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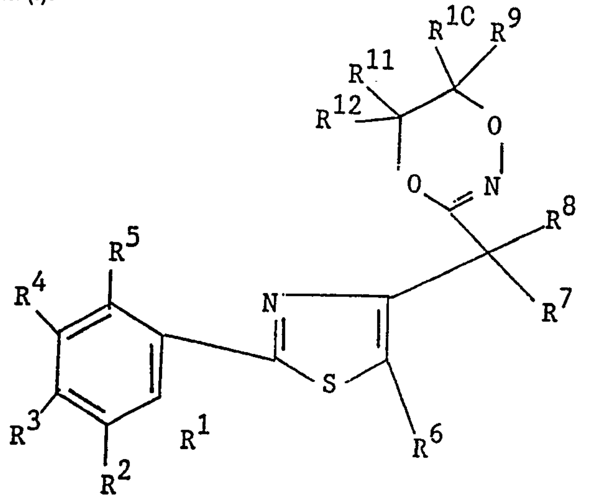
(54) Dioxazine derivatives

(57) Compounds of formula (I):



(I)

or salts thereof: wherein R^1, R^2, R^3, R^4 and R^5 are independently selected from hydrogen, hydroxy, alkyl, alkoxy, alkylcarbonyl, halogen, nitrile, nitro, haloakyl and haloalkoxy; R^6 is hydrogen, hydroxy, amino, lower alkyl, halogen, nitrile, haloalkyl, nitro, aryl, or a group C(O)$_m$R^{13}, wherein R^{13} is hydrogen, alkyl, alkenyl, alkynyl or phenyl any of which may be optionally substituted and m is 1 or 2; R^7 is hydrogen, lower alkyl, haloalkyl, C(O)$_m$R^{13} or halogen; or R^6 and R^7 together form an optionally substituted alkylene chain of 2 or 3 carbon atoms; R^8 is hydrogen, lower alkyl or halogen or the group R^7 and R^8 together form an oxo group; and R^9, R^{10}, R^{11} and R^{12} are independently selected from hydrogen or alkyl.

These compounds are active as *herbicides*.

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HERBICIDAL COMPOUNDS

The present invention relates to certain thiazole derivatives useful as herbicides, to herbicidal compositions containing these compounds and to processes for their preparation.

A large number of thiazole derivatives are known in particular as pharmaceuticals (see for example British Patent Number 1,099,389). British Patent Number 1,022,750 and US Patent Number 3,418,331 show that some are also known as herbicides. Further thiazole derivatives which are useful as herbicides are described in EP-A-368592.

According to the present invention there is provided a compound of formula (I); or a salt thereof: wherein R^1, R^2, R^3, R^4 and R^5 are independently selected from hydrogen, hydroxy, alkyl, alkoxy, alkylcarbonyl, halogen, nitrile, nitro, haloalkyl and haloalkoxy; R^6 is hydrogen, hydroxy, amino, mono- or di-alkyl amino, lower alkyl, halogen, nitrile, haloalkyl, nitro, aryl, or a group $C(O)_mR^{13}$ wherein R^{13} is hydrogen, alkyl, alkenyl, alkynyl or phenyl any of which may be optionally substituted and m is 1 or 2; R^7 is hydrogen, lower alkyl, haloalkyl, $C(O)_mR^{13}$ or halogen; or R^6 and R^7 together form an optionally substituted alkylene chain of 2 or 3 carbon atoms; R^8 is hydrogen, lower alkyl or halogen or the group R^7 and R^8 together form an oxo group; and the groups R^9, R^{10}, R^{11}, R^{12}, are independently selected from hydrogen or alkyl.

Salts of the compounds of formula (I) are available when the compound includes a carboxy group. Suitable salts are agriculturally acceptable salts such as sodium, potassium, calcium, ammonium or sulphonium salts. Examples of ammonium salts are those of formula $NR^aR^bR^cR^d$ wherein R^a, R^b, R^c, and R^d, are independently selected from hydrogen or C_{1-10} alkyl optionally substituted with for example hydroxy.

Examples of sulphonium salts include those of formula $R^aR^bR^cS$ where R^a, R^b and R^c are independently selected from optionally substituted C_{1-10} alkyl.

As used herein the term "alkyl" includes straight or branched chains suitably containing from 1 to 10 carbon atoms, preferably from 1 to 6 carbon atoms. The expression "lower alkyl" refers to alkyl groups having from 1 to 3 carbon atoms. Similarly the terms "alkenyl" and "alkynyl" refer to unsaturated straight or branched chains having from 2 to 10, preferably from 2 to 6 carbon atoms.

In addition the term "alkoxy" refers to group O-alkyl as defined above. The terms "haloalkyl" and "haloalkoxy" refer to the described alkyl groups and alkoxy groups respectively which are substituted by at least one halogen atom such as fluorine, chlorine, bromine or iodine. A particular haloalkyl group is trifluoromethyl and a particular haloalkoxy group is trifluoromethoxy.

As used herein the term "aryl" includes phenyl and naphthyl.

Suitable groups R^1, R^2, R^3, R^4 and R^5 are hydrogen, $C_{(1-6)}$ alkyl, $C_{(1-6)}$alkoxy, lower alkyl carbonyl, halo $C_{(1-6)}$ alkyl, halo (C_{1-6}) alkoxy or halo wherein the halo groups are selected from fluorine, chlorine, bromine and iodine.

Particular examples of the groups R^1, R^2, R^3,R^4 and R^5 are hydrogen, methyl, methoxy, trifluormethyl trifluoromethoxy, fluoro, chloro, bromo, iodo or nitrile.

In a particular embodiment R^1 and/or R^5 is other than hydrogen. Preferably R^1 and/or R^5 are halogen such as chlorine or fluorine and R^2, R^3 and R^4 are hydrogen.

In another embodiment, R^3 is other than hydrogen. In particular R^3 is halogen and R^1, R^2, R^4 and R^5 are hydrogen.

Suitably R^6 is hydrogen, lower alkyl such as methyl or ethyl, halogen such as fluorine, chlorine, bromine or iodine, amino, hydroxy, nitro, nitrile, carboxy or lower alkyl esters thereof or trifluoromethyl. Examples of R^6 are hydrogen, bromine or chlorine in particular hydrogen.

Suitably R^7 is selected from hydrogen, alkyl in particular lower alkyl, carboxy or lower alkyl esters thereof or haloalkyl such as trifluoromethyl or bromomethyl.

Suitably R^8 is selected from hydrogen or methyl or haloalkyl such as trifluoromethyl.

Preferably both R^7 and R^8 are hydrogen or methyl.

When R^6 and R^7 form an optionally substituted alkylene chain, the substituents are suitably selected from those described for R^{13} below.

Preferably R^9, R^{10}, R^{11} and R^{12} are hydrogen.

Suitable substituents for R^{13} include one or more groups selected from halo such as fluoro, chloro, bromo or iodo; hydroxy; C_{1-6} alkoxy; nitro; cycloalkyl; heterocyclic optionally substituted by oxo; nitrile; phenyl optionally substituted by nitro, halo such as chloro, alkoxy or carboxy or salts or C_{1-6} alkyl esters thereof; or alkylsilyl groups such as trimethylsilyl.

Examples of compounds of formula (I) are set out in Table I.

TABLE I

Compound No	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R12
1	Cl	H	H	H	Cl	H	H	H	H	H	H	H
2	Cl	H	H	H	F	H	H	H	H	H	H	H
3	F	H	H	H	F	H	H	H	H	H	H	H
4	H	H	H	H	H	H	H	H	H	H	H	H
5	H	H	H	H	F	H	CH_3	CH_3	H	H	H	H
6	H	H	Br	H	H	H	H	H	H	H	H	H
7	H	H	CH_3	H	H	H	H	H	H	H	H	H
8	H	H	Cl	H	H	H	H	H	H	H	H	H
9	H	H	Cl	H	H	Cl	H	H	H	H	H	H
10	H	Cl	Cl	H	H	H	H	H	H	H	H	H
11	H	CH_3	Cl	H	H	H	H	H	H	H	H	H
12	H	H	Cl	H	H	H	CH_3	CH_3	H	H	H	H
13	H	H	Cl	H	H	Br	H	H	H	H	H	H
14	H	H	H	H	H	H	CH_3	H	H	H	H	H

TABLE I (continued)

Compound No	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R12
15	H	H	H	H	H	Cl	H	H	H	H	H	H
16	Cl	H	H	H	H	H	H	H	H	H	H	H
17	H	H	H	H	H	H	CH_3	CH_3	H	H	H	H
18	Cl	H	H	H	Cl	H	CH_3	H	H	H	H	H
19	Cl	H	H	H	H	H	CH_3	CH_3	H	H	H	H
20	CH_3	H	H	H	H	H	H	H	H	H	H	H
21	CH_3	H	H	H	H	H	CH_3	H	H	H	H	H
22	CF_3	H	H	H	H	H	H	H	H	H	H	H
23	Br	H	H	H	H	H	H	H	H	H	H	H
24	Cl	H	H	CF_3	H	H	H	H	H	H	H	H
25	CH_2CH_3	H	H	H	H	H	H	H	H	H	H	H
26	H	Br	Br	H	H	H	H	H	H	H	H	H
27	H	H	Cl	H	H	CH_2CH_3	H	H	H	H	H	H
28	H	H	Cl	H	H	CH_3	H	H	H	H	H	H
29	H	H	Cl	H	H	H	$CH(CH_3)_2$	H	H	H	H	H

TABLE I (continued)

Compound No	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R12
30	H	H	Cl	H	H	Br	$CH(CH_3)_2$	H	H	H	H	H
31	H	H	Cl	H	H	Cl	CH_3	H	H	H	H	H
32	H	H	CF_3	H	H	H	H	H	H	H	H	H
33	H	H	I	H	H	H	H	H	H	H	H	H
34	H	H	I	H	H	Br	H	H	H	H	H	H
35	H	H	Cl	H	H	Cl	Br	H	H	H	H	H
36	H	H	Cl	H	H	Cl	$CO_2C_2H_5$	H	H	H	H	H
37	H	H	Cl	H	H	Cl	=0		H	H	H	H
38	H	H	Cl	H	H	NO_2	H	H	H	H	H	H
39	H	H	F	H	H	Br	H	H	H	H	H	H
40	F	H	H	H	F	Br	Br	H	H	H	H	H
41	H	CH_3	H	H	H	H	H	H	H	H	H	H
42	H	H	F	H	H	NO_2	H	H	H	H	H	H
43	H	H	F	H	H	H	H	H	H	H	H	H

TABLE I (continued)

Compound No	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R12
44	H	Cl	H	H	H	Br	H	H	H	H	H	H
45	H	H	Br	H	H	Br	H	H	H	H	H	H
46	H	H	Cl	H	H	Br	Br	H	H	H	H	H
47	H	H	CF_3	H	H	Br	H	H	H	H	H	H
48	F	H	Cl	H	H	NH_2	H	H	H	H	H	H
49	H	H	F	H	H	Br	H	H	H	H	H	H
50	H	F	F	H	H	Br	H	H	H	H	H	H
51	H	H	NO_2	H	H	H	H	H	H	H	H	H
52	F	H	H	H	F	Br	H	H	H	H	H	H
53	H	H	CH_3	H	H	Br	H	H	H	H	H	H
54	H	H	OCH_3	H	H	Br	H	H	H	H	H	H
55	H	H	$COCH_3$	H	H	Br	H	H	H	H	H	H
56	H	H	OH	H	H	Br	H	H	H	H	H	H
57	H	H	Cl	H	H	CO_2CH_3	H	H	H	H	H	H

TABLE I (continued)

Compound No	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	R^{10}	R^{11}	R12
58	H	H	Cl	H	H	CO_2H	H	H	H	H	H	H
59	H	H	OCH_3	H	H	OH	H	H	H	H	H	H
60	H	H	Cl	H	H	CH_3	CH_3	H	H	H	H	H
61	H	H	Cl	H	H	CH_2Br	CH_3	H	H	H	H	H
62	H	H	$C(CH_3)_3$	H	H	H	H	H	H	H	H	H
63	H	Cl	F	H	H	H	H	H	H	H	H	H
64	H	H	CH_3	H	H	H	H	H	H	H	H	H

Compounds of formula (I) can be prepared by reacting a compound of formula (II); wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are as defined in relation to formula (I) above; with a compound of formula (III): where R^9, R^{10}, R^{11} and R^{12} are as defined in relation to formula (I) and X and X^1 are may be the same or different and are leaving groups.

Suitable leaving groups X and X^1 are halogen atoms in particular chlorine, bromine, or mesylate or tosylate groups.

The reaction is suitably carried out in the presence of a base such as anhydrous potassium carbonate, or sodium hydride in a polar organic solvent such as dimethylformamide or dimethylsulphoxide. Moderate temperatures of from 20 to 80°C, conveniently at room temperature can be employed. The reaction may take some time to effect in significant yields, for example from 1 to 5 days.

Compounds of formula (I) where R^6 is halo can be prepared by reacting the corresponding compound where R^6 is hydrogen with a halogen such as chlorine or bromine.

The reaction is suitably carried out in a solvent such as glacial acetic acid and/ or chloroform at temperatures of from 20°-80°C.

Compounds of formula I where R^6 is nitrile can be prepared by subjecting the compound of formula (I) wherein R^6 is $-CO_2R^{13}$ to conventional procedures for transforming an alkoxy- carbonyl group to a -CN group.

Compounds of formula (I) where R^6 is nitro can be prepared by reacting an compound of formula (I) where R^6 is hydrogen with a mild nitrating agent such as nitronium tetrafluoroborate. The reaction is suitably effected in an organic solvent such as CH_3CN. Low temperatures of from 0°C - 15°C are suitably employed.

These nitro compounds can be converted to compounds of formula (I) where R^6 is amino by hydrogenation using conventional conditions. For instance, the compound can be reacted with hydrogen in the presence of a catalyst such as palladium on charcoal. The reaction is suitably effected in an organic solvent such as methanol or dichloromethane. Alkylation of the amino compound for example by reaction with an alkyl halide in the presence of base gives a compound of formula (I) where R^6 is the mono- or di-alkyl amino group.

Compounds of formula II can be prepared by reacting a compound of formula (IV): where R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are as defined in relation to formula (I) and R^{14} is an alkyl group such as methyl, with hydroxylamine which is generated in situ using an acid addition salt for example hydroxylamine hydrochloride and a base such as potassium hydroxide.

The reaction is suitably effected in an organic solvent such as methanol in the presence of a base such as potassium hydroxide. Moderate temperatures of from 20 to 60°C, conveniently room temperature are suitably employed.

Compounds of formula (IV) can be prepared by reacting a compound of formula (V): where R^1, R^2, R^3, R^4 and R^5 are as defined in relation to formula (I), with a compound of formula (VI): where R^6, R^7 and R^8 are as defined in relation to formula (I), R^{14} is as defined in relation to formula (IV) and X^2 is a leaving group.

Suitable leaving groups X^2 include halogen such as chlorine, mesylate or tosylate. The reaction is suitably effected in an organic solvent such as isopropylalcohol, toluene, methanol or ethanol at elevated temperatures of from 60 to 120°C. Compounds of formula (IV) and process for their preparation are described and claimed in EP-A-368592.

Compounds of formula (III), (V) and (VI) are either known compounds or they can be prepared from known compounds by conventional methods.

The compounds of formula (I) are active as herbicides and therefore, in a further aspect the invention provides a process for severely damaging or killing unwanted plants which process comprises applying to the plants, or to the growth medium of the plants, an effective amount of a compound of formulae (I) as hereinbefore defined.

The compounds of formula (I) are active against a broad range of weed species including monocotyledenous and dicotyledonous species. The compounds may show a useful selectivity into monocotyledonous crops, in particular cereal crops and rice.

The compounds of formula (I) may be applied directly to the plant (post -emergence application) or to the soil before the emergence of the plant (pre-emergence application) Preferably the compounds are applied post emergent.

The compounds of formulae (I) may be used on their own to inhibit the growth of, severely damage, or kill plants but are preferably used in the form of a herbicidal composition in combination with a carrier or diluent. These compositions from a further aspect of the invention.

Compositions containing compounds of formula (I) include both dilute compositions, which are ready for immediate use, and concentrated compositions, which require to be diluted before use, usually with water.

Preferably the compositions contain from 0.01% to 90% by weight of the active ingredient. Dilute compositions ready for use preferably contain from 0.01% to 2% of active ingredient, while concentrated compositions may contain from 20 to 90% of active ingredient, although from 20 to 70% is usually preferred.

The solid compositions may be in the form of granules, or dusting powders wherein the active ingredient is mixed with a finely divided solid diluent, eg, kaolin, bentonite, kieselguhr, dolomite, calcium carbonate, talc, powdered magnesia Fuller's earth and gypsum. They may also be in the form of dispersible powders or grains, comprising a wetting agent to facilitate the dispersion of the powder or grain in liquid. Solid compositions in the form of a powder may be applied as foliar dusts.

Liquid compositions may comprise a solution or dispersion of an active ingredient in water optionally containing a surface- active agent, or may comprise a solution or dispersion of an active ingredient in a water-immiscible organic solvent which is dispersed as droplets in water.

Surface-active agents may be of the cationic, anionic, or non-ionic type. The cationic agents are, for example, quaternary ammonium compounds (eg cetyltrimethylammonium bromide). Suitable anionic agents are soaps; salts or aliphatic mono esters of sulphuric acid, for example sodium lauryl sulphate; and salts of sulphonated aromatic compounds, for example sodium dodecylbenzenesulphonate, sodium, calcium and ammonium lignosulphonate, butylnaphthalene sulphonate, and .a mixture of the sodium of diisopropyl and triisoproplnaphthalenesulphonic acid. Suitable non-ionic agents are the condensation products of ethylene oxide with fatty alcohols such as oleyl alcohol and cetyl alcohol, or with alkylphenols such as octyl- or nonyl-phenol or octyl-cresol. Other non-ionic agents are the partial esters derived from long chain fatty acids and hexitol anhydrides, for example sorbitan monolaurate; the condensation products of the partial ester with ethylene oxide; and the lecithins.

The aqueous solutions or dispersions may be prepared by dissolving the active ingredient in water or an organic solvent optionally containing wetting or dispersing agent(s) and then, when organic solvents are used, adding the mixture so obtained to water optionally containing wetting or dispersing agent(s). Suitable organic solvents include, for example, ethylene di- chloride, isopropyl. alcohol, propylene glycol, diacetone alcohol, toluene, kerosene, methylnaphthalene, the xylenes and trichloroethylene.

The compositions for use in the form of aqueous solutions or dispersions are generally supplied in the form of a concentrate containing a high proporation of the active ingredient, and the concentrate is then diluted with water before use. The concentrates are usally required to withstand storage for prolonged periods and after such storage, to be capable of dilution with water to form aqueous preparations which remain homogeneous for a sufficient time to enable them to be applied by conventional spray equipment. Concentrates conveniently contain 20-90%, preferably 20-70%, by weight of the active ingredient(s). Dilute preparations ready for use may contain varying amounts of the active ingredient(s) depending upon the intended purpose; amounts of 0.01% to 10.0% and preferably 0.1% to 2%, by weight of active ingredient(s) are normally used.

A preferred form of concentrated composition comprising the active ingredient which has been finely divided and which has been dispersed in water in the presence of a surface-active agent and a suspending agent. Suitable suspending agents are hydrophilic colloids and include, for example, polyvinylpyrrolidone and sodium carboxymethylcellulose, and the vegetable gums, for example gum acacia and gum tragacanth. Preferred suspending agents are those which impart thixotropic properties too, and increase the viscosity of the concentrate. Examples of preferred suspending agents include hydrated colloidal mineral silicates, such as montmorillonite, beidellite, nontronite, hectorite, saponite, and saucorite. Bentonite is especially preferred. Other suspending agents include cellulose derivatives and polyvinyl alcohol.

The rate of application of the compounds of the invention will depend on a number of factors including, for example, the compound chosen for use, the idenity of the plants whose growth is to be inhibited, the formulations selected for use and whether the compound is to be applied for foliage or root uptake. As a general guide, however, an application rate of from 0.01 to 10 kilogrames per hectare is suitable.

The compositions of the invention may comprise, in addition to one or more compounds of formula (I) one or more compounds not of the invention but which possess biological activity. Accordingly in yet a still further embodiment the invention provides a herbicidal composition comprising a mixture of at least one herbicidal compound of formula (I) as hereinbefore defined with at least one other herbicide.

The other herbicide may be any herbicide not having the formula (I). It will generally be a herbicide having a complementary action in the particular application.

For example it may be desirable in certain circumstances to use the compound of formula (I) in admixture with a contact herbicide.

Examples of useful complementary herbicides include:

A. benzo-2,1,3-thiadiazin-4-one-2,2-dioxides such as bentazone;

B. hormone herbicides, particularly the phenoxy alkanoic acids such as MCPA, MCPA-thioethyl, dichlorprop, 2,4,5-T, MCPB, 2,4-D, 2,4-DB, mecoprop, trichlopyr, clopyralid, and their derivatives (eg. salts, esters and amides);

C. 1,3 dimethylpyrazole derivatives such as pyrazoxyfen, pyrazolate and benzofenap;

D. Dinitrophenols and their derivatives (eg. acetates) such as dinoterb, dinoseb and its ester, dinoseb acetate;

E. dinitroaniline herbicides such as dinitramine, trifluralin, ethalflurolin, pendimethalin, oryzalin;

F. arylurea herbicides such as diuron, flumeturon, metoxuron, neburon, isoproturon, chlorotoluron, chloroxuron, linuron, monolinuron, chlorobromuron, daimuron, methabenzthiazuron;

G. phenylcarbamoyloxyphenylcarbamates such as phenmedipham and desmedipham;

H. 2-phenylpyridazin-3-ones such as chloridazon and norflurazon;

I. uracil herbicides such as lenacil, bromacil and terbacil;

J. triazine herbicides such as atrazine, simazine, aziprotryne, cyanazine, prometryn, dimethametryn, simetryne, and terbutryn;

K. phosphorothioate herbicides such as piperophos, bensulide, and butamifos;

L. thiolcarbamate herbicides such as cycloate, vernolate, molinate, thiobencarb, butylate*, EPTC*, tri-allate, di-allate, esprocarb, tiocarbazil, pyridate, and dimepiperate;

M. 1,2,4-triazin-5-one herbicides such as metamitron and metribuzin;

N. benzoic acid herbicides such as 2,3,6-TBA, dicamba and chloramben;

O. anilide herbicides such as pretilachlor, butachlor, alachlor, propachlor, propanil, metazachlor, metolachlor, acetochlor, and dimethachlor;

P. dihalobenzonitrile herbicides such as dichlobenil, bromoxynil and ioxynil;

Q. haloalkanoic herbicides such as dalapon, TCA and salts thereof;

R. diphenylether herbicides such as lactofen, fluroglycofen or salts or ester thereof, nitrofen, bifenox, aciflurofen and salts and esters thereof, oxyfluorfen, fomesafen, chlornitrofen and chlomethoxyfen;

S. phenoxyphenoxypropionate herbicides such as diclofop and esters thereof such as the methyl ester, fluazifop and esters thereof, haloxyfop and esters thereof, quizalofop and esters thereof and fenoxaprop and esters thereof such as the ethyl ester;

T. cyclohexanedione herbicides such as alloxydim and salts thereof, sethoxydim, cycloxyidim, tralkoxydim, and clethodim;

U. sulfonyl urea herbicides such as chlorosulfuron, sulfometuron, metsulfuron and esters thereof; benzsulfuron and esters thereof such as DPX-M6313, chlorimuron and esters such as the ethyl ester thereof pirimisulfuron and esters such as the methyl ester thereof, 2-[3-(4-methoxy-6-methyl-1,3,5-triazin-zyl)-3-methylureidosulphonyl) benzoic acid esters such as the methyl ester thereof (DPX-LS300) and pyrazosulfuron;

V. imidazolidinone herbicides such as imazaquin, imazamethabenz, imazapyr and isopropylammonium salts thereof, imazethapyr;

W. arylanilide herbicides such as flamprop and esters thereof, benzoylprop-ethyl, diflufenican;

X. amino acid herbicides such as glyphosate and glufosinate and their salts and esters, sulphosate and bialaphos;

Y. organoarsenical herbicides such as monosodium methanearsonate (MSMA);

Z. herbicidal amide derivative such as napropamide, propyzamide, carbetamide, tebutam, bromobutide, isoxaben, naproanilide and naptalam;

AA. miscellaneous herbicides including ethofumesate, cinmethylin, difenzoquat and salts thereof such as the methyl sulphate salt, clomazone, oxadiazon, bromofenoxim, barban, tridiphane, flurochloridone, quinchlorac and mefanacet;

BB. Examples of useful contact herbicides include:
bipyridylium herbicides such as those in which the active entity is paraquat and those in which the active entity is diquat;

* These compounds are preferably employed in combination with a safener such as dichlormid.

The following examples illustrate the invention.

EXAMPLE 1

This Example illustrates the preparation of compound 1 in Table I.

Stage a

Preparation of 2-(2,6-dichlorophenyl)thiazol-4-ylacetohydroxamic acid

Potassium hydroxide (8g, 142 mmol) dissolved in hot MeoH (20 ml) was added dropwise to $H_2NOH.HCl$ (2 equiv., 5.7g, 82 mmol) dissolved in MeoN (60 ml) and the resulting mixture stirred at room temparature for 30 minutes. Ethyl-2-(2,6-dichlorophenyl)-thiazol-4-ylacetic ester (13g, 41 mmol) in MeoH (50 mml) was added to the reaction stirred at room temperature overnight. The precipitate was filtered off and the filtrate concentrated *in vacuo*. H_2O (100 ml) was added to the residue and the resulting solution acidified (dil. HCl). The precipitate was filtered off and air dried to yield the pot (10g, 75%).

^{1}HNMR (D_6-DMSO) 3.6(2H,s, $CH_2CONNOH$), 7.7 (4H, m, aromatic C-H and thiazolyl-H), 9.0(1H, bs, $CH_2CON\underline{H}OH$) and 10.8 (1H,bs, $CH_2CONHO\underline{H}$).

Stage b

Preparation of Dioxazine derivative

2-(2,6-dichlorophenyl)thiazol-4-ylacetohydroxamic acid (5.84g, 20 mmol) from step (a) dissolved in dry DMF (40 ml) and 1,2-dibromoethane (11.28g, 20 mmol) suspended in dry DMF (60 ml) and the resulting solution stirred at room temperature for 6 days. The reaction mixture was filtered through celite (or mghHo) and the filtrate concentrated *in vacuo*. H_2O (100 ml) was added to the residue, then extracted with Et_2O. The combined organic extracts were washed with brine, dried ($MgSO_4$) and concentrated *in vacuo*. The product (3g, 68%) was purified by flash chromatography (in Et_2O).

^{1}H NMR ($CDCl_3$) 3.8(2H,s, CH_2), 4.1(2H,t, OCH_2 CH_2O), 4.35(2H,t, OCH_2CH_2O), 7.35(4H,m, aromatic C-H and thiasolyl-H).

EXAMPLE 2

This Example illustrates the preparation of compound 2 in Table I.

Stage a

Preparation of 2-(2-chloro-6-fluorophenyl)thiazol-4-yl- acetohydroxamic acid

The reaction as described in Example 1(a) was carried out using methyl 2-(2-chloro-6-fluorophenyl)thiazol-4-yl acetic ester (7.9g, 28 mmol) to give the desired product (3.7g, 46%).

^{1}H NMR (d$_6$-DMSO) 3.75(2H,s, CH$_2$), 7.7(3H,m, aromatic C-H), 7.9(1H,s, thiazolyl-H 9.15(1H,bs, $\overset{O}{\text{C}}$-MHon), and 10.9 (1H, bs, $\overset{O}{\text{C}}$-MHon).

Stage b

Preparation of (2-chloro-6-fluoro-phenyl) dioxazine derivative

The reaction as described in Example 1(b) was carried out using 2-(2-chloro-6-fluorophenyl)thiazol-4-yl acetohydroxamic acid (3.4g, 12 mmol) to give the desired product (1.9g, 51%).

^{1}H NMR CDCl$_3$ 3.8(2H,s, CH$_2$), 4.1(2H,t, OCH$_2$CH$_2$O), 4.35(2H,t, OCH$_2$CH$_2$O), and 7.25(4H,m, aromatic C-H and thiazoly-H).

EXAMPLE 3

This Example illustrate the preparation of compound 3 in Table I.

Stage a

Preparation of 2(2,6-difluorophenyl)thiazol-4-yl acetohydroxamic acid

The reaction as described out in Example 1(a) was carried out using methyl-2-(2,6-difluorophenyl)thiazol-4-yl acetic ester (6.1g, 23 mmol) to give the desired product (2.8g, 45%).

^{1}H NMR (d$_6$-DMSO) 3.75(2H,s, CH$_2$), 7.65(3H,m, aromatic C-H), 7.9(1H,s, thiazolyl-H), 9.1(1H,s, $\overset{O}{\text{C}}$-NH-OH), and 10.9(1H,bs, $\overset{O}{\text{C}}$-NHOH).

Stage b

Preparation of (2,6-difluorophenyl)diaxazine derivative

The reaction as described in Example 1b was carried out using 2-(2,6-difluorophenyl) thiazol-4-yl acetohydroxamic acid (2.5g, 9.25 mmol) to give the desired product (1.75g, 62%).

^{1}H NMR CDCl$_3$ 3.8(2H,s, CH$_2$), 4.1(2H,t, OCH$_2$CH$_2$O), 4.35(2H,t, OCH$_2$CH$_2$O), 72(4H,m, aromatic C-H and thiazolyl-H).

EXAMPLE 4

This Example illustrates the preparation of compound No. 4 in Table 1.

Step a

Preparation of Ethyl-2-phenyl-thiazol-4-acetic ester

Thiobenzamide (15g), ethyl-γ-chloroacetoacetate (18.03g), toluene (300ml) and piperidine (trace) when heated under reflux for several hours. The reaction mixture was then washed with water, dried over magnesium sulphate, filtered and evaporated to give a brown oil. This was distilled under reduced pressure to give one main fraction boiling at 143-160°C (16.24g).

Step b

Preparation of 2-phenyl-thiazol-4-ylacetohydroxamic acid

Hydroxylamine hydrochloride (C.14g) was dissolved in methanol (MeOH) (50ml) and potassium hydroxide (16.8g) added together with more methanol (25ml) at room temperature with stirring. The flask was cooled in an ice-bath for 5 minutes. The product of step (a) (16.24g) was added with stirring and the mixture filtered. The remaining solution was cooled in a refridgerator for 2 hours after which the methanol was removed under reduced pressure. The resultant yellow oil was dissolved in water (100ml) and diethylether (15ml) and remaining solid filtered off. The aqueous phase ws acidified to a pH of 6 with glacial acetic acid and the solid product filtered, dried and crystallised from ethyl acetate/ethanol to give a crystalline solid (8.58g).

Step c

The hydroxamic acid from step (b) and 1,2 dibromoethane (4.02g) were dissolved in dimethylformamide (30ml) together with finely ground potassium carbonate (5.93g). The reaction was stirred vigously overnight after which the solvent was removed under reduced pressure. The residue was extracted into chloroform and water. The chloroform layer was dried over magesium sulphate, filtered and evaporated to give a brown oil. Distallation under reduced pressure (0.01 torr) at 210-215°C give the desired product (1.26g) as an orange oil.

EXAMPLE 5

Compound 5 in Table 1 was obtained by a method analogous to that described in Example 4, as a white solid (mp 54-6°C).

The herbicidal activity of some of the compounds was tested as follows:-

Each compound in the appropriate concentration was incorporated into a 4% emulsion of methylcylohexanone and 0.4% blend of 3.6 parts Tween 20 and 1 part Span 80. Tween 20 is a Trade Mark for a surface active agent comprising a condensate of 20 molar proportions of ethylene oxide with sorbitan laurate. Span 80 is a Trade Mark for a surface-active agent comprising sorbitan monolaurate. Formulation was effected by dissolving the compound in the requisite amount of solvent/surfactant blend. If necessary, glass beads were added, the total liquid volume adjusted to 5ml with water, and the mixture shaken to effect complete dissolution of the compound. The formulation so prepared, after removal of beads where necessary, was then diluted to final spray volume (45ml) with water.

The spray compositions so prepared were sprayed onto young pot plants (post-emergence test) at a rate equivalent to 1000 litres per hectare. Damage to plants was assessed 13 days after spraying by comparison with untreated plants, on a scale of 0 to 9 where 0 is 0% damage, 1 is 1-5% damage, 2 is 6-15% damage, 3 is 16-25% damage, 4 is 26-35% damage, 5 is 36-59% damage, 6 is 60-69% damage, 7 is 70-79% damage, 8 is 80-89% damage and 9 is 90-100% damage.

In a test carried out to detect pre-emergence herbicidal activity, crop seeds were sown at 2 cm depth (i.e. Sb, Ct, Rp, Ww, Mz,Rc, Sy) and weed seeds at 1cm depth beneath compost and sprayed with the compositions at the rate of 1000 litres per hectate. 20 days after spraying, the seedlings in the sprayed plastic trays were compared with the seedlings in unsprayed control trays, the damage being assessed on the same scale of 0 - 9.

The results of the tests are given in Table II below.

TABLE II

COMPOUND NO.	RATE OF APPLN. kg/ha	PRE- OR POST EMERGENCE APPLN.	Sb	Rp	Ct	Sy	Mz	Ww	Rc	Sn	Ip	Am	Pi	Ca	Ga	Xa	Po	Ab	Cv	Co	Ot/ AV	Dg	Pu	Al	St	Ec	Sh	Ag	Cn
1	5	Pre	3	2	1	4	5	5	5	2	1	3	3	2	3	2	-	3	-	1	5	5	-	5	4	4	4	5	3
		Post	3	2	3	2	4	4	2	3	1	3	3	3	3	2	-	3	-	4	4	4	-	3	3	4	3	4	1
4	5	Pre	1	1	0	0	2	3	3	4	0	3	-	2	-	0	2	0	-	-	4	5	5	-	4	4	0	0	0
		Post	1	1	0	1	0	0	0	3	-	2	0	3	-	0	2	2	0	-	0	3	0	-	2	0	0	0	0
5	5	Pre	1	2	0	2	3	4	5	4	0	3	-	2	-	-	2	2	-	-	4	4	5	-	4	5	4	5	5
		Post	0	2	0	0	0	3	0	2	0	1	-	0	-	2	2	0	0	-	2	2	1	-	0	0	0	2	0

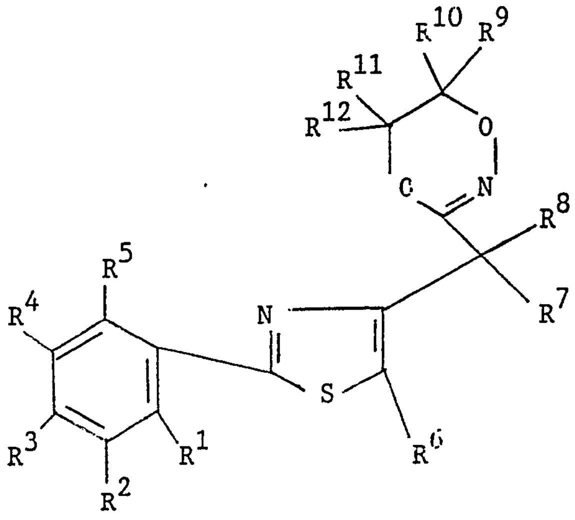
TABLE III

Abbreviations used for Test Plants in Table II

Sb - Sugar beet
Rp - Rape
Ct - Cotton
Sy - Soybean
Mz - Maize
Rc - Rice
Ww - Winter wheat
Bd - *Senecio vulgaris*
Ip - *Ipomoea purpurea*
Am - *Amaranthus retroflexus*
Pi - *Polygonum aviculare*
Ca - *Chenopodium album*
Ga - *Galium aparine*
Xa - *Xanthium spinosum*
Po - *Portulaca oleracea*
Ab - *Abutilon theophrasti*
Ot/Av - Oats cultivated in pre-emergence test and *Avena fatua* (wild oats) in post-emergence test
Dg - *Digitaria sanguinalis*
Pu - *Poa annua*
Al - *Alopecuris myosuroides*
St - *Setaria viridis*
Ec - *Echinochloa crus-galli*
Sh - *Sorghum halepense*
Ag - *Agropyron repens*
Ce - *Cyperus rotundus*

CHEMICAL FORMULAE

(in description)



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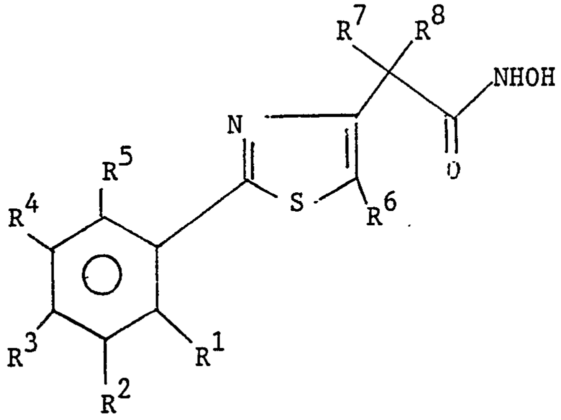

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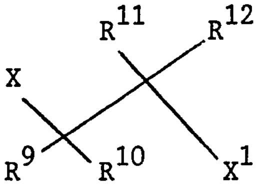

(III)

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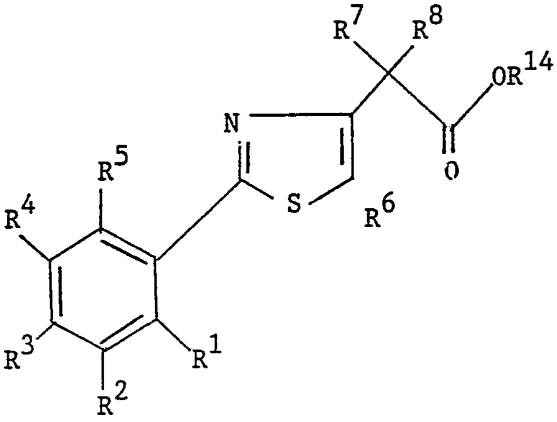

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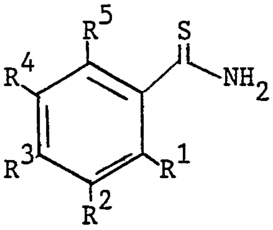

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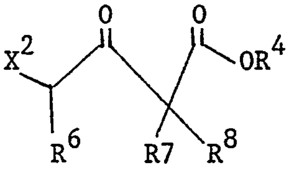
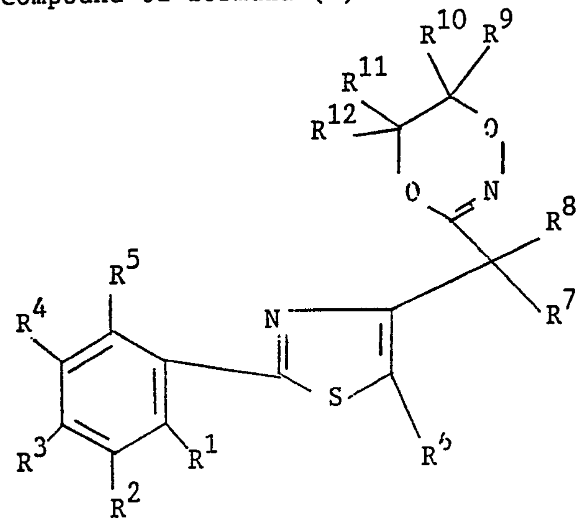


(VI)

CLAIMS

1. A compound of formula (I):



(I)

or a salt thereof: wherein R^1, R^2, R^3, R^4 and R^5 are independently selected from hydrogen, hydroxy, alkyl, alkoxy, alkylcarbonyl, halogen, nitrile, nitro, haloalkyl and haloalkoxy; R^6 is hydrogen, hydroxy, amino, lower alkyl, halogen, nitrile, haloalkyl, nitro, aryl, or a group $C(O)_mR^{13}$, wherein R^{13} is hydrogen, alkyl, alkenyl, alkynyl or phenyl any of which may be optionally substituted and m is 1 or 2; R^7 is hydrogen, lower alkyl, haloalkyl, $C(O)_mR^{13}$ or halogen; or R^6 and R^7 together form an optionally substituted alkylene chain of 2 or 3 carbon atoms; R^8 is hydrogen, lower alkyl or halogen or the group R^7 and R^8 together form an oxo group; and R^9, R^{10}, R^{11} and R^{12} are independently selected from hydrogen or alkyl.

2. A compound according to claim 1 wherein R^6 is hydrogen, bromine or chlorine.

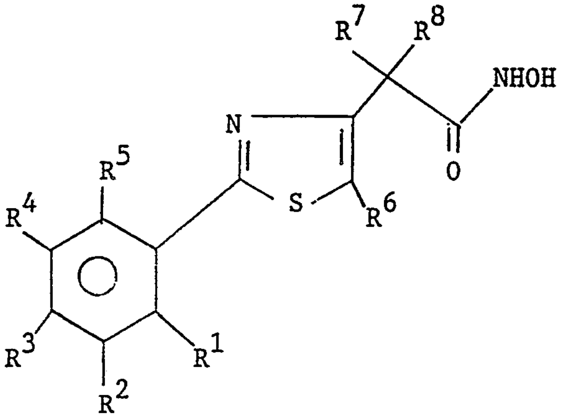
3. A compound according to claim 1 or claim 2 wherein R^1 and/or R^5 are other than hydrogen.

4. A compound according to claim 3 wherein at least one of R^1 and R^5 is halogen and the other as well as R^2, R^3 and R^4 are hydrogen.

5. A compound according to claim 1 or claim 2 wherein R^3 is halogen, and R^1, R^2, R^4 and R^5 are hydrogen.

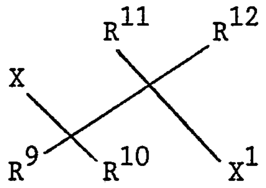
6. A compound according to any one of the preceding claims where R^7 and R^8 are selected from hydrogen or methyl.

7. A process for preparing a compound according to claim 1 which process comprises reacting a compound of formula (II):



(II)

wherein R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are as defined in claim 1 above; with a compound of formula (III):



(III)

where R^9, R^{10}, R^{11} and R^{12} are as defined in relation to formula (I) and X and X^1 are may be the same or different and are leaving groups.

8. A herbicidal composition comprising a compound of formula (I) as defined in claim 1 in combination with an agriculturally acceptable carrier or diluent.

9. A herbicidal composition according to claim 8 which further comprises a herbicide not of formula (I).

10. A method for killing or controlling unwanted plants which method comprises applying to the plant or to a locus thereof, any effective amount of a compound of formula (I) as defined in claim 1.

Examiner's report to the Comptroller under Section 17 (The Search Report)	Application number 9209121.4

Relevant Technical fields

(i) UK Cl (Edition K) C2C

(ii) Int CL (Edition 5) C07D

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASE: CAS ONLINE

Search Examiner

D S LUCAS

Date of Search

24.6.92

Documents considered relevant following a search in respect of claims 1 TO 10

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
A	GB 1022750 A (SHELL) see Claims 1 and 21	1 to 10
A	EP 0368592 A (ICI) see Claims 3 and 8	1 to 10

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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