischer Ring ist, ausgewählt aus

a) einer Pyridylgruppe, die an ihrer[b]- oder [c]-Seite an einen Benzolring kondensiert sein kann,

b) 2-Pyridyl-N-oxid oder 2-Pyrazinyl-N¹-oxid,

c) einer Pyrimidinylgruppe,

d) einer Pyrazinylgruppe,

e) einer 3- oder 4-Cinnolyl- oder 2-Chinoxalinyllgruppe und

f) einem fünfgliedrigen heteroaromatischen Ring, der mit einem seiner Ring-C-Atome an die CR^3 -Gruppe, ausgewählt aus Thienyl, Furanyl, Pyrrolyl, Oxazolyl, Thiazolyl, Isoxazolyl, Isothiazolyl, Imidazolyl oder Pyrazolyl gebunden ist; wobei der fünfgliedrige heteroaromatische Ring an seiner[b]-Seite an einen Benzolring kondensiert sein kann;

wobei die Gruppe R mit der Gruppe R' ortho-substituiert ist und zusätzlich einen weiteren Substituenten Y trägt und sowohl R' als auch Y an ein Ringkohlenstoffatom gebunden sind; R' die Carboxygruppe in freier Form oder in Salzform oder die Gruppe $COOR^5$ ist, R^3 H oder eine C_{1-5} -Alkylgruppe ist und R^2 , R^4 , R^5 , R^{10} , R^{11} , X, Y, Z und Z^1 wie in Anspruch 2 definiert sind.

4. Zusammensetzung nach Anspruch 3, worin der heteroaromatische Ring R ausgewählt ist aus Pyridyl, Chinolyl, 2-Pyridyl-N-oxid, Pyrimidinyl, Pyrazinyl, Thienyl und Furyl, substituiert mit R' und Y wie in Anspruch 3 definiert.

5. Zusammensetzung nach Anspruch 4, worin R ausgewählt ist aus Pyridyl oder Thienyl, substituiert mit R' und Y, wie in Anspruch 3 angegeben, und R^4 H ist.

6. Zusammensetzung nach Anspruch 5, worin R^3 eine C_{1-5} -Alkylgruppe ist, X Sauerstoff ist, R^{10} eine Z, Z^1 -substituierte Phenylgruppe ist, Z H, Halogen, eine C_{1-5} -Alkyl-, C_{1-5} -Alkoxy- oder CF_3 -Gruppe ist und Z^1 H, Chlor, Fluor, eine Methyl- oder Methoxygruppe ist.

7. Zusammensetzung nach Anspruch 6, worin R ein mit wie in Anspruch 3 definiertem R' ortho-substituierter 2-Pyridylrest ist und Y H ist.

8. Zusammensetzung nach Anspruch 6, worin R ein mit wie in Anspruch 3 definiertem R' ortho-substituierter Thienylrest ist und Y H ist.

9. Zusammensetzung nach Anspruch 7, worin R^{10} eine Phenyl-, 3-Chlorphenyl oder 3-Fluorphenylgruppe ist.

10. Zusammensetzung nach einem der Ansprüche 1 bis 9, worin R' die Carboxygruppe in freier Form oder in Salzform ist oder eine $COO-CH(R^{11})-O-C(=O)-C_{1-5}$ -Alkylgruppe, worin R^{11} wie in Anspruch 2 definiert ist.

11. Zusammensetzung nach Anspruch 10, umfassend eine Verbindung, ausgewählt aus

a) 2-Acetylnicotinsäure-4-phenylsemicarbazon in freier Säureform oder in Salzform,

b) 2-Acetylnicotinsäure-4-(3-chlorphenyl)semicarbazon in freier Form oder in Salzform,

c) 2-Acetylnicotinsäure-4-(3-fluorphenyl)semicarbazon in freier Form oder in Salzform,

d) Butyryloxymethyl-2-acetylnicotinat-4-(3-fluorphenyl)semicarbazon,

e) Butyryloxymethyl-2-acetylnicotinat-4-(3-chlorphenyl)semicarbazon.

12. Verfahren zur Herstellung einer Verbindung der Formel (A), wie in Anspruch 1 definiert, das umfaßt, daß man

a) eine Verbindung der Formel I

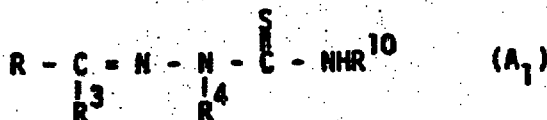


worin R und R^3 wie in Anspruch 1 definiert sind, mit einer Verbindung der Formel II



worin R^2 und R^4 wie in Anspruch 1 definiert sind, umgesetzt und anschließend, falls erwünscht, die Verbindungen der Formel (A), worin R' die Carboxylgruppe ist, zu Verbindungen (A) verestert, worin R' eine Carboxylestergruppe ist, oder

b) eine Verbindung der Formel A₁

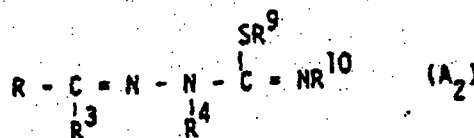




10 worin R , R^3 , R^4 und R^{10} wie in Anspruch 1 definiert sind, mit einem Alkylhalogenid der Formel III



15 worin R^9 wie in Anspruch 1 definiert ist und Hal Halogen ist, oder einem reaktiven funktionellen Derivat der Verbindung der Formel III S-alkyliert, um eine Verbindung der Formel (A₂)

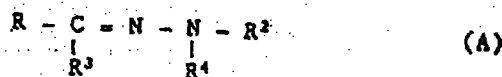


20 zu erhalten, worin R , R^3 , R^4 , R^9 und R^{10} wie in Anspruch 1 definiert sind.

Revendications

25 Revendications pour les Etats contractants : BE, CH, DE, FR, GB, IT, LI, LU, NL, SE.

1. Les composés de formule (A) :



dans laquelle

R signifie phényle ou naphtyle ou un cycle hétéroaromatique choisi parmi les cycles

a) pyridyle qui peut être condensé par son côté [b] ou [c] avec un cycle benzénique,

b) 2-pyridyl-N-oxyde ou 2-pyrazinyl-N¹-oxyde,

c) pyrimidinyle,

d) pyrazinyle,

e) 3- ou 4-cinnolinyle ou 2-quinoxalinyne et

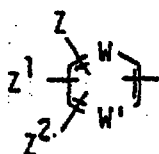
f) un cycle hétéroaromatique à 5 chaînons fixé par l'un de ses atomes de carbone du cycle au groupe CR^3 , choisi parmi les cycles thiényle, furannyle, pyrrolyle, oxazolyne, thiazolyne, isoxazolyne, isothiazolyne, imidazolyne et pyrazolyne, ledit cycle hétéroaromatique à 5 chaînons pouvant être condensé par son côté [b] avec un cycle benzénique,

lequel groupe R est substitué en ortho par le groupe R' et porte en plus un autre substituant Y, les deux substituants R' et Y étant fixés sur un atome de carbone du cycle,

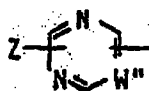
R' signifie un groupe carboxy sous forme libre, sous forme d'un sel ou sous forme d'ester ou signifie le groupe $CO-SR^6$ ou $CO-NR^7R^8$;

Y signifie H, alkyle en C_1-C_8 , haloalkyle en C_1-C_8 , alcoxy en C_1-C_8 , haloalcoxy en C_1-C_8 , alcényloxy en C_2-C_8 , haloalcényloxy en C_2-C_8 , alcynyloxy en C_2-C_8 , phényle, phénoxy, alkylthio en C_1-C_8 , OH, un halogène, nitro ou cyano ;

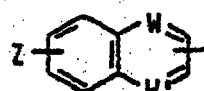
R² signifie le groupe $-C(=NR^{10})-SR^9$ ou $-C(=X)-NHR^{10}$, chaque symbole R^3 , R^4 , R^7 et R^8 signifie indépendamment l'hydrogène ou alkyle en C_1-C_8 ; chaque symbole R^6 et R^9 signifie indépendamment alkyle en C_1-C_8 , R^{10} signifie l'un des groupes



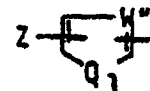
(G-1) ,



(G-2) ,



(G-3)



ou (G-4)

chaque symbole W, W' et W'' signifie indépendamment N ou CH,
Q₁ signifie l'oxygène, le soufre ou NH,



X signifie l'oxygène ou le soufre,
chaque symbole Z, Z¹ et Z² a indépendamment l'une des significations spécifiées pour Y, mais indépendante de Y,

avec la condition que lorsque R signifie phényle mono-substitué en ortho par le groupe carboxy sous forme libre ou sous forme d'un sel ou par un groupe alcoxycarbonyle en C₁-C₄, R³ signifie alors alkyle en C₁-C₈.

2. Un composé de la revendication 1, dans lequel R signifie un groupe 2-COOH-phényle ou 2-COOR⁵-phényle, lequel groupe phényle est substitué par Y, R² signifie un groupe -C(=X)-NHR¹⁰, R³ signifie alkyle en C₁-C₈, R⁴ signifie H ou alkyle en C₁-C₈, R⁵ signifie alkyle en C₁-C₈, haloalkyle en C₁-C₈, alcoxyalkyle en C₂-C₁₀ ou -CH(R¹¹)-O-C(=O)-alkyle en C₁-C₈, R¹⁰ signifie phényle ou pyridyle, lesquels groupes sont substitués par Z et Z¹, R¹¹ signifie H ou alkyle en C₁-C₈, X signifie O ou S, chaque symbole Y et Z signifie indépendamment H, un halogène, alkyle en C₁-C₈, alcoxy en C₁-C₈, CF₃, phényle, phénoxy, nitro, cyano ou hydroxy et Z¹ signifie H, un halogène, alkyle en C₁-C₈ ou alcoxy en C₁-C₈, tout groupe carboxy dans R étant sous forme libre ou sous forme d'un sel.

3. Un composé de la revendication 1, dans lequel R signifie un cycle hétéroaromatique choisi parmi les cycles

a) pyridyle qui peut être condensé par son côté [b] ou [c] avec un cycle benzénique,

b) 2-pyridyl-N-oxyde ou 2-pyrazinyl-N¹-oxyde,

c) pyrimidinyle,

d) pyrazinyle,

e) 3- ou 4-cinnolinyle ou 2-quinoxalinyle et

f) un cycle hétéroaromatique à 5 chaînons fixé par l'un de ses atomes de carbone du cycle au groupe CR³, choisi parmi les cycles thiényl, furanyl, pyrrolyl, oxazolyle, thiazolyle, isoxazolyle, isothiazolyle, imidazolyle et pyrazolyle; ledit cycle hétéroaromatique à 5 chaînons pouvant être condensé par son côté [b] avec un cycle benzénique;

lequel groupe R est substitué en ortho par le groupe R' et porte en plus un autre substituant Y, les deux substituants R' et Y étant fixés sur un atome de carbone du cycle;

R' signifie un groupe carboxy sous forme libre ou sous forme d'un sel ou signifie le groupe COOR⁵;

R³ signifie H ou alkyle en C₁-C₈, et R², R⁴, R⁵, R¹⁰, R¹¹, X, Y, Z et Z¹ sont tels que spécifiés à la revendication

2.

4. Un composé de la revendication 3, dans lequel le cycle hétéroaromatique R est choisi parmi les cycles pyridyle, quinolyle, 2-pyridyl-N-oxyde, pyrimidinyle, pyrazinyle, thiényl et furyl, substitués par R' et Y tels que spécifiés à la revendication 3.

5. Un composé de la revendication 4, dans lequel R est choisi parmi pyridyle et thiényl, substitués par R' et Y tels que spécifiés à la revendication 3 et R⁴ signifie H.

6. Un composé de la revendication 5, dans lequel R³ signifie alkyle en C₁-C₈, X signifie l'oxygène, R¹⁰ signifie phényle substitué par Z, Z¹, Z signifie H, un halogène, alkyle en C₁-C₈, alcoxy en C₁-C₈ ou CF₃ et Z¹ signifie H, chloro, fluoro, méthyle ou méthoxy.

7. Un composé de la revendication 6, dans lequel R signifie 2-pyridyle substitué en ortho par R' tel que spécifié à la revendication 3 et Y signifie H.

8. Un composé de la revendication 6, dans lequel R signifie thiényl substitué en ortho par R' tel que spécifié à la revendication 3 et Y signifie H.

9. Un composé de la revendication 7, dans lequel R¹⁰ signifie phényle, 3-chlorophényle ou 3-fluorophényle.

10. Un composé selon l'une quelconque des revendications 1 à 9, dans lequel R' signifie un groupe carboxy sous forme libre ou sous forme d'un sel ou signifie un groupe COO-CH(R¹¹)-O-C(=O)-alkyle en C₁-C₈, où R¹¹ est tel que spécifié à la revendication 2.

11. Un composé de la revendication 10 choisi parmi

a) la 4-phénylsemicarbazone de l'acide 2-acétylnicotinique sous forme libre ou sous forme d'un sel,

b) la 4-(3-chlorophényl)semicarbazone de l'acide 2-acétylnicotinique sous forme libre ou sous forme d'un sel,

c) la 4-(3-fluorophényl)-semicarbazone de l'acide 2-acétylnicotinique sous forme libre ou sous forme d'un sel,

d) la 4-(3-fluorophényl)-semicarbazone du 2-acétylnicotinate de butyryloxyméthyle,

e) la 4-(3-chlorophényl)-semicarbazone du 2-acétylnicotinate de butyryloxyméthyle.

12. Un procédé de préparation d'un composé de formule (A) spécifié à la revendication 1, qui comprend

a) la réaction d'un composé de formule I



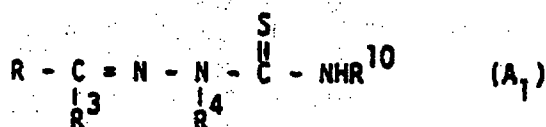


où R et R³ sont tels que définis à la revendication 1, avec un composé de formule II



où R² et R⁴ sont tels que définis à la revendication 1, suivie, si on le désire, de l'estérification des composés de formule (A) où R' signifie un groupe carboxy en composés (A) où R' signifie un groupe carboxy-ester, ou

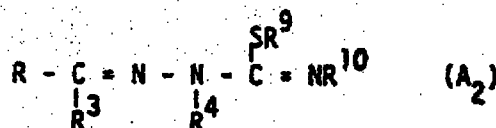
b) la S-alkylation d'un composé de formule A₁



où R, R³, R⁴ et R¹⁰ sont tels que définis à la revendication 1, avec un halogénure d'alkyle de formule III



où R⁹ est tel que défini à la revendication 1 et Hal signifie un halogène, ou un dérivé fonctionnel réactif dudit composé de formule III, pour obtenir un composé de formule (A₂)



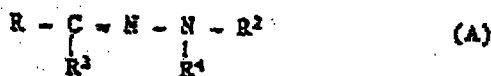
où R, R³, R⁴, R⁹ et R¹⁰ sont tels que définis à la revendication 1.

13. Une composition herbicide, comprenant un composé de formule (A) selon l'une quelconque des revendications 1 à 11 et un diluant acceptable en agriculture.

14. Un procédé pour combattre les mauvaises herbes, qui comprend l'application sur leur lieu de croissance d'une quantité efficace du point de vue herbicide d'un composé de formule (A) selon l'une quelconque des revendications 1 à 11.

Revendications pour l'Etat contractant : AT.

1. Une composition herbicide comprenant un composé de formule (A) :



dans laquelle

R signifie phényle ou naphthyle ou un cycle hétéroaromatique choisi parmi les cycles

a) pyridyle qui peut être condensé par son côté [b] ou [c] avec un cycle benzénique,

b) 2-pyridyl-N-oxyde ou 2-pyrazinyl-N¹-oxyde,

c) pyrimidinyle,

d) pyrazinyle,

e) 3- ou 4-cinnolinyle ou 2-quinoxalinyne et

f) un cycle hétéroaromatique à 5 chaînons fixé par l'un de ses atomes de carbone du cycle au groupe CR², choisi parmi les cycles thiényl, furanyl, pyrrolyl, oxazolyle, thiazolyle, isoxazolyle, isothiazolyle, imidazolyle et pyrazolyle, ledit cycle hétéroaromatique à 5 chaînons pouvant être condensé par son côté [b] avec un cycle benzénique,

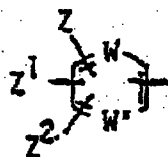
lequel groupe R est substitué en ortho par le groupe R' et porte en plus un autre substituant Y, les deux substituant R' et Y étant fixés sur un atome de carbone du cycle,

R' signifie un groupe carboxy sous forme libre, sous forme d'un sel ou sous forme d'ester ou signifie le groupe CO-SR⁶ ou CO-NR⁷R⁸ ;

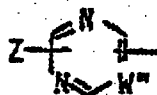


Y signifie H, alkyle en C₁-C₈, haloalkyle en C₁-C₈, alcoxy en C₁-C₈, haloalcoxy en C₁-C₈, alcényloxy en C₂-C₈, haloalcényloxy en C₂-C₈, alcynyloxy en C₂-C₈, phényle, phénoxy, alkylthio en C₁-C₈, OH, un halogène, nitro ou cyano ;

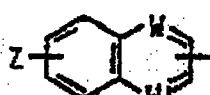
R² signifie le groupe -C(=NR¹⁰)-SR⁹ ou -C(=X)-NHR¹⁰, chaque symbole R³, R⁴, R⁷ et R⁸ signifie indépendamment l'hydrogène ou alkyle en C₁-C₈ ; chaque symbole R⁶ et R⁹ signifie indépendamment alkyle en C₁-C₈, R¹⁰ signifie l'un des groupes



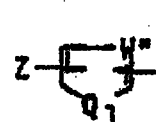
(G-1) ,



(G-2) ,



(G-3)



(G-4)

chaque symbole W, W' et W'' signifie indépendamment N ou CH,

Q₁ signifie l'oxygène, le soufre ou NH,

X signifie l'oxygène ou le soufre, chaque symbole Z, Z' et Z'' a indépendamment l'une des significations spécifiées pour Y, mais indépendante de Y, avec la condition que lorsque R signifie phényle mono-substitué en ortho par le groupe carboxy sous forme libre ou sous forme d'un sel ou par un groupe alcoxycarbonyle en C₁-C₄, R³ signifie alors alkyle en C₁-C₈.

2. Une composition selon la revendication 1, dans laquelle R signifie un groupe 2-COOH-phényle ou 2-COOR⁵-phényle, lequel groupe phényle est substitué par Y, R² signifie un groupe -C(=X)-NHR¹⁰, R³ signifie alkyle en C₁-C₈, R⁴ signifie H ou alkyle en C₁-C₈, R⁵ signifie alkyle en C₁-C₈, haloalkyle en C₁-C₈, alcoxy-alkyle en C₂-C₁₀ ou -CH(R¹¹)-O-O(=O)-alkyle en C₁-C₈, R¹⁰ signifie phényle ou pyridyle, lesquels groupes sont substitués par Z et Z', R¹¹ signifie H ou alkyle en C₁-C₈, X signifie O ou S, chaque symbole Y et Z signifie indépendamment H, un halogène, alkyle en C₁-C₈, alcoxy en C₁-C₈, CF₃, phényle, phénoxy, nitro, cyano ou hydroxy et Z' signifie H, un halogène, alkyle en C₁-C₈ ou alcoxy en C₁-C₈, tout groupe carboxy dans R étant sous forme libre ou sous forme d'un sel.

3. Une composition selon la revendication 1, dans laquelle R signifie un cycle hétéroaromatique choisi parmi les cycles

a) pyridyle qui peut être condensé par son côté [b] ou [c] avec un cycle benzénique,

b) 2-pyridyl-N-oxyde ou 2-pyrazinyl-N'-oxyde,

c) pyrimidinyle,

d) pyrazinyle,

e) 3- ou 4-cinnolinyne ou 2-quinoxalinyne et

f) un cycle hétéroaromatique à 5 chaînons fixé par l'un de ses atomes de carbone du cycle au groupe CR³, choisi parmi les cycles thiényne, furannyle, pyrrolyle, oxazolyle, thiazolyle, isoxazolyle, isothiazolyle, imidazolyle et pyrazolyle ; ledit cycle hétéroaromatique à 5 chaînons pouvant être condensé par son côté [b] avec un cycle benzénique ;

lequel groupe R est substitué en ortho par le groupe R' et porte en plus un autre substituant Y, les deux substituants R' et Y étant fixés sur un atome de carbone du cycle ;

R' signifie un groupe carboxy sous forme libre ou sous forme d'un sel ou signifie le groupe COOR⁵ ;

R³ signifie H ou alkyle en C₁-C₈, et

R², R⁴, R⁵, R¹⁰, R¹¹, X, Y, Z et Z' sont tels que spécifiés à la revendication 2.

4. Une composition selon la revendication 3, dans laquelle le cycle hétéroaromatique R est choisi parmi les cycles pyridyle, quinolyle, 2-pyridyl-N-oxyde, pyrimidinyle, pyrazinyle, thiényne et furyle, substitués par R' et Y tels que spécifiés à la revendication 3.

5. Une composition selon la revendication 4, dans laquelle R est choisi parmi pyridyle et thiényne, substitués par R' et Y tels que spécifiés à la revendication 3 et R⁴ signifie H.

6. Une composition selon la revendication 5, dans laquelle R³ signifie alkyle en C₁-C₈, X signifie l'oxygène, R¹⁰ signifie phényle substitué par Z, Z', Z signifie H, un halogène, allyle en C₁-C₈, alcoxy en C₁-C₈ ou CF₃ et Z' signifie H, chloro, fluoro, méthyle ou méthoxy.

7. Une composition selon la revendication 6, dans laquelle R signifie 2-pyridyle substitué en ortho par R' tel que spécifié à la revendication 3 et Y signifie H.

8. Une composition selon la revendication 6, dans laquelle R signifie thiényne substitué en ortho par R' tel que spécifié à la revendication 3 et Y signifie H.

9. Une composition selon la revendication 7, dans laquelle R¹⁰ signifie phényle, 3-chlorophényle ou 3-fluo-



rophényle.

10. Une composition selon l'une quelconque des revendications 1 à 9, dans laquelle R' signifie un groupe carboxy sous forme libre ou sous forme d'un sel ou signifie un groupe $\text{COO-CH(R}^{11}\text{)-O-C(=O)-alkyle en C}_1\text{-C}_6$, où R¹¹ est tel que spécifié à la revendication 2.

11. Une composition selon la revendication 10 comprenant un composé choisi parmi

- a) la 4-phénylsemicarbazone de l'acide 2-acétylnicotinique sous forme libre ou sous forme d'un sel,
- b) la 4-(3-chlorophényl)semicarbazone de l'acide 2-acétylnicotinique sous forme libre ou sous forme d'un sel,
- c) la 4-(3-fluorophényl)-semicarbazone de l'acide 2-acétylnicotinique sous forme libre ou sous forme d'un sel,
- d) la 4-(3-fluorophényl)-semicarbazone du 2-acétylnicotinate de butyryloxyméthyle,
- e) la 4-(3-chlorophényl)-semicarbazone du 2-acétylnicotinate de butyryloxyméthyle.

12. Un procédé de préparation d'un composé de formule (A) spécifié à la revendication 1, qui comprend

- a) la réaction à un composé de formule I

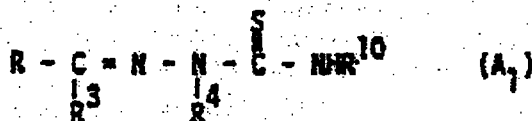


où R et R³ sont tels que définis à la revendication 1, avec un composé de formule II



où R² et R⁴ sont tels que définis à la revendication 1, suivie, si on le désire, de l'estérification des composés de formule (A) où R' signifie un groupe carboxy en composés (A) où R' signifie un groupe carboxy-ester, ou

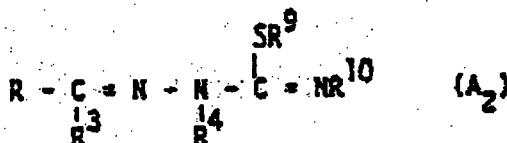
- b) la S-alkylation d'un composé de formule A₁



où R, R³, R⁴ et R¹⁰ sont tels que définis à la revendication 1, avec un halogénure d'alkyle de formule III



où R⁹ est tel que défini à la revendication 1 et Hal signifie un halogène, ou un dérivé fonctionnel réactif dudit composé de formule III, pour obtenir un composé de formule (A₂)



où R, R³, R⁴, R⁹ et R¹⁰ sont tels que définis à la revendication 1.