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HERBICIDAL CARBOXAMIDE DERIVATIVES

The present invention relates to herbicidal carboxamide derivatives, their preparation, herbicidal compositions containing such derivatives and their use in combating undesired plant growth.

5 The herbicidal activity of 2-phenoxy-3-pyridine carboxamide compounds is well known. In 1981 and 1982 three U.S. patent specifications were published , Nos. 4 251 263, 4 270 946 and 4 327 218, directed to A.D. Gutman's work on 2-phoxynicotinamide
10 herbicides. His later review article, Chapter 5 of "Synthesis and Chemistry of Agrochemicals" (1987) published by the American Chemical Society, shows that his investigations started with 2-phoxynicotinic acids (which were found to be inactive) progressed to
15 N-alkyl amide derivatives (found to have weak herbicidal activity), and then concentrated on N-phenyl and N-benzyl amides as the most active of the compound type. Indeed, Diflufenican[N-(2,4-difluoro-phenyl)-2-(3-trifluoromethylphenoxy)-3-pyridine
20 carboxamide] was subsequently developed, by a different research group, as a commercial herbicide for use against broad-leaved weeds in winter cereals, such as winter wheat and barley.

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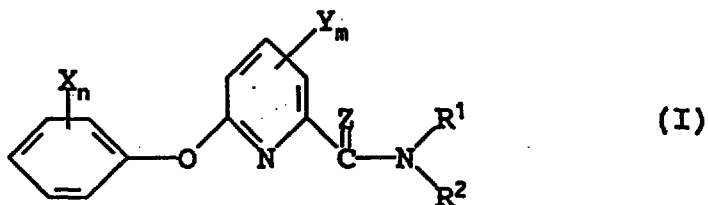
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U.S. Patent Specification No. 4 251 263 is concerned with the N-alkyl amides of Gutman, and related N-alkenyl and N-alkynyl amides. The compound documented as being the most active of the aliphatic amides prepared and tested is N-(1,1-dimethylprop-2-ynyl)-2-(3-trifluoromethylphenoxy)-3-pyridine carboxamide, which gives 85% control preemergence and only 57% control postemergence on specified narrow- and broad-leaved species.

Suprisingly, it has now been found that 2-phenoxy-6-pyridine carboxamide compounds with aliphatic (both straight chain and alicyclic) and other substitution of the amide nitrogen atom have unexpectedly high levels of herbicidal activity against representative narrow- and broad-leaved test species in pre- and/or post-emergence application; certain examples exhibiting 90 to 100% effectiveness against test species both pre- and post-emergence.

The present invention accordingly provides a compound of the general formula I



wherein

n is an integer from 1 to 5 and the or each X independently represents a hydrogen or halogen atom, an alkyl or alkoxy group optionally substituted by one or more of the same or different substituents selected from halogen atoms and cyano, hydroxy and alkoxy groups, or a cyano, nitro, alkenyloxy, alkynyloxy, alkylthio, haloalkylthio, alkenylthio or alkynylthio group;

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m is 0 or an integer from 1 to 3 and the or each Y independently represents a halogen atom or an alkyl or haloalkyl group;

Z represents an oxygen atom or a sulphur atom;

5 and

R¹ and R² each, independently, represents a hydrogen atom, an alkyl group optionally substituted by one or more of the same or different substituents selected from halogen atoms or hydroxy, cyano, 10 alkoxy, alkylthio, alkoxycarbonyl, or mono- or di-alkylamino groups, an alkenyl, alkynyl, cycloalkyl, or optionally substituted cycloalkylalkyl group, or a hydroxy, alkoxy, alkenyloxy, alkynyloxy, alkoxycarbonyl, amino, 15 mono- or di-alkylamino, alkoxycarbonylamino group, an arylamino group optionally substituted by a halogen atom, or a dialkylcarbonyl group;

or

R¹ and R² together represent an alkylene chain which is optionally interrupted by an oxygen or sulphur atom or by a group -NR- in which R represents a hydrogen atom or an alkyl group.

When any of the substituents X, Y, R¹ and R² represents or contains an alkyl, alkenyl or alkynyl 25 substituent group, this may be linear or branched and suitably has up to 12, preferably up to 8 and especially up to 5, carbon atoms. Thus, for example, an alkyl group R² may be butyl, e.g. i-butyl, n-butyl, sec-butyl or tert-butyl. Where a cycloalkyl 30 substituent group is present, this suitably has from 3 to 8, preferably 3 to 6, carbon atom ring atoms. An aryl group is suitably phenyl. An alkylene chain suitably has 3 to 6, preferably 4 or 5, chain members. A halogen atom suitably denotes a fluorine, chlorine,



bromine or iodine atom; preferred haloalkyl groups are trifluoromethyl, trifluoroethyl and fluoroethyl.

The substituent(s) X_n may be at any free position or combination of positions on the phenoxy ring.

5 One phenoxy substituent X is desirably located at the 3- (or meta-) position and is preferably a hydrogen, fluorine, chlorine or bromine atom or a nitro, ethyl, methoxy or, especially, a trifluoromethyl group. When additional substituents X
10 are present, they are suitably located at the 4- and/or 5- position and may be the same as, or, preferably, different to the meta-substituent. Such additional substituent(s), X, are preferably selected from chlorine and, especially, fluorine atoms.

15 Substituent(s) X_n may, of course, be at other positions, and may be, for example, 2, 3- or 2,5-dimethyl.

Preferably only one or two substituents X are present and, most preferably one of or the X
20 represents a 3-trifluoromethyl substituent.

Preferably m is 0.

Preferably Z represents an oxygen atom.

The radicals, R^1 and R^2 , when individually present may be the same or different. Preferably R^1
25 represents a hydrogen atom or a C_{1-4} alkyl or C_{2-4} alkenyl, suitably allyl, group, most preferably hydrogen or C_{1-4} alkyl, while R^2 represents an unsubstituted C_{1-8} alkyl group, especially C_{1-6} alkyl, a C_{1-4} alkyl group substituted by fluorine, hydroxy, cyano, C_{1-2} alkoxy, (C_{1-2} alkoxy)carbonyl, or mono- or
30 di-(C_{1-2} alkyl)amino, for example fluoroethyl, trifluoroethyl, cyanopropyl, hydroxyethyl, methoxyethyl, ethoxycarbonylmethyl, or dimethylaminoethyl, a C_{3-8} cycloalkyl group, especially cyclopropyl,
35 cyclobutyl, cyclopentyl or cyclohexyl, a C_{2-4} alkenyl



group, for example allyl or methylallyl, a C_{2-4} alkynyl group, for example propynyl, a C_{1-4} alkoxy group, for example ethoxy, a $(C_{1-4} \text{ alkyl})$ amino group, for example methylamino, a C_{2-4} alkenyloxy group, for
5 example propenyloxy, a $(C_{1-2} \text{ alkoxy})$ carbonyl group, for example ethoxycarbonyl, a $(C_{1-2} \text{ alkoxy})$ carbonyl-amino group, for example ethoxycarbonylamino, a $di(C_{1-2} \text{ alkyl})$ carbamoyl group, for example dimethylcarbamoyl, an arylamino group, for example
10 phenylamino or p-chlorophenylamino, or a halo-substituted $(C_{3-6} \text{ cycloalkyl})C_{1-4}$ alkyl group, for example chloro-substituted cyclopropylmethyl.

It is especially preferred that either R^1 represents a hydrogen atom while R^2 represents an
15 unsubstituted C_{1-5} alkyl group, a C_{1-2} alkyl group substituted by fluorine or methoxy, a C_{3-6} cycloalkyl group, a C_3 alkenyl group, a C_3 alkynyl group, a C_{1-2} alkoxy group, a C_3 alkenyloxy group or a chloro-substituted cyclopropylmethyl group, or R^1
20 represents a C_{1-3} alkyl group while R^2 represents the same C_{1-3} alkyl group or a chloro-substituted cyclopropylmethyl group.

Particularly preferred are compounds in which R^1 represents a hydrogen atom and R^2 represents an ethyl,
25 propyl, cyclopropyl or cyclobutyl group.

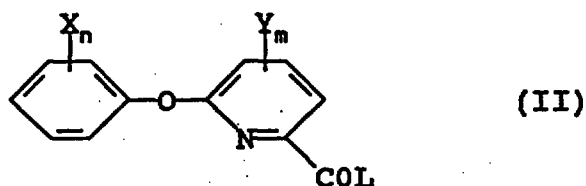
When R^1 and R^2 together represent an alkylene chain, suitably the chain consists of 4 or 5 chain atoms, and is for example a group $-(CH_2)_4-$,
30 $-(CH_2)_2O(CH_2)_2-$ or $-(CH_2)_2NR(CH_2)_2-$ in which R is a C_{1-2} alkyl group, suitably methyl. Preferably R^1 and R^2 is a $-(CH_2)_4-$ group.

The compounds of general formula I may be prepared either by reaction of an appropriate phenoxypicolinic acid derivative with an appropriate
35 amine (method A) or by reaction of an appropriate



2-halo-6-pyridine carboxamide derivative with an appropriate alkali metal phenolate (method B). Such methods constitute further aspects of the present invention.

- 5 In accordance with method A, a compound of the general formula I in which Z is oxygen, is prepared by reacting a compound of the general formula II



- 10 in which X_n and Y_m are as hereinbefore defined and L represents a leaving group, with an amine of the general formula NHR^1R^2 in which R^1 and R^2 are as defined above.

- 15 A leaving group is any group that will, under the reaction conditions, cleave from the starting material thus promoting reaction at a specific site.

The leaving group L may suitably be a halogen atom, for example a bromine or, especially, a chlorine atom or an alkoxy group, suitably C_{1-4} alkoxy, especially methoxy.

- 20 The process variant A is suitably carried out in the presence of an inert organic solvent, for example dimethylformamide or an aromatic hydrocarbon, for example benzene or toluene, or a halogenated hydrocarbon, for example dichloromethane or an ether, 25 for example diethyl ether, or an ester, for example ethyl acetate; suitably at a temperature in the range of from 0 to 100°C.

Suitably, the reaction is carried out using substantially equimolar amounts of the reactants.

- 30 However, it can be expedient to use one reactant in

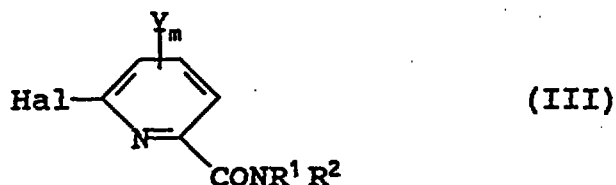


excess, conveniently the amine, for example such that the molar ratio of phenoxypicolinic acid derivative to amine is in the range 1:1 to 1.1.

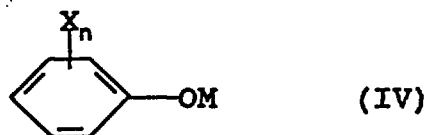
5 When L represents a halogen atom the reaction is suitably carried out at a temperature in the range 0 to 50°C, preferably at ambient temperature, and suitably in the presence of a base, for example potassium carbonate or, preferably, an amine base, such as triethylamine or excess amine starting
10 material.

When L represents an alkoxy group the reaction is suitably carried out at a temperature in the range 0 to 100°C, preferably at room temperature (or 20°C) and in the absence of an added base.

15 In accordance with method B, a compound of the general formula I in which Z is oxygen, is prepared by reacting a compound of the general formula III



20 in which Y_m , R^1 and R^2 are as defined above and Hal represents a halogen atom with a compound of the general formula IV



in which X_n is as defined above and M represents an alkali metal atom.

25 Suitably, Hal represents a bromine atom or, especially, a chlorine atom. Suitably, R represents a



potassium atom or, especially, a sodium atom.

The reaction B may be carried out by preparation of the alkali metal phenolate from the phenol using an alkali metal alkoxide, such as sodium methoxide,
5 followed by treatment of the phenolate with a substantially equimolar amount of reactant III, suitably at an elevated temperature, for example under reflux, with a copper catalyst, such as cuprous chloride, in pyridine in the presence of an aromatic
10 hydrocarbon, such as xylene, as is described in U.K. Patent Specification No. 2 050 168A.

Alternatively the process variant B could be carried out in the presence of an alkali metal hydride, for example sodium hydride, in a dry solvent,
15 such as dimethylformamide, suitably at an elevated temperature, for example at a temperature in the range of from 50°C to 125°C, or in the presence of an alkali metal carbonate, for example sodium or potassium carbonate, followed by treatment with cuprous oxide
20 and/or copper powder in an organic solvent, such as dimethylformamide or quinoline, suitably at a temperature in the range of from 20 to 150°C and conveniently at the reflux temperature of the reaction mixture.

25 Compounds of the general formula I wherein Z represents a sulphur atom are suitably prepared by reaction of a compound of the general formula I wherein Z represents an oxygen atom, with phosphorous pentasulphide under standard conditions, for example
30 by heating, suitably under reflux, in the presence of an inert aromatic solvent, for example benzene, toluene, pyridine or quinoline.

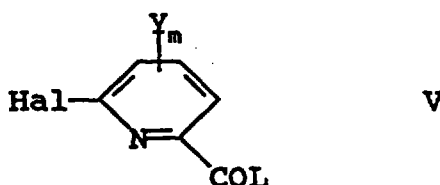
The compounds of the present invention may be isolated and purified by conventional techniques, for
35 example by solvent extraction, evaporation followed by



recrystallisation or by chromatography on silica.

Compounds of formula II may be prepared from corresponding phenoxy-substituted picolinic acids by standard methods for the preparation or, for example, esters, using, for example, alcohols and acid catalysts or thionyl chloride, or of acid chlorides and acid bromides, using, for example, thionyl chloride or thionyl bromide. The acid compounds themselves can be prepared by standard methods from chloropicolinic acid or ester thereof. Chloropicolinic acid, or ester thereof, may be prepared by the methods described in J. Pharm. Belg. (1980), 35 1, 5-11.

Compounds of formula III may suitably be prepared by an analogous method to that of method A, by reacting a substituted amine of formula NHR^1R^2 with a 2-halo-6-pyridine carboxylic acid derivative of the general formula V



in which Y_m , Hal and L are as defined above. Compounds of formula V may be prepared by conventional techniques from picolinic acid.

The substituted amines NHR^1R^2 and the phenolates of formula IV are either known or can be prepared by conventional techniques.

The compounds of the invention have been found to have a surprisingly high herbicidal activity with a wide spectrum of activity against grasses and, especially, broadleaved weeds, including Alopecurus myosuroides (blackgrass), Avena fatua (wild oat),



Sterea faberii (giant foxtail), Setaria viridis (green foxtail), Ipomoea purpurea (morning glory), Galium aparine (cleavers), Solanum nigrum (black nightshade), Veronica persica (speedwell) and Stellaria media (chickweed), when applied pre- and post-emergence. Examples have been found to show selectivity to small grain cereals, for example maize, wheat, barley and rice, and to broad-leaved crops, for example soya, sunflower and cotton, indicating that they may be useful in combating weeds growing in such crops.

The invention further provides a herbicidal composition comprising a compound of formula I as defined above in association with a carrier, and a method of making such a composition which comprises bringing a compound of formula I into association with a carrier.

The invention also provides the use of such a compound or composition according to the invention as a herbicide. Further in accordance with the invention there is provided a method of combating undesired plant growth at a locus by treating the locus with a compound or composition according to the invention. Application to the locus may be pre-emergence or post-emergence. The dosage of active ingredient used, may, for example, be in the range of from 0.01 to 10 kg/ha, suitably 0.05 to 4 kg/ha. The locus may, for example, be the soil or plants in a crop area, typical crops being cereals such as wheat and barley, and broad-leaved crops, such as soya, sunflower and cotton.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage,



transport or handling. A carrier may be a solid or a liquid, including a material which is normally gaseous but which has been compressed to form a liquid, and any of the carriers normally used in formulating
5 herbicidal compositions may be used. Preferably compositions according to the invention contain 0.5 to 95% by weight of active ingredient.

Suitable solid carriers include natural and synthetic clays and silicates, for example natural
10 silicas such as diatomaceous earths; magnesium silicates, for example talcs; magnesium aluminium silicates, for example attapulgites and vermiculites; aluminium silicates, for example kaolinites, montmorillonites and micas; calcium carbonate; calcium
15 sulphate; ammonium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements, for example carbon and sulphur; natural and synthetic resins, for example coumarone resins, polyvinyl chloride, and styrene polymers and
20 copolymers; solid polychlorophenols; bitumen; waxes; and solid fertilisers, for example superphosphates.

Suitable liquid carriers include water; alcohols, for example isopropanol and glycols; ketones, for example acetone, methyl ethyl ketone, methyl isobutyl
25 ketone and cyclohexanone; ethers; aromatic or araliphatic hydrocarbons, for example benzene, toluene and xylene; petroleum fractions, for example kerosine and light mineral oils; chlorinated hydrocarbons, for example carbon tetrachloride, perchloroethylene and
30 trichloroethane. Mixtures of different liquids are often suitable.

Agricultural compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application.
35 The presence of small amounts of a carrier which is a



surface-active agent facilitates this process of dilution. Thus preferably at least one carrier in a composition according to the invention is a surface-active agent. For example the composition may
5 contain at least two carriers, at least one of which is a surface-active agent.

A surface-active agent may be an emulsifying agent, a dispersing agent or a wetting agent; it may be nonionic or ionic. Examples of suitable
10 surface-active agents include the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation products of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene
15 oxide; fatty acid esters of glycerol, sorbitol, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty alcohol or alkyl phenols, for example p-octylphenol or p-octylcresol, with ethylene
20 oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example sodium
25 lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

30 The compositions of the invention may for example be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 25, 50 or 75% w of active
35 ingredient and usually contain in addition to solid

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inert carrier, 3-10% w of a dispersing agent and, where necessary, 0-10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing $\frac{1}{2}$ -10% w of active ingredient. Granules are usually prepared to have a size between 10 and 100 BS mesh (1.676 - 0.152 mm), and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain $\frac{1}{2}$ -75% w active ingredient and 0-10% w of additives such as stabilisers, surfactants, slow release modifiers and binding agents. The so-called "dry flowable powders" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent and, when necessary, co-solvent, 10-50% w/v active ingredient, 2-20% w/v emulsifiers and 0-20% w/v of other additives such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are usually compounded so as to obtain a stable, non-sedimenting flowable product and usually contain 10-75% w active ingredient, 0.5-15% w of dispersing agents, 0.1-10% w of suspending agents such as protective colloids and thixotropic agents, 0-10% w of other additives such as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as anti-freeze agents for water.



Aqueous dispersions and emulsions, for example compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the invention. The said emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonnaise'-like consistency.

The composition of the invention may also contain other ingredients, for example compounds possessing insecticidal or fungicidal properties or other herbicides.

The following Examples illustrate the invention. Example 1 illustrates the preparation of an ester of general formula II and Examples 2 to 63 relate to the preparation of compounds of general formula I; Examples 2 to 61 by Method A, Example 62 by Method B, and Example 63 by conversion of a compound of general formula I in which Z is oxygen to one in which Z is sulphur. All structures were confirmed by mass spectroscopy and/or 300'H nmr.

Example 1

Preparation of methyl-6-(3- α,α,α -trifluoromethylphenoxy)picolinate

A solution of sodium methoxide (from 1.3g sodium in 20 ml methanol) was added to a solution of 3- α,α,α -trifluoromethylphenol (8.9g) in xylene (50ml). The solvents were evaporated in vacuo to give the dry sodium phenolate. Pyridine (25ml) and xylene (50ml) were added, followed by cuprous chloride (1.5g) and the mixture heated to reflux. A solution of methyl-6-chloropicolinate (8.5g) in xylene (50ml) was added dropwise. The mixture was refluxed for a further 14 hours. After cooling, the mixture was poured into water (500ml) and acidified with dilute



5 sulphuric acid. The xylene layer was separated and the aqueous layer further extracted with diethyl ether. The combined extracts were washed with brine, dried over anhydrous magnesium sulphate and evaporated. The residue was purified on a silica gel column using 5% (v/v) diethyl ether/dichloromethane as eluant to give the title compound (7.4g) as a yellow solid of melting point 43-44°C.

Analysis (%) :

10 $C_{14}H_{10}O_3NF_3$: Calc. : C 56.6 H 3.4 N 4.7
Found : C 55.6 H 3.4 N 4.8

m/e: Theory: 297
Found : 297

Example 2

15 N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

(a) Preparation of 6-(3- α,α,α -trifluoromethylphenoxy) picolinic acid

20 A solution of methyl-6-(3- α,α,α -trifluoromethylphenoxy)-picolinate (8g) in 50% aqueous methanol (45 ml) containing sodium hydroxide (2.5g) was refluxed for 3 hours. The methanol was evaporated, more water added to the residue and the aqueous solution extracted with diethyl
25 ether. The aqueous phase was then acidified with dilute hydrochloric acid to precipitate 6-(3- α,α,α -trifluoromethylphenoxy)picolinic acid (7.1g) as a white solid of melting point 92-93°C.

Analysis (%) :

30 $C_{13}H_8NO_3F_3$: Calc : C 55.1 H 2.8 N 4.9
Found : C 53.3 H 3.0 N 5.0

m/e Theory : 283
Found : 283



b) Preparation of N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

5 6-(3- α,α,α -trifluoromethylphenoxy)picolinic acid (1.5g) in thionyl chloride (20ml) was refluxed for 1 hour. The excess thionyl chloride was evaporated in vacuo and dichloromethane (20ml) added to the residual picolinoyl chloride. A solution of n-propylamine (0.6g) and triethylamine (1.0g) in dichloromethane (20ml)
10 was added dropwise at ambient temperature. After stirring for a further $\frac{1}{2}$ hour, the reaction mixture was washed with water, dried over anhydrous magnesium sulphate and the dichloromethane evaporated off. The residue was
15 purified on a silica gel column using 5% (v/v) diethyl ether/dichloromethane as eluant to give N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide (1.5g) as an oil.

Analysis (%) :

20 $C_{16}H_{15}O_2N_2F_3$: Calc. : C 59.3 H 4.6 N 8.6
Found : C 60.0 H 5.0 N 8.7

m/e Theory: 324

Found : 324

Example 2A

25 Preparation of N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

Methyl-6-(3- α,α,α -trifluoromethylphenoxy) picolinate (0.8g) and n-propylamine (1.4g, excess) were allowed to stand at room temperature for one
30 hour. The excess n-propylamine was evaporated leaving the title compound (0.7g) as a colourless oil.



Analysis (%):

$C_{16}H_{15}O_2N_2F_3$: Calc. : C 59.2 H 4.6 N 8.6
Found : C 58.6 H 4.9 N 8.8

m/e Theory: 324

5 Found : 324

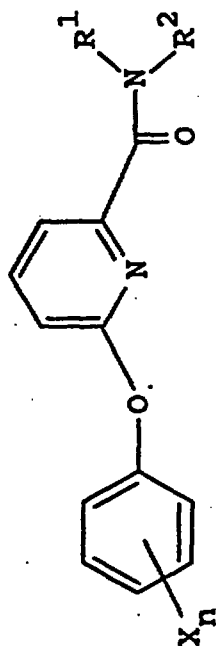
Examples 3 to 61

10 Further compounds of the general formula I were prepared by the procedure of Example 2 above, with the appropriate selection of starting materials. Details of the compounds of formula I prepared are given in Table 1 below, and of the starting acids are given in Table 2.

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Table 1



Example No.	X _n	R ¹	R ²	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
3	3-CF ₃	H	nC ₄ H ₉	60.3 59.8	5.0 5.2	8.3 8.5		oil	338 338
4	3-CF ₃	H	sC ₄ H ₉	60.3 60.1	5.0 5.4	8.3 8.5		oil	338 338
5	3-CF ₃	H	tC ₄ H ₉	60.3 60.0	5.0 5.2	8.3 8.6		oil	338 338
6	3-Cl	H	nC ₄ H ₉	63.1 62.6	5.6 5.9	9.2 9.1		oil	304 304



Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}C$)	m/e (Theory Found)
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			
7	3-CF ₃	C ₂ H ₅	C ₂ H ₅	60.4 59.7	5.0 5.3	8.3 8.3		oil	338 338
8	3-CF ₃	H	CH ₂ CH=CH ₂	59.6 57.7	4.0 3.9	8.7 8.7		34-36	322 322
9	3-CF ₃	H	CH ₂ CH ₂ OCH ₃	56.5 55.1	4.4 4.5	8.2 7.9		oil	340 340
10	3-CF ₃	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -		58.0 57.3	4.3 4.5	8.0 7.8		oil	352 352
11	3-CF ₃	-CH ₂ -CH ₂ -CH ₂ -CH ₂ -		60.7 61.1	4.5 4.6	8.3 8.3		98-99	336 336
12	3-CF ₃	nC ₃ H ₇	nC ₃ H ₇	62.3 62.3	5.7 6.1	7.7 7.7		oil	366 366
13	3-CF ₃	H	CH ₂ CH ₂ N(CH ₃) ₂	57.8 57.6	5.1 5.2	11.9 11.9		58-59	353 353



Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
14	3,4-diCl	H	nC_4H_9	56.8 59.2	4.7 6.1	8.3 8.9		oil	338 338
15	3-CF ₃ ,4-F	H	nC_4H_9	57.3 57.5	4.5 5.1	7.9 8.0		oil	356 356
16	3-Br	H	nC_4H_9	55.0 58.0	4.9 5.3	8.0 8.1		oil	349 349
17	3,5-diCl	H	nC_4H_9	56.8 53.0	4.7 5.2	8.3 7.6		oil	338 338
18	3-NO ₂	H	nC_4H_9	61.0 57.3	5.4 6.0	13.3 12.3		oil	315 315
19	3-CF ₃	H	iC_3H_7	59.3 58.9	4.6 4.9	8.6 8.4		oil	324 324
20	3-CF ₃	H	nC_5H_{11}	61.4 60.8	5.4 5.4	8.0 9.7		oil	352 352

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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			
21	3-CF ₃	H	nC ₆ H ₁₃	62.3	5.7	7.6		44-45	366
				62.1	5.7	7.5			366
22	3-CF ₃	H	C ₂ H ₅	58.1	4.2	9.0		30	310
				58.4	4.1	8.9			310
23	3-CF ₃	H	CH ₂ C≡CH	60.0	3.4	8.7		70-72	320
				59.8	3.7	8.3			320
24	3-CF ₃	H	CH ₂ CH ₂ F	54.9	3.7	8.5		74-75	328
				55.4	4.0	8.2			328
25	3-CF ₃	H	nC ₇ H ₁₅	63.2	6.1	7.4		59-60	380
				63.9	5.6	7.1			380
26	3-CF ₃	H	nC ₈ H ₁₇	64.0	6.4	7.1		50-51	394
				64.1	6.4	7.0			394
27	3-CF ₃	H	cyclobutyl	60.7	4.5	8.3		46-48	336
				60.5	4.5	8.2			336

This Sheet Has Been Replaced



Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}C$)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
28	3-CF ₃	$-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-$ $\quad$							



Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)		
				C		H				N	
				(Calc. Found)	(Calc. Found)	(Calc. Found)	(Calc. Found)				
33	3-CF ₃	H	O-CH ₂ CH=CH ₂	56.8 56.3	3.8 4.0	8.3 8.2		oil	338 338		
34	3-CF ₃	H	CH ₂ CF ₃	49.4 49.9	2.7 2.9	7.7 7.6		89-90	364 364		
35	3-CF ₃	H	CH ₃	56.7 54.2	3.7 4.2	9.5 10.5		67-68	296 296		
36	3-CF ₃	H	cyclopropyl	59.6 60.2	4.0 4.1	8.7 8.7		53-54	322 322		
37	3-CF ₃	H	CH ₂ CO ₂ C ₂ H ₅	55.4 56.0	4.1 4.5	7.6 7.6		66-67	368 368		
38	3-CF ₃	H	CON(CH ₃) ₂	54.4 57.1	4.0 4.7	11.9 11.9		136-137	353 353		
39	3-CF ₃	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	62.9 62.7	4.7 4.9	7.7 7.7		55-56	362 362		

This Sheet Has Been Replaced



Table 1 (continued)

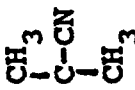
Example No.	X _n	R ¹	R ²	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			
40	3-CF ₃	H		58.4 57.3	4.0 4.2	12.0 11.7		91-92	349 349
41	3-CF ₃	H		61.1 58.5	3.7 3.6	11.3 10.3		oil	373 373
42	3-CF ₃	H		56.0 55.7	3.2 3.2	10.3 9.9		100-101	407
43	3-CF ₃	H	NHCH ₃	54.0 55.3	3.8 4.3	13.5 13.4		oil	311 311
44	3-CF ₃	H	CO ₂ C ₂ H ₅	54.2 55.4	3.7 4.0	7.9 7.9		142-143	354 354



Table 1 (continued)

Example No.	X _n	R ¹	R ²	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)		
				C		H				N	
				(Calc. Found)	(Calc. Found)	(Calc. Found)	(Calc. Found)				
45	3-CF ₃	H	H	55.3	3.2	9.9	134-135	282			
46	3-C ₂ H ₅	H	CH ₂ CF ₃	56.2	3.6	9.7		282			
47	H	H	CH ₂ CF ₃	59.2	4.6	8.6	oil	324			
48	3-CF ₃	H	cyclopentyl	58.8	4.8	8.2		324			
49	3-CF ₃	H	cyclohexyl	56.7	3.7	9.5	104-105	296			
50	3-OCH ₃	H	n-C ₃ H ₇	56.9	4.1	9.1		296			
				61.7	4.8	8.0	oil	350			
				60.2	4.9	7.8		350			
				62.6	5.2	7.7	oil	364			
				61.4	5.2	7.5		364			
				67.1	6.3	9.8	oil	286			
				66.6	6.5	9.8		286			



Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}C$)	m/e (Theory Found)
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			
51	3-CF ₃	H	2,2-Cl ₂ -cyclopropyl-methyl	50.4	3.2	6.9		oil	-
				50.0	3.4	6.4			
52	3-CF ₃	CH ₃	2,2-Cl ₂ -cyclopropyl-methyl	51.6	3.6	6.7		oil	-
				51.3	3.8	6.3			
53	3-Cl	H	iC ₃ H ₇	62.0	5.2	9.6		oil	-
				62.1	5.1	9.4			
54	3-Cl	H	nC ₃ H ₇	62.0	5.2	9.6		oil	-
				61.6	5.0	9.9			
55	3-Cl	nC ₃ H ₇	nC ₃ H ₇	65.0	6.4	8.4		oil	-
				64.6	6.2	8.1			
56	3-Cl	H	CH ₂ CF ₃	50.9	3.1	8.5		oil	-
				51.3	2.9	8.9			

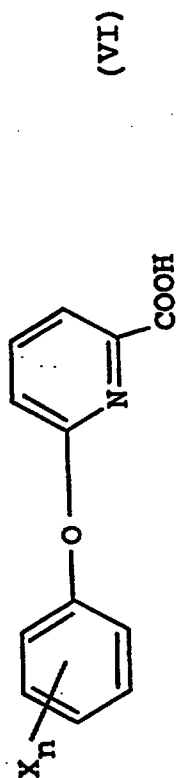


Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}C$)	m/e (Theory Found)
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			
57	3-Cl	H	H	58.0	3.7	11.3		186	-
58	3-Cl	H	CH_2CH_2F	58.0	3.8	11.7			-
59	3-Cl	CH_3	$2,2-Cl_2-$ cyclopropyl- methyl	57.0	4.1	9.5		oil	-
				56.6	4.2	9.1			
				52.9	3.9	7.3		oil	-
				52.4	3.6	6.9			
60	3-Cl	H	$2,2-Cl_2-$ cyclopropyl methyl	51.7	3.5	7.5		oil	-
				51.5	3.2	7.0			
61	3-Cl	C_2H_5	$CH_2C=CH_2$ CH_3	65.4	5.8	8.5		oil	-
				65.4	6.1	8.5			



Table 2



X_n	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
	C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
3-Cl	57.8	3.2	5.6	not recorded		249
3,4-diCl	57.4	3.2	5.5			249
	50.9	2.5	4.9	110-111		283
	52.3	3.7	5.4			283
3-CF ₃ , 4-F	51.8	2.3	4.7	86-87		301
	51.9	3.0	4.3			301
3-Br	49.0	2.7	4.8	76-77		294
	53.0	3.2	4.8			294

Table 2 (continued)

X _n	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
	C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
3,5-diCl	50.9	2.5	4.9		140-141	283
	51.0	2.9	5.8			283
3-NO ₂	55.4	3.1	10.8		147-149	260
	54.4	2.6	10.8			260
3-C ₂ H ₅	69.1	5.3	5.7		50-51	243
	66.5	5.1	5.7			243
H	66.9	4.2	6.5		104-105	215
	66.6	4.2	6.4			215
3-OCH ₃	63.7	4.5	5.7		102-103	245
	61.9	4.1	5.5			245

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Example 62

Preparation of N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

5 (a) 6-chloropicolinic acid (3g) and thionyl chloride (50 ml) was refluxed for one hour. The excess thionyl chloride was evaporated in vacuo and dichloromethane added to the residual picolinoyl chloride. This solution was poured into an excess of n-propylamine in dichloromethane. The
10 solution was then washed with water, dried over anhydrous magnesium sulphate and the dichloromethane evaporated to give 6-chloro-2-N-n-propyl pyridine carboxamide (3g) as a yellow oil.

15 Analysis (%):

$C_9H_{11}N_2OCl$:	Calc :	C 54.5	H 5.5	N 14.1
	Found :	C 54.2	H 5.9	N 14.0

m/e: Theory: 198

Found : 198

20 (b) A solution of sodium methoxide (from 0.4g of sodium in 20 ml of methanol) was added to a solution of 3- α,α,α -trifluoromethylphenol (2.6g) in xylene (20 ml). The solvents were evaporated
25 in vacuo to give the dry sodium phenolate. Pyridine (14 ml) and xylene (30 ml) were added, followed by cuprous chloride (0.4g) and the mixture heated to reflux. A solution of
30 6-chloro-2-N-n-propyl pyridine carboxamide (3g) in xylene (20 ml) was added dropwise and the resultant mixture refluxed a further 18 hours. After cooling, the mixture was poured into water and acidified with dilute hydrochloric acid. The whole was extracted with diethyl ether. The combined extracts were dried over anhydrous

35



magnesium sulphate and evaporated. The residue was purified on a silica gel column using 5% (v/v) diethyl ether/dichloromethane as eluant to give recovered starting material (6-chloro-2-N-n-propyl pyridine carboxamide, 60%) and the title compound (40%) as a colourless oil.

Example 63

Preparation of N-n-butyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridinethiocarboxamide

A mixture of N-n-butyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide (0.6g) and phosphorus pentasulphide (1.0g) in pyridine (50 ml) was refluxed for 2 hours. The pyridine was evaporated and water added to the residue. The aqueous solution was then extracted with methylene chloride. The extracts were washed with dilute hydrochloric acid, water and dried over anhydrous magnesium sulphate. The dichloromethane was evaporated and the residue purified on a silica gel column using dichloromethane as eluant to give the title compound (0.5g) as a yellow solid of melting point 61-62°C.

Analysis (%):

$C_{17}H_{17}N_2OSF_3$: Calc : C 57.6 H 4.8 N 7.9
Found : C 61.0 H 4.7 N 8.1

m/e: Theory: 354
Found : 354

Example 64

Herbicidal Activity

To evaluate their herbicidal activity, compounds according to the invention were tested using as representative range of plants: maize, Zea mays (Mz); rice, Oryza sativa (R); barnyard grass, Echinochloa crusgalli (BG); oat, Avena sativa (O); linseed, Linum



usitatissimum (L); mustard, Sinapsis alba (M); sugar beet, Beta vulgaris (SB) and soya bean, Glycine max (S).

5 The tests fall into two categories, pre-emergence and post-emergence. The pre-emergence tests involved spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above had recently been sown. The post-emergence tests involved two types of test, viz., soil drench and foliar spray tests. In the soil drench tests the soil in which the seedling plants of the above species were growing was drenched with a liquid formulation containing a compound of the invention, and in the foliar spray tests the seedling plants were sprayed with such a formulation.

15 The soil used in the tests was a prepared horticultural loam.

The formulations used in the tests were prepared from solutions of the test compounds in acetone containing 0.4% by weight of an alkylphenol/ethylene oxide condensate available under the trade mark TRITON X-155. These acetone solutions were diluted with water and the resulting formulations applied at dosage levels corresponding to 5 kg or 1 kg of active material per hectare in a volume equivalent to 900 litres per hectare in the soil spray and foliar spray test, and at a dosage of level equivalent to 10 kilograms of active material per hectare in a volume equivalent to approximately 3,000 litres per hectare in the soil drench tests.

25 In the pre-emergence tests untreated sown soil and in the post-emergence tests untreated soil bearing seedling plants were used as controls.

The herbicidal effects of the test compounds were assessed visually twelve days after spraying the



foliage and the soil, and thirteen days after
drenching the soil and were recorded on a 0-9 scale.

A rating 0 indicates growth as untreated control, a
rating 9 indicates death (i.e. 100% effectiveness).

- 5 An increase of 1 unit on the linear scale approximates
to a 10% increase in the level of effect.

The results of the tests are set out in the
following Table 3 in which the compounds are
identified by reference to the preceding examples. In
10 the Table, a blank space indicates a 0 rating, and an
asterisk indicates that no result was obtained.

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TABLE 3

Compound of Ex. No.	Soil drench 10 kg/ha					Dosage kg/ha	Foliar spray					Pre-emergence													
	Mz	R	BG	O	L		M	SB	S	Mz	R	BG	O	L	M	SB	S								
2	6	6	8	7	3	9	9	4	5	9	7	9	9	9	9	8	8	8	8	9	9	8	9	9	7
									1	6	5	9	7	8	9	9	8	6	6	9	8	6	9	9	7
3	3	3	7	6	5	9	7	3	5	8	8	9	8	8	9	9	8	7	6	9	9	7	9	9	5
									1	6	6	8	7	7	9	9	8	6	5	9	6	4	9	9	3
4	1	1	5	4	5	8	6	3	5	6	6	8	7	8	9	9	8	6	5	9	8	7	9	9	2
									1	5	4	8	7	7	9	9	8	5	4	9	7	6	9	9	1
5									5	7	2	8	7	6	9	9	8		6	4	1	9	8	3	
									1	3		6	4	5	9	9	7		1			7	6		
6	2		5	3	3	7	6	1	5	7	6	8	6	8	9	9	7	2	4	9	2	3	9	8	2
									1	5	3	6	3	7	8	8	6	1	2	8		1	8	8	

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TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha					Dosage kg/ha	Foliar spray					Pre-emergence				
	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
7	6	3	6	5	2	7	9	4	5	7	6	9	6	8	9	3
									1	5	2	7	4	7	9	9
8	5	5	6	4	5	7	7	2	5	5	4	9	7	8	9	5
									1	3	2	7	5	8	9	8
9	6	5	7	3	4	8	8	5	5	7	5	9	7	8	9	4
									1	6	5	9	6	8	9	2
10									5	5	3	6	4	6	9	4
									1	4	*	*	5	7	*	2
11	4	4			4	4	2	5	7	3	8	5	6	9	9	4
								1	6	2	7	4	5	8	9	5

This Sheet Has Been Replaced



TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha	Foliar spray				Pre-emergence															
	Mz	R	BG	O		L	M	SB	S	Mz	R	BG	O	L	M	SB	S								
12	5		5	1	4	*	9	1	5	8	5	9	6	8	9	9	8	6	4	9	7	7	9	9	5
									1	7	4	9	5	8	9	9	7	4	3	9	4	4	9	9	2
13									5	5	3	8	5	6	9	9	8	2	2	2				7	5
									1	2		7	2	5	8	9	6							5	4
14									5	5	3	7	5	5	7	8	5			4	1	1	7	7	
									1	3	1	3	2	3	6	6	3							4	
15	4		3	2	1	2	2	1	5	5	4	8	7	7	9	9	7	4	2	9	5	4	9	9	2
									1	3	2	5	4	6	8	9	5	1	6	2	2	8	7		
16	2		4	2	3	3	4		5	4	5	8	5	7	8	9	6	3	3	9	5	3	9	8	
									1	2	2	6	2	6	7	7	4	2	7	2			8	7	



TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha	Foliar spray				Pre-emergence											
	Mz	R	BG	O		L	M	SB	S	Mz	R	BG	O	L	M	SB	S				
17					1	1			5	6	3	4	2	6	8	9	6	2	2		
									1	2	2	1	1	4	7	7	5	1	1		
18	3	3	5	1	3	5	6		5	6	6	6	4	7	9	9	7	1	4	3	1
									1	4	2	3	2	6	8	9	7		2	2	1
19	4	3	5	4	5	6	6	3	5	7	6	9	6	8	9	9	8	*	*	*	*
									1	6	5	6	5	8	9	9	7	*	*	*	*
20									5	7	6	8	7	8	9	9	7	*	*	*	*
									1	5	4	6	4	7	9	9	6	*	*	*	*
21									5	6	4	7	5	7	9	9	7	1	*	8	2
									1	4	2	6	3	5	9	9	6	*	*	*	*



TABLE 3 (cont'd)

Compound of Ex. No.		Soil drench 10 kg/ha					Dosage kg/ha	Foliar spray					Pre-emergence												
		Mz	R	BG	O	L		M	SB	S	Mz	R	BG	O	L	M	SB	S							
22		5	6	7	6	6	8	8	4	5	7	6	8	7	8	9	9	8	*	*	*	*	*	*	*
										1	5	4	7	4	8	9	9	7	*	*	*	*	*	*	*
23		3	2	5	3	4	6	7	3	5	5	4	8	4	8	9	9	7	4	3	9	7	5	9	2
										1	3	2	5	3	7	9	9	6	1	7	5	3	8	8	
24		*	*	*	*	*	*	*	*	5	8	7	9	7	8	9	9	7	6	5	9	8	9	9	9
										1	6	5	7	5	7	9	9	6	4	3	9	6	5	9	7
25									2	5	3	2	5	3	4	9	9	6		5		1	7	8	
										1	3	1	3	1	2	9	9	4		3			3	7	
26										5	5	2	4	3	5	9	9	6		1	7	2	4	8	1
										1	3	1	2	1	3	9	9	6		2		2	6	9	



TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha					Dosage kg/ha	Foliar spray					Pre-emergence													
	Mz	R	BG	O	L		M	SB	S	Mz	R	BG	O	L	M	SB	S								
27	6	6	6	6	5	8	4	2	5	8	7	8	8	8	9	9	8	7	7	9	9	9	9	9	8
					1	6	5	7	6	8	9	9	9	9	7	6	5	9	8	8	9	9	9	8	
28					2	2			5	4	4	4	6	3	5	9	9	7		2		1	7	8	
									1	3	2	5	2	4	8	8	5		1			5	7		
29	5		4	2	5	7	7	5	5	4	3	7	4	7	9	9	7	7	3	9	6	3	9	9	2
									1	3	1	4	2	5	9	9	6	3	1	6		1	8	9	
30	5	2	2		4	7	5	2	5	7	5	7	3	6	9	9	7	7	2	9		8	9	9	1
									1	5	3	5	2	4	9	9	5	4		7		7	9	9	
31	4		2			4			5	2	1	9	5	5	9	9	6	4		7		1	7	5	3
									1			4	2	3	8	8	4		4			4	3	1	

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TABLE 3 (cont'd)

Compound of Ex. No.		Soil drench 10 kg/ha					Dosage	Foliar spray					Pre-emergence														
		Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S	
32		6	3	6	2	7	4		5	5	3	9	5	6	9	9	7	5	7	3				8	8	5	
									1	3		7	4	3	9	9	5	2	4				6	5	4		
33		7	*	*	*	3	7	3	5	7	4	9	6	8	9	9	8	6	8	3	6	9	9	2			
									1	5	3	7	4	7	9	9	7	4	7		4	9	8	1			
34		6	6	8	7	6	8	7	5	8	8	8	8	8	9	9	8	8	7	9	9	9	9	8			
									1	8	8	8	8	8	9	9	8	7	6	9	9	7	9	9	7		
35		6	6	8	5	5	6	9	5	8	6	9	9	8	9	9	8	7	7	9	8	9	9	6			
									1	5	3	8	5	7	8	9	7	5	4	9	6	9	9	3			
36		*	*	*	*	*	*	*	5	9	8	9	9	8	9	9	8	7	6	9	8	9	9	7			
									1	7	6	8	6	8	9	9	8	*	4	9	7	6	8	9	6		

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TABLE 3 (cont'd)

Compound of Ex. No.		Soil drench 10 kg/ha					Dosage kg/ha					Foliar spray					Pre-emergence								
		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
37									5	7	4	9	6	6	9	9	7							5	
									1	3	2	6	2	5	8	8	5							3	
38	2	4	1	2	4	1			5	6	1	7	3	7	7	8	7	4	1	7	1	4	7	8	4
									1	4	1	5	1	5	7	7	6	1	2			1	5	4	
39	1	1	1	1	5	6	3		5	8	3	7	5	7	9	8	7	4		8	3	5	8	8	7
									1	5		6	2	6	8	7	6	1	6			1	7	5	3
40	4	3	6	5	4	7	4	2	5	7	4	7	5	7	8	8	7	4	1	8	4	5	8	9	4
									1	4		6	2	6	8	8	6	1	7	3	3	7	8		
41									5	4		4	2	5	9	7	5					4		2	
									1	2		2		2	8	6	5					1			



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TABLE 3 (cont'd)

Compound of		Soil drench 10 kg/ha				Dosage	Foliar spray				Pre-emergence														
Ex. No.	Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
47	4				4		1		5	3	1	7	4	6	9	8	7	1		5		3	8	7	2
									1	1		4	2	3	8	7	6		2			1		2	
48	5	2	8	6	4	6	8	5	5	6	7	9	8	8	9	9	7	5	5	9	7	6	9	9	8
									1	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*	*
49	2		8	6	4	7	7	3	5	6	7	9	7	8	9	9	7	5	4	9	6	6	9	9	5
									1	5	4	9	6	7	9	9	7	2	1	8	5	4	8	8	2
50	1	5			1	3	7	3	5	3		9	3	6	8	9	6		3			2	2	2	
									1	2		8	1	4	7	8	6					1			
51	3	4	3	4	4	4	3		5	6	5	8	6	7	9	9	9	6	8	6	4	8	9	6	
									1	5	2	7	5	6	9	9	8	2	7	4	2	8	9	5	

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TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha				Foliar spray				Pre-emergence			
	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
52					3	4	7		5	7	3	9	5	7	1	
								1	4	4	2	4	4	7	9	6
53																
54																
55																
56																

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TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha				Foliar spray				Pre-emergence			
	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
57					3	2			5	5	2	3	2	5	8	7
									1	3		2		4	8	5
58									5	7	5	8	5	8	9	7
									1	4	3	6	3	6	9	8
59									5	5	2	5	2	6	9	8
									1	2		2	1	4	8	5
60									5	6	5	6	2	5	9	6
									1	3	2	3		5	8	9
61									5	5	2	7	2	6	9	9
									1	3		3		3	7	7



TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage	Foliar spray				Pre-emergence									
	Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S		
63	4	2	4	4	2	4	3		5	5	6	8	6	8	2	8	9	4	
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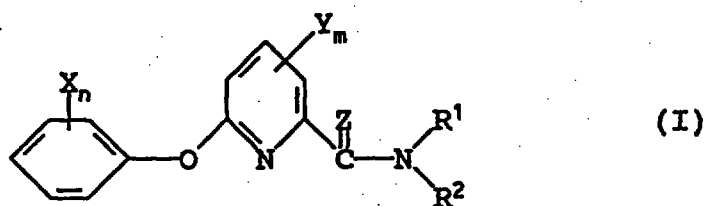




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CLAIMS

1. A compound of the general formula I



wherein

n is an integer from 1 to 5 and the or each X independently represents a hydrogen or halogen atom, an alkyl or alkoxy group optionally substituted by one or more of the same or different substituents selected from halogen atoms and cyano, hydroxy and alkoxy groups, or a cyano, nitro, alkenyloxy, alkynyloxy, alkylthio, haloalkylthio, alkenylthio or alkynylthio group;

m is 0 or an integer from 1 to 3 and the or each Y independently represents a halogen atom or an alkyl or haloalkyl group;

Z represents an oxygen atom or a sulphur atom;
and

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5 R^1 and R^2 each, independently, represents a hydrogen atom, an alkyl group optionally substituted by one or more of the same or different substituents selected from halogen atoms or hydroxy, cyano, alkoxy, alkylthio, alkoxy carbonyl, or mono- or di-alkylamino groups, an alkenyl, alkynyl, cycloalkyl, or optionally substituted cycloalkylalkyl group, or a hydroxy, alkoxy, alkenyloxy, 10 alkynyloxy, alkoxy carbonyl, amino, mono- or di-alkylamino, alkoxy carbonylamino group, an arylamino group optionally substituted by a halogen atom, or a dialkylcarbamoyl group;

15 or
 R^1 and R^2 together represent an alkylene chain which is optionally interrupted by an oxygen or sulphur atom or by a group -NR- in which R represents a hydrogen atom or an alkyl group.

20 2. A compound as claimed in claim 1, wherein n is 1 or 2 and the or each X independently represents a hydrogen, fluorine, chlorine or bromine atom or a nitro, ethyl, methoxy or trifluoromethyl group.

25 3. A compound as claimed in claim 2, wherein n is 1 and X represents a 3-trifluoromethyl or 3-methoxy group or a 3-chlorine atom.

 4. A compound as claimed in any one of claims 1 to 3, wherein either
30 R^1 represents a hydrogen atom or a C_{1-4} alkyl or C_{2-4} alkenyl group, while R^2 represents a hydrogen atom or an unsubstituted C_{1-8} alkyl group, a C_{1-4} alkyl group substituted by fluorine, hydroxy, cyano, C_{1-2} alkoxy, (C_{1-2} alkoxy)carbonyl or mono- or di-(C_{1-2} alkyl)amino,
35 a C_{3-6} cycloalkyl group, a C_{2-4} alkenyl group, a

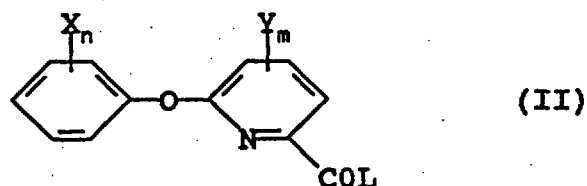


- 5 C₂₋₄ alkynyl group, a C₁₋₄ alkoxy group, a (C₁₋₄ alkyl)amino group, a C₂₋₄ alkenyloxy group, a (C₁₋₂ alkoxy)carbonyl group, a (C₁₋₂ alkoxy) carbonylamino group, a di(C₁₋₂ alkyl) carbamoyl group, an arylamino group in which the aryl group is optionally halo-substituted, or a halo-substituted (C₃₋₆ cycloalkyl)C₁₋₄ alkyl group;
- 10 or
R¹ and R² together represent a group -(CH₂)₄-, -(CH₂)₂O(CH₂)₂- or -(CH₂)₂NR(CH₂)₂- in which R is a C₁₋₂ alkyl group.
- 15 5. A compound as claimed in claim 4, wherein either R¹ represents a hydrogen atom while R² represents an unsubstituted C₁₋₅ alkyl group, a C₁₋₂ alkyl group substituted by fluorine or methoxy, a C₃₋₆ cycloalkyl group, a C₃ alkenyl group, a C₃ alkynyl group, a C₁₋₂ alkoxy group, a C₃ alkenyloxy group or a chloro-substituted cyclopropylmethyl group, or R¹ represents a C₁₋₃ alkyl group while R² represents the same C₁₋₃ alkyl group or a chloro-substituted cyclopropylmethyl group.
- 20 6. A compound as claimed in claim 5, wherein R¹ represents a hydrogen atom and R² represents an ethyl, propyl, cyclopropyl or cyclobutyl group.
- 25 7. A process for the preparation of a compound of general formula I as claimed in claim 1, which comprises preparing a compound of general formula I in which Z represents an oxygen atom, by
- 30 a) reacting a compound of the general



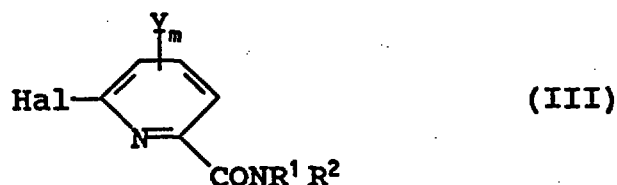


formula II

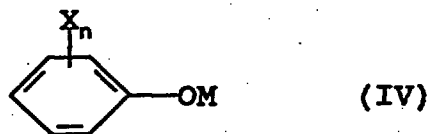


in which X_n and Y_m are as defined in claim 1, and L represents a leaving group, with an amine of the general formula NHR^1R^2 , in which R^1 and R^2 are as defined in claim 1; or

- b) reacting a compound of the general formula III



in which Y_m , R^1 and R^2 are as defined in claim 1, and Hal represents a halogen atom with a compound of the general formula IV



in which X_n is as defined in claim 1 and M represents an alkali metal atom; and optionally converting the product into a compound of general formula I in which Z represents a sulphur atom.





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8. A herbicidal composition which comprises a compound as claimed in anyone of claims 1 to 6, together with a carrier.
- 5 9. A method of combating undesired plant growth at a locus, which comprises treating the locus with a compound as claimed in any one of claims 1 to 6, or with a composition as claimed in claim 8.
- 10 10. The use of a compound as claimed in any one of claims 1 to 7, or a composition as claimed in claim 8, as a herbicide.

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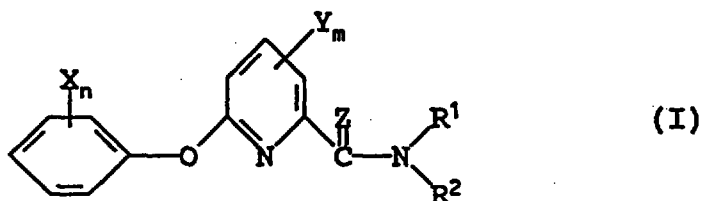


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ABSTRACT

HERBICIDAL CARBOXAMIDE DERIVATIVES

Compounds of the formula



wherein

- 5 n is 1 to 5 and the/each X is hydrogen, halogen, cyano, nitro, optionally substituted alkyl or alkoxy alkenyloxy, alkynyloxy, haloalkylthio, alkenylthio or alkynylthio;
- m is 0 or 1 to 3 and the/each Y is halogen, alkyl or haloalkyl;
- 10 z is oxygen or sulphur;
- and
- R¹ and R² each, independently, is hydrogen, alkyl optionally substituted by halogen, hydroxy, cyano, alkoxy, alkylthio, alkoxycarbonyl, or
- 15 mono- or di-alkylamino, alkenyl, alkynyl, hydroxy, alkoxy, alkenyloxy, alkynyloxy, alkoxycarbonyl, amino, mono- or di-alkylamino,



alkoxycarbonylamino, arylamino, dialkylcarbamoyl, cycloalkyl, or optionally substituted cycloalkylalkyl;

or

- 5 R^1 and R^2 together form an alkylene chain optionally interrupted by oxygen, sulphur or -NR-, R being hydrogen or alkyl;

are herbicides.

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☒ Claim(s) : paged 4... to paged 5.....	
☐ Drawing(s) : paged to paged	
☐ Abstract : paged to paged	
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REPLACEMENT SHEETS	SG
☒ Description : paged 1... to paged 4.....	
☒ Claim(s) : paged 4... to paged 5.....	
☐ Drawing(s) : paged to paged	
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HERBICIDAL CARBOXAMIDE DERIVATIVES

The present invention relates to herbicidal carboxamide derivatives, their preparation, herbicidal compositions containing such derivatives and their use in combating undesired plant growth.

- 5 The herbicidal activity of 2-phenoxy-3-pyridine carboxamide compounds is well known. In 1981 and 1982 three U.S. patent specifications were published , Nos. 4 251 263, 4 270 946 and 4 327 218, directed to A.D. Gutman's work on 2-phenoxy nicotinamide
- 10 herbicides. His later review article, Chapter 5 of "Synthesis and Chemistry of Agrochemicals" (1987) published by the American Chemical Society, shows that his investigations started with 2-phenoxy nicotinic
- 15 N-alkyl amide derivatives (found to have weak herbicidal activity), and then concentrated on N-phenyl and N-benzyl amides as the most active of the compound type. Indeed, Diflufenican[N-(2,4-difluoro-
- 20 phenyl)-2-(3-trifluoromethylphenoxy)-3-pyridine carboxamide] was subsequently developed, by a different research group, as a commercial herbicide for use against broad-leaved weeds in winter cereals, such as winter wheat and barley.

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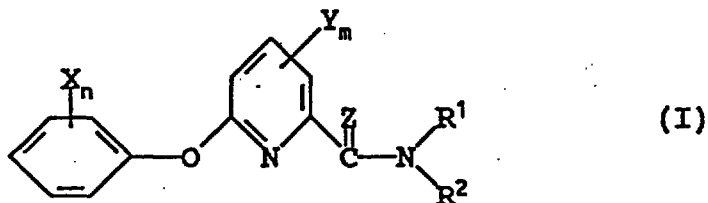


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U.S. Patent Specification No. 4 251 263 is concerned with the N-alkyl amides of Gutman, and related N-alkenyl and N-alkynyl amides. The compound documented as being the most active of the aliphatic amides prepared and tested is N-(1,1-dimethylprop-2-ynyl)-2-(3-trifluoromethylphenoxy)-3-pyridine carboxamide, which gives 85% control preemergence and only 57% control postemergence on specified narrow- and broad-leaved species.

Suprisingly, it has now been found that 2-phenoxy-6-pyridine carboxamide compounds with aliphatic (both straight chain and alicyclic) and other substitution of the amide nitrogen atom have unexpectedly high levels of herbicidal activity against representative narrow- and broad-leaved test species in pre- and/or post-emergence application; certain examples exhibiting 90 to 100% effectiveness against test species both pre- and post-emergence.

The present invention accordingly provides a compound of the general formula I



wherein

n is an integer from 1 to 5 and the or each X independently represents a hydrogen or halogen atom, an alkyl or alkoxy group optionally substituted by one or more of the same or different substituents selected from halogen atoms and cyano, hydroxy and alkoxy groups, or a cyano, nitro, alkenyloxy, alkynyloxy, alkylthio, haloalkylthio, alkenylthio or alkynylthio group;

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m is 0 or an integer from 1 to 3 and the or each Y independently represents a halogen atom or an alkyl or haloalkyl group;

Z represents an oxygen atom or a sulphur atom;

5 and

R¹ and R² each, independently, represents a hydrogen atom, an alkyl group optionally substituted by one or more of the same or different substituents selected from halogen atoms or hydroxy, cyano, 10 alkoxy, alkylthio, alkoxycarbonyl, or mono- or di-alkylamino groups, an alkenyl, alkynyl, cycloalkyl, or optionally substituted cycloalkylalkyl group, or a hydroxy, alkoxy, alkenyloxy, alkynyloxy, alkoxycarbonyl, amino, 15 mono- or di-alkylamino, alkoxycarbonylamino group, an arylamino group optionally substituted by a halogen atom, or a dialkylcarbamoyl group;

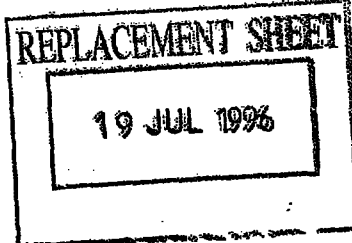
or

R¹ and R² together represent an alkylene chain which 20 is optionally interrupted by an oxygen or sulphur atom or by a group -NR- in which R represents a hydrogen atom or an alkyl group.

When any of the substituents X, Y, R¹ and R² represents or contains an alkyl, alkenyl or alkynyl 25 substituent group, this may be linear or branched and suitably has up to 12, preferably up to 8 and especially up to 5, carbon atoms. Thus, for example, an alkyl group R² may be butyl, e.g. i-butyl, n-butyl, sec-butyl or tert-butyl. Where a cycloalkyl 30 substituent group is present, this suitably has from 3 to 8, preferably 3 to 6, carbon atom ring atoms. An aryl group is suitably phenyl. An alkylene chain suitably has 3 to 6, preferably 4 or 5, chain members. A halogen atom suitably denotes a fluorine, chlorine,

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bromine or iodine atom; preferred haloalkyl groups are trifluoromethyl, trifluoroethyl and fluoroethyl.

The substituent(s) X_n may be at any free position or combination of positions on the phenoxy ring.

5 One phenoxy substituent X is desirably located at the 3- (or meta-) position and is preferably a hydrogen, fluorine, chlorine or bromine atom or a nitro, ethyl, methoxy or, especially, a trifluoromethyl group. When additional substituents X
10 are present, they are suitably located at the 4- and/or 5- position and may be the same as, or, preferably, different to the meta-substituent. Such additional substituent(s), X, are preferably selected from chlorine and, especially, fluorine atoms.

15 Substituent(s) X_n may, of course, be at other positions, and may be, for example, 2, 3- or 2,5-dimethyl.

Preferably only one or two substituents X are present and, most preferably one of or the X
20 represents a 3-trifluoromethyl substituent.

Preferably m is 0.

Preferably Z represents an oxygen atom.

The radicals, R^1 and R^2 , when individually present may be the same or different. Preferably R^1
25 represents a hydrogen atom or a C_{1-4} alkyl or C_{2-4} alkenyl, suitably allyl, group, most preferably hydrogen or C_{1-4} alkyl, while R^2 represents an unsubstituted C_{1-8} alkyl group, especially C_{1-6} alkyl, a C_{1-4} alkyl group substituted by fluorine, hydroxy, cyano, C_{1-2} alkoxy, (C_{1-2} alkoxy)carbonyl, or mono- or
30 di- (C_{1-2} alkyl)amino, for example fluoroethyl, trifluoroethyl, cyanopropyl, hydroxyethyl, methoxyethyl, ethoxycarbonylmethyl, or dimethylaminoethyl, a C_{3-8} cycloalkyl group, especially cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, a C_{2-4} alkenyl
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group, for example allyl or methylallyl, a C_{2-4} alkynyl group, for example propynyl, a C_{1-4} alkoxy group, for example ethoxy, a $(C_{1-4}$ alkyl)amino group, for example methylamino, a C_{2-4} alkenyloxy group, for
5 example propenyloxy, a $(C_{1-2}$ alkoxy)carbonyl group, for example ethoxycarbonyl, a $(C_{1-2}$ alkoxy)carbonylamino group, for example ethoxycarbonylamino, a $di(C_{1-2}$ alkyl)carbamoyl group, for example dimethylcarbamoyl, an arylamino group, for example
10 phenylamino or p-chlorophenylamino, or a halo-substituted $(C_{3-6}$ cycloalkyl) C_{1-4} alkyl group, for example chloro-substituted cyclopropylmethyl.

It is especially preferred that either R^1 represents a hydrogen atom while R^2 represents an
15 unsubstituted C_{1-5} alkyl group, a C_{1-2} alkyl group substituted by fluorine or methoxy, a C_{3-6} cycloalkyl group, a C_3 alkenyl group, a C_3 alkynyl group, a C_{1-2} alkoxy group, a C_3 alkenyloxy group or a chloro-substituted cyclopropylmethyl group, or R^1
20 represents a C_{1-3} alkyl group while R^2 represents the same C_{1-3} alkyl group or a chloro-substituted cyclopropylmethyl group.

Particularly preferred are compounds in which R^1 represents a hydrogen atom and R^2 represents an ethyl,
25 propyl, cyclopropyl or cyclobutyl group.

When R^1 and R^2 together represent an alkylene chain, suitably the chain consists of 4 or 5 chain atoms, and is for example a group $-(CH_2)_4-$,
30 $-(CH_2)_2O(CH_2)_2-$ or $-(CH_2)_2NR(CH_2)_2-$ in which R is a C_{1-2} alkyl group, suitably methyl. Preferably R^1 and R^2 is a $-(CH_2)_4-$ group.

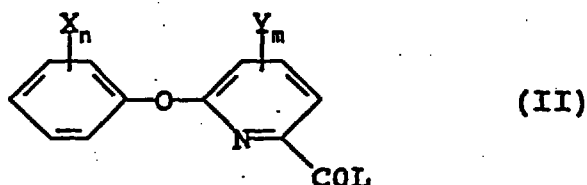
The compounds of general formula I may be prepared either by reaction of an appropriate
phenoxypicolinic acid derivative with an appropriate
35 amine (method A) or by reaction of an appropriate

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2-halo-6-pyridine carboxamide derivative with an appropriate alkali metal phenolate (method B). Such methods constitute further aspects of the present invention.

- 5 In accordance with method A, a compound of the general formula I in which Z is oxygen, is prepared by reacting a compound of the general formula II



- 10 in which X_n and Y_m are as hereinbefore defined and L represents a leaving group, with an amine of the general formula NHR^1R^2 in which R^1 and R^2 are as defined above.

- 15 A leaving group is any group that will, under the reaction conditions, cleave from the starting material thus promoting reaction at a specific site.

The leaving group L may suitably be a halogen atom, for example a bromine or, especially, a chlorine atom or an alkoxy group, suitably C_{1-4} alkoxy, especially methoxy.

- 20 The process variant A is suitably carried out in the presence of an inert organic solvent, for example dimethylformamide or an aromatic hydrocarbon, for example benzene or toluene, or a halogenated hydrocarbon, for example dichloromethane or an ether, 25 for example diethyl ether, or an ester, for example ethyl acetate; suitably at a temperature in the range of from 0 to 100°C.

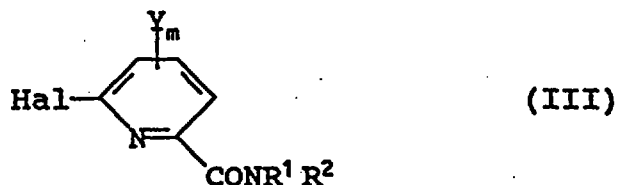
- Suitably, the reaction is carried out using substantially equimolar amounts of the reactants. 30 However, it can be expedient to use one reactant in

excess, conveniently the amine, for example such that the molar ratio of phenoxycolinic acid derivative to amine is in the range 1:1 to 1.1.

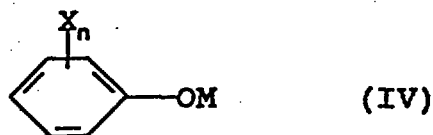
When L represents a halogen atom the reaction is suitably carried out at a temperature in the range 0 to 50°C, preferably at ambient temperature, and suitably in the presence of a base, for example potassium carbonate or, preferably, an amine base, such as triethylamine or excess amine starting material.

When L represents an alkoxy group the reaction is suitably carried out at a temperature in the range 0 to 100°C, preferably at room temperature (or 20°C) and in the absence of an added base.

In accordance with method B, a compound of the general formula I in which Z is oxygen, is prepared by reacting a compound of the general formula III



in which Y_m , R^1 and R^2 are as defined above and Hal represents a halogen atom with a compound of the general formula IV



in which X_n is as defined above and M represents an alkali metal atom.

Suitably, Hal represents a bromine atom or, especially, a chlorine atom. Suitably, R represents a

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potassium atom or, especially, a sodium atom.

The reaction B may be carried out by preparation of the alkali metal phenolate from the phenol using an alkali metal alkoxide, such as sodium methoxide,
5 followed by treatment of the phenolate with a substantially equimolar amount of reactant III, suitably at an elevated temperature, for example under reflux, with a copper catalyst, such as cuprous chloride, in pyridine in the presence of an aromatic
10 hydrocarbon, such as xylene, as is described in U.K. Patent Specification No. 2 050 168A.

Alternatively the process variant B could be carried out in the presence of an alkali metal hydride, for example sodium hydride, in a dry solvent,
15 such as dimethylformamide, suitably at an elevated temperature, for example at a temperature in the range of from 50°C to 125°C, or in the presence of an alkali metal carbonate, for example sodium or potassium carbonate, followed by treatment with cuprous oxide
20 and/or copper powder in an organic solvent, such as dimethylformamide or quinoline, suitably at a temperature in the range of from 20 to 150°C and conveniently at the reflux temperature of the reaction mixture.

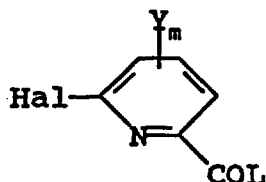
25 Compounds of the general formula I wherein Z represents a sulphur atom are suitably prepared by reaction of a compound of the general formula I wherein Z represents an oxygen atom, with phosphorous pentasulphide under standard conditions, for example
30 by heating, suitably under reflux, in the presence of an inert aromatic solvent, for example benzene, toluene, pyridine or quinoline.

The compounds of the present invention may be isolated and purified by conventional techniques, for
35 example by solvent extraction, evaporation followed by

recrystallisation or by chromatography on silica.

Compounds of formula II may be prepared from corresponding phenoxy-substituted picolinic acids by standard methods for the preparation or, for example, esters, using, for example, alcohols and acid catalysts or thionyl chloride, or of acid chlorides and acid bromides, using, for example, thionyl chloride or thionyl bromide. The acid compounds themselves can be prepared by standard methods from chloropicolinic acid or ester thereof. Chloropicolinic acid, or ester thereof, may be prepared by the methods described in J. Pharm. Belg. (1980), 35 1, 5-11.

Compounds of formula III may suitably be prepared by an analogous method to that of method A, by reacting a substituted amine of formula NHR^1R^2 with a 2-halo-6-pyridine carboxylic acid derivative of the general formula V



in which Y_m , Hal and L are as defined above. Compounds of formula V may be prepared by conventional techniques from picolinic acid.

The substituted amines NHR^1R^2 and the phenolates of formula IV are either known or can be prepared by conventional techniques.

The compounds of the invention have been found to have a surprisingly high herbicidal activity with a wide spectrum of activity against grasses and, especially, broadleaved weeds, including Alopecurus myosuroides (blackgrass), Avena fatua (wild oat),

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Sterea faberii (giant foxtail), Setaria viridis (green foxtail), Ipomoea purpurea (morning glory), Galium aparine (cleavers), Solanum nigrum (black nightshade), Veronica persica (speedwell) and Stellaria media (chickweed), when applied pre- and post-emergence. Examples have been found to show selectivity to small grain cereals, for example maize, wheat, barley and rice, and to broad-leaved crops, for example soya, sunflower and cotton, indicating that they may be useful in combating weeds growing in such crops.

The invention further provides a herbicidal composition comprising a compound of formula I as defined above in association with a carrier, and a method of making such a composition which comprises bringing a compound of formula I into association with a carrier.

The invention also provides the use of such a compound or composition according to the invention as a herbicide. Further in accordance with the invention there is provided a method of combating undesired plant growth at a locus by treating the locus with a compound or composition according to the invention. Application to the locus may be pre-emergence or post-emergence. The dosage of active ingredient used, may, for example, be in the range of from 0.01 to 10 kg/ha, suitably 0.05 to 4 kg/ha. The locus may, for example, be the soil or plants in a crop area, typical crops being cereals such as wheat and barley, and broad-leaved crops, such as soya, sunflower and cotton.

A carrier in a composition according to the invention is any material with which the active ingredient is formulated to facilitate application to the locus to be treated, which may for example be a plant, seed or soil, or to facilitate storage,

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transport or handling. A carrier may be a solid or a liquid, including a material which is normally gaseous but which has been compressed to form a liquid, and any of the carriers normally used in formulating herbicidal compositions may be used. Preferably compositions according to the invention contain 0.5 to 95% by weight of active ingredient.

Suitable solid carriers include natural and synthetic clays and silicates, for example natural silicas such as diatomaceous earths; magnesium silicates, for example talcs; magnesium aluminium silicates, for example attapulgites and vermiculites; aluminium silicates, for example kaolinites, montmorillonites and micas; calcium carbonate; calcium sulphate; ammonium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminium silicates; elements, for example carbon and sulphur; natural and synthetic resins, for example coumarone resins, polyvinyl chloride, and styrene polymers and copolymers; solid polychlorophenols; bitumen; waxes; and solid fertilisers, for example superphosphates.

Suitable liquid carriers include water; alcohols, for example isopropanol and glycols; ketones, for example acetone, methyl ethyl ketone, methyl isobutyl ketone and cyclohexanone; ethers; aromatic or aliphatic hydrocarbons, for example benzene, toluene and xylene; petroleum fractions, for example kerosine and light mineral oils; chlorinated hydrocarbons, for example carbon tetrachloride, perchloroethylene and trichloroethane. Mixtures of different liquids are often suitable.

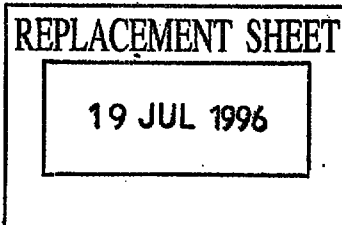
Agricultural compositions are often formulated and transported in a concentrated form which is subsequently diluted by the user before application. The presence of small amounts of a carrier which is a

surface-active agent facilitates this process of dilution. Thus preferably at least one carrier in a composition according to the invention is a surface-active agent. For example the composition may
5 contain at least two carriers, at least one of which is a surface-active agent.

A surface-active agent may be an emulsifying agent, a dispersing agent or a wetting agent; it may be nonionic or ionic. Examples of suitable
10 surface-active agents include the sodium or calcium salts of polyacrylic acids and lignin sulphonic acids; the condensation products of fatty acids or aliphatic amines or amides containing at least 12 carbon atoms in the molecule with ethylene oxide and/or propylene
15 oxide; fatty acid esters of glycerol, sorbitol, sucrose or pentaerythritol; condensates of these with ethylene oxide and/or propylene oxide; condensation products of fatty alcohol or alkyl phenols, for example p-octylphenol or p-octylcresol, with ethylene
20 oxide and/or propylene oxide; sulphates or sulphonates of these condensation products; alkali or alkaline earth metal salts, preferably sodium salts, of sulphuric or sulphonic acid esters containing at least 10 carbon atoms in the molecule, for example sodium
25 lauryl sulphate, sodium secondary alkyl sulphates, sodium salts of sulphonated castor oil, and sodium alkylaryl sulphonates such as dodecylbenzene sulphonate; and polymers of ethylene oxide and copolymers of ethylene oxide and propylene oxide.

The compositions of the invention may for example
30 be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols. Wettable powders usually contain 25, 50 or 75% w of active
35 ingredient and usually contain in addition to solid

inert carrier, 3-10% w of a dispersing agent and, where necessary, 0-10% w of stabiliser(s) and/or other additives such as penetrants or stickers. Dusts are usually formulated as a dust concentrate having a similar composition to that of a wettable powder but without a dispersant, and are diluted in the field with further solid carrier to give a composition usually containing $\frac{1}{2}$ -10% w of active ingredient. Granules are usually prepared to have a size between 10 and 100 BS mesh (1.676 - 0.152 mm), and may be manufactured by agglomeration or impregnation techniques. Generally, granules will contain $\frac{1}{2}$ -75% w active ingredient and 0-10% w of additives such as stabilisers, surfactants, slow release modifiers and binding agents. The so-called "dry flowable powders" consist of relatively small granules having a relatively high concentration of active ingredient. Emulsifiable concentrates usually contain, in addition to a solvent and, when necessary, co-solvent, 10-50% w/v active ingredient, 2-20% w/v emulsifiers and 0-20% w/v of other additives such as stabilisers, penetrants and corrosion inhibitors. Suspension concentrates are usually compounded so as to obtain a stable, non-sedimenting flowable product and usually contain 10-75% w active ingredient, 0.5-15% w of dispersing agents, 0.1-10% w of suspending agents such as protective colloids and thixotropic agents, 0-10% w of other additives such as defoamers, corrosion inhibitors, stabilisers, penetrants and stickers, and water or an organic liquid in which the active ingredient is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as anti-freeze agents for water.



Aqueous dispersions and emulsions, for example compositions obtained by diluting a wettable powder or a concentrate according to the invention with water, also lie within the scope of the invention. The said
5 emulsions may be of the water-in-oil or of the oil-in-water type, and may have a thick 'mayonnaise'-like consistency.

The composition of the invention may also contain other ingredients, for example compounds possessing
10 insecticidal or fungicidal properties or other herbicides.

The following Examples illustrate the invention. Example 1 illustrates the preparation of an ester of general formula II and Examples 2 to 63 relate to the
15 preparation of compounds of general formula I; Examples 2 to 61 by Method A, Example 62 by Method B, and Example 63 by conversion of a compound of general formula I in which Z is oxygen to one in which Z is sulphur. All structures were confirmed by mass
20 spectroscopy and/or ^{300}H nmr.

Example 1

Preparation of methyl-6-(3- CF_3 -trifluoromethylphenoxy)picolinate

A solution of sodium methoxide (from 1.3g sodium
25 in 20 ml methanol) was added to a solution of 3- CF_3 -trifluoromethylphenol (8.9g) in xylene (50ml). The solvents were evaporated in vacuo to give the dry sodium phenolate. Pyridine (25ml) and xylene (50ml) were added, followed by cuprous chloride (1.5g) and
30 the mixture heated to reflux. A solution of methyl-6-chloropicolinate (8.5g) in xylene (50ml) was added dropwise. The mixture was refluxed for a further 14 hours. After cooling, the mixture was poured into water (500ml) and acidified with dilute

5 sulphuric acid. The xylene layer was separated and the aqueous layer further extracted with diethyl ether. The combined extracts were washed with brine, dried over anhydrous magnesium sulphate and evaporated. The residue was purified on a silica gel column using 5% (v/v) diethyl ether/dichloromethane as eluant to give the title compound (7.4g) as a yellow solid of melting point 43-44°C.

Analysis (%) :

10 $C_{14}H_{10}O_3NF_3$: Calc. : C 56.6 H 3.4 N 4.7
Found : C 55.6 H 3.4 N 4.8

m/e: Theory: 297
Found : 297

Example 2

15 N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

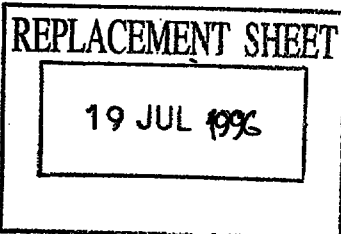
(a) Preparation of 6-(3- α,α,α -trifluoromethylphenoxy) picolinic acid

20 A solution of methyl-6-(3- α,α,α -trifluoromethylphenoxy)-picolinate (8g) in 50% aqueous methanol (45 ml) containing sodium hydroxide (2.5g) was refluxed for 3 hours. The methanol was evaporated, more water added to the residue and the aqueous solution extracted with diethyl
25 ether. The aqueous phase was then acidified with dilute hydrochloric acid to precipitate 6-(3- α,α,α -trifluoromethylphenoxy)picolinic acid (7.1g) as a white solid of melting point 92-93°C.

Analysis (%) :

30 $C_{13}H_8NO_3F_3$: Calc : C 55.1 H 2.8 N 4.9
Found : C 53.3 H 3.0 N 5.0

m/e Theory : 283
Found : 283



b) Preparation of N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

5 6-(3- α,α,α -trifluoromethylphenoxy)picolinic acid (1.5g) in thionyl chloride (20ml) was refluxed for 1 hour. The excess thionyl chloride was evaporated in vacuo and dichloromethane (20ml) added to the residual picolinoyl chloride. A solution of n-propylamine (0.6g) and triethylamine (1.0g) in dichloromethane (20ml) 10 was added dropwise at ambient temperature. After stirring for a further $\frac{1}{2}$ hour, the reaction mixture was washed with water, dried over anhydrous magnesium sulphate and the dichloromethane evaporated off. The residue was 15 purified on a silica gel column using 5% (v/v) diethyl ether/dichloromethane as eluant to give N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide (1.5g) as an oil.

Analysis (%):

20 $C_{16}H_{15}O_2N_2F_3$: Calc. : C 59.3 H 4.6 N 8.6
Found : C 60.0 H 5.0 N 8.7

m/e Theory: 324

Found : 324

Example 2A

25 Preparation of N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

Methyl-6-(3- α,α,α -trifluoromethylphenoxy) 30 picolinate (0.8g) and n-propylamine (1.4g, excess) were allowed to stand at room temperature for one hour. The excess n-propylamine was evaporated leaving the title compound (0.7g) as a colourless oil.

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Analysis (%):

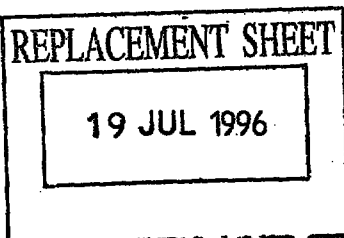
$C_{16}H_{15}O_2N_2F_3$: Calc. : C 59.2 H 4.6 N 8.6
Found : C 58.6 H 4.9 N 8.8

m/e Theory: 324

5 Found : 324

Examples 3 to 61

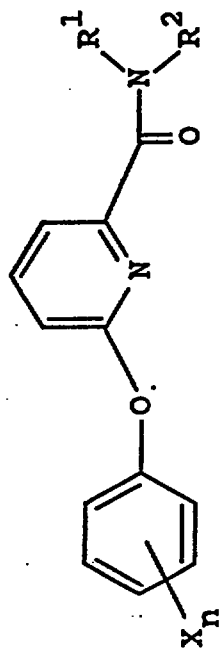
Further compounds of the general formula I were prepared by the procedure of Example 2 above, with the appropriate selection of starting materials. Details of the compounds of formula I prepared are given in Table 1 below, and of the starting acids are given in Table 2.



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Table 1



Example No.	X _n	R ¹	R ²	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)	
				C		H				N
				(Calc. Found)	(Calc. Found)	(Calc. Found)	(Calc. Found)			
3	3-CF ₃	H	nC ₄ H ₉	60.3	5.0	8.3	oil	338		
				59.8	5.2	8.5		338		
4	3-CF ₃	H	sC ₄ H ₉	60.3	5.0	8.3	oil	338		
				60.1	5.4	8.5		338		
5	3-CF ₃	H	tC ₄ H ₉	60.3	5.0	8.3	oil	338		
				60.0	5.2	8.6		338		
6	3-Cl	H	nC ₄ H ₉	63.1	5.6	9.2	oil	304		
				62.6	5.9	9.1		304		

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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}\text{C}$)	m/e
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			(Theory Found)
7	3-CF ₃	C ₂ H ₅	C ₂ H ₅	60.4 59.7	5.0 5.3	8.3 8.3		oil	338 338
8	3-CF ₃	H	CH ₂ CH=CH ₂	59.6 57.7	4.0 3.9	8.7 8.7		34-36	322 322
9	3-CF ₃	H	CH ₂ CH ₂ OCH ₃	56.5 55.1	4.4 4.5	8.2 7.9		oil	340 340
10	3-CF ₃	-CH ₂ -CH ₂ -O-CH ₂ -CH ₂ -		58.0 57.3	4.3 4.5	8.0 7.8		oil	352 352
11	3-CF ₃	-CH ₂ -CH ₂ -CH ₂ -CH ₂ -		60.7 61.1	4.5 4.6	8.3 8.3		98-99	336 336
12	3-CF ₃	nC ₃ H ₇	nC ₃ H ₇	62.3 62.3	5.7 6.1	7.7 7.7		oil	366 366
13	3-CF ₃	H	CH ₂ CH ₂ N(CH ₃) ₂	57.8 57.6	5.1 5.2	11.9 11.9		58-59	353 353

Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
14	3,4-diCl	H	nC_4H_9	56.8 59.2	4.7 6.1	8.3 8.9		oil	338 338
15	3-CF ₃ , 4-F	H	nC_4H_9	57.3 57.5	4.5 5.1	7.9 8.0		oil	356 356
16	3-Br	H	nC_4H_9	55.0 58.0	4.9 5.3	8.0 8.1		oil	349 349
17	3,5-diCl	H	nC_4H_9	56.8 53.0	4.7 5.2	8.3 7.6		oil	338 338
18	3-NO ₂	H	nC_4H_9	61.0 57.3	5.4 6.0	13.3 12.3		oil	315 315
19	3-CF ₃	H	iC_3H_7	59.3 58.9	4.6 4.9	8.6 8.4		oil	324 324
20	3-CF ₃	H	nC_5H_{11}	61.4 60.8	5.4 5.4	8.0 9.7		oil	352 352

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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}\text{C}$)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
21	3-CF ₃	H	nC ₆ H ₁₃	62.3	5.7	7.6		44-45	366
				62.1	5.7	7.5			366
22	3-CF ₃	H	C ₂ H ₅	58.1	4.2	9.0		30	310
				58.4	4.1	8.9			310
23	3-CF ₃	H	CH ₂ C $\equiv$ CH	60.0	3.4	8.7		70-72	320
				59.8	3.7	8.3			320
24	3-CF ₃	H	CH ₂ CH ₂ F	54.9	3.7	8.5		74-75	328
				55.4	4.0	8.2			328
25	3-CF ₃	H	nC ₇ H ₁₅	63.2	6.1	7.4		59-60	380
				63.9	5.6	7.1			380
26	3-CF ₃	H	nC ₈ H ₁₇	64.0	6.4	7.1		50-51	394
				64.1	6.4	7.0			394
27	3-CF ₃	H	cyclobutyl	60.7	4.5	8.3		46-48	336
				60.5	4.5	8.2			336

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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point (°C)	m/e
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			(Theory Found)
28	3-CF ₃		$-\text{CH}_2-\text{CH}_2-\text{N}(\text{CH}_3)-\text{CH}_2-\text{CH}_2-$	59.2 58.9	4.9 5.5	11.5 11.1		oil	365 365
29	3-CF ₃	CH ₃	CH ₃	58.1 54.5	4.2 4.6	9.0 8.7		oil	310 310
30	3-CF ₃	H	OC ₂ H ₅	55.2 55.9	4.0 4.0	8.6 8.4		oil	326 326
31	3-CF ₃	H	NHCO ₂ C ₂ H ₅	52.0 51.9	3.8 4.0	11.4 11.3		100-101	369 369
32	3-CF ₃	H	CH ₂ CH ₂ OH	55.2 55.0	4.0 4.9	8.6 8.6		48-49	326 326

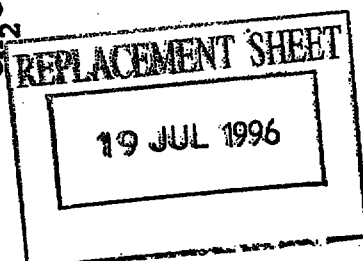


Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}\text{C}$)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
33	3-CF ₃	H	O-CH ₂ CH=CH ₂	56.8 56.3	3.8 4.0	8.3 8.2	oil		338 338
34	3-CF ₃	H	CH ₂ CF ₃	49.4 49.9	2.7 2.9	7.7 7.6	89-90		364 364
35	3-CF ₃	H	CH ₃	56.7 54.2	3.7 4.2	9.5 10.5	67-68		296 296
36	3-CF ₃	H	cyclopropyl	59.6 60.2	4.0 4.1	8.7 8.7	53-54		322 322
37	3-CF ₃	H	CH ₂ CO ₂ C ₂ H ₅	55.4 56.0	4.1 4.5	7.6 7.6	66-67		368 368
38	3-CF ₃	H	CON(CH ₃) ₂	54.4 57.1	4.0 4.7	11.9 11.9	136-137		353 353
39	3-CF ₃	CH ₂ CH=CH ₂	CH ₂ CH=CH ₂	62.9 62.7	4.7 4.9	7.7 7.7	55-56		362 362

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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}\text{C}$)	m/e
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			(Theory Found)
40	3-CF ₃	H	$\begin{array}{c} \text{CH}_3 \\ \\ \text{C-CN} \\ \\ \text{CH}_3 \end{array}$	58.4 57.3	4.0 4.2	12.0 11.7		91-92	349 349
41	3-CF ₃	H		61.1 58.5	3.7 3.6	11.3 10.3		oil	373 373
42	3-CF ₃	H		56.0 55.7	3.2 3.2	10.3 9.9		100-101	407
43	3-CF ₃	H	NHCH ₃	54.0 55.3	3.8 4.3	13.5 13.4		oil	311 311
44	3-CF ₃	H	CO ₂ C ₂ H ₅	54.2 55.4	3.7 4.0	7.9 7.9		142-143	354 354

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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point ($^{\circ}\text{C}$)	m/e
				C	H	N			
				(Calc. Found)	(Calc. Found)	(Calc. Found)			(Theory Found)
45	3-CF ₃	H	H	55.3	3.2	9.9	134-135	282	282
46	3-C ₂ H ₅	H	CH ₂ CF ₃	56.2	3.6	9.7		282	282
				59.2	4.6	8.6	oil	324	324
				58.8	4.8	8.2		324	324
47	H	H	CH ₂ CF ₃	56.7	3.7	9.5	104-105	296	296
				56.9	4.1	9.1		296	296
48	3-CF ₃	H	cyclopentyl	61.7	4.8	8.0	oil	350	350
				60.2	4.9	7.8		350	350
49	3-CF ₃	H	cyclohexyl	62.6	5.2	7.7	oil	364	364
				61.4	5.2	7.5		364	364
50	3-OCH ₃	H	n-C ₃ H ₇	67.1	6.3	9.8	oil	286	286
				66.6	6.5	9.8		286	286

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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
51	3-CF ₃	H	2,2-Cl ₂ - cyclopropyl- methyl	50.4 50.0	3.2 3.4	6.9 6.4		oil	-
52	3-CF ₃	CH ₃	2,2-Cl ₂ - cyclopropyl- methyl	51.6 51.3	3.6 3.8	6.7 6.3		oil	-
53	3-Cl	H	iC ₃ H ₇	62.0 62.1	5.2 5.1	9.6 9.4		oil	-
54	3-Cl	H	nC ₃ H ₇	62.0 61.6	5.2 5.0	9.6 9.9		oil	-
55	3-Cl	nC ₃ H ₇	nC ₃ H ₇	65.0 64.6	6.4 6.2	8.4 8.1		oil	-
56	3-Cl	H	CH ₂ CF ₃	50.9 51.3	3.1 2.9	8.5 8.9		oil	-

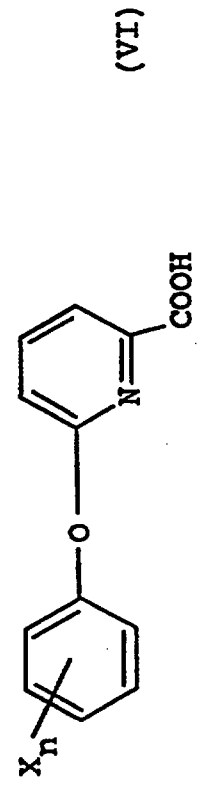
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Table 1 (continued)

Example No.	X_n	R^1	R^2	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
				C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
57	3-Cl	H	H	58.0	3.7	11.3		186	-
				58.0	3.8	11.7			
58	3-Cl	H	CH_2CH_2F	57.0	4.1	9.5		oil	27
				56.6	4.2	9.1			
59	3-Cl	CH_3	2,2- Cl_2 - cyclopropyl-	52.9	3.9	7.3		oil	-
			methyl	52.4	3.6	6.9			
60	3-Cl	H	2,2- Cl_2 - cyclopropyl	51.7	3.5	7.5		oil	-
			methyl	51.5	3.2	7.0			
61	3-Cl	C_2H_5	$CH_2C=CH_2$ CH_3	65.4	5.8	8.5		oil	-
				65.4	6.1	8.5			

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Table 2



X_n	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
	C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
3-Cl	57.8 57.4	3.2 3.2	5.6 5.5		not recorded	249 249
3,4-diCl	50.9 52.3	2.5 3.7	4.9 5.4		110-111	283 283
3-CF ₃ ,4-F	51.8 51.9	2.3 3.0	4.7 4.3		86-87	301 301
3-Br	49.0 53.0	2.7 3.2	4.8 4.8		76-77	294 294

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Table 2 (continued)

X_n	Elementary Analysis (%)				Melting Point (°C)	m/e (Theory Found)
	C (Calc. Found)	H (Calc. Found)	N (Calc. Found)			
3,5-diCl	50.9	2.5	4.9		140-141	283
	51.0	2.9	5.8			283
3-NO ₂	55.4	3.1	10.8		147-149	260
	54.4	2.6	10.8			260
3-C ₂ H ₅	69.1	5.3	5.7		50-51	243
	66.5	5.1	5.7			243
H	66.9	4.2	6.5		104-105	215
	66.6	4.2	6.4			215
3-OCH ₃	63.7	4.5	5.7		102-103	245
	61.9	4.1	5.5			245

Example 62

Preparation of N-n-propyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide

- 5 (a) 6-chloropicolinic acid (3g) and thionyl chloride (50 ml) was refluxed for one hour. The excess thionyl chloride was evaporated in vacuo and dichloromethane added to the residual picolinoyl chloride. This solution was poured into an excess of n-propylamine in dichloromethane. The solution was then washed with water, dried over anhydrous magnesium sulphate and the dichloromethane evaporated to give 6-chloro-2-N-n-propyl pyridine carboxamide (3g) as a yellow oil.

15 Analysis (%):

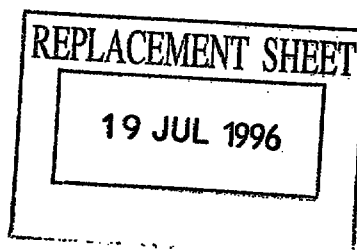
$C_9H_{11}N_2OCl$:	Calc :	C 54.5	H 5.5	N 14.1
	Found :	C 54.2	H 5.9	N 14.0

m/e: Theory: 198

Found : 198

- 20 (b) A solution of sodium methoxide (from 0.4g of sodium in 20 ml of methanol) was added to a solution of 3- α,α,α -trifluoromethylphenol (2.6g) in xylene (20 ml). The solvents were evaporated in vacuo to give the dry sodium phenolate.
- 25 Pyridine (14 ml) and xylene (30 ml) were added, followed by cuprous chloride (0.4g) and the mixture heated to reflux. A solution of 6-chloro-2-N-n-propyl pyridine carboxamide (3g) in xylene (20 ml) was added dropwise and the resultant mixture refluxed a further 18 hours.
- 30 After cooling, the mixture was poured into water and acidified with dilute hydrochloric acid. The whole was extracted with diethyl ether. The combined extracts were dried over anhydrous

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magnesium sulphate and evaporated. The residue was purified on a silica gel column using 5% (v/v) diethyl ether/dichloromethane as eluant to give recovered starting material

- 5 (6-chloro-2-N-n-propyl pyridine carboxamide, 60%) and the title compound (40%) as a colourless oil.

Example 63

Preparation of N-n-butyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridinethiocarboxamide

- 10 A mixture of N-n-butyl-2-(3- α,α,α -trifluoromethylphenoxy)-6-pyridine carboxamide (0.6g) and phosphorus pentasulphide (1.0g) in pyridine (50 ml) was refluxed for 2 hours. The pyridine was evaporated and water added to the residue. The aqueous solution
15 was then extracted with methylene chloride. The extracts were washed with dilute hydrochloric acid, water and dried over anhydrous magnesium sulphate. The dichloromethane was evaporated and the residue purified on a silica gel column using dichloromethane
20 as eluant to give the title compound (0.5g) as a yellow solid of melting point 61-62°C.

Analysis (%):

- | | | | | | |
|----|--------------------------|---------|--------|-------|-------|
| | $C_{17}H_{17}N_2OSF_3$: | Calc : | C 57.6 | H 4.8 | N 7.9 |
| | | Found : | C 61.0 | H 4.7 | N 8.1 |
| 25 | <u>m/e</u> : Theory: | 354 | | | |
| | Found : | 354 | | | |

Example 64

Herbicidal Activity

- 30 To evaluate their herbicidal activity, compounds according to the invention were tested using as representative range of plants: maize, Zea mays (Mz); rice, Oryza sativa (R); barnyard grass, Echinochloa crusgalli (BG); oat, Avena sativa (O); linseed, Linum

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usitatissimum (L); mustard, Sinapsis alba (M); sugar beet, Beta vulgaris (SB) and soya bean, Glycine max (S).

5 The tests fall into two categories, pre-emergence and post-emergence. The pre-emergence tests involved spraying a liquid formulation of the compound onto the soil in which the seeds of the plant species mentioned above had recently been sown. The post-emergence tests involved two types of test, viz., soil drench
10 and foliar spray tests. In the soil drench tests the soil in which the seedling plants of the above species were growing was drenched with a liquid formulation containing a compound of the invention, and in the foliar spray tests the seedling plants were sprayed
15 with such a formulation.

The soil used in the tests was a prepared horticultural loam.

The formulations used in the tests were prepared from solutions of the test compounds in acetone
20 containing 0.4% by weight of an alkylphenol/ethylene oxide condensate available under the trade mark TRITON X-155. These acetone solutions were diluted with water and the resulting formulations applied at dosage levels corresponding to 5 kg or 1 kg of active
25 material per hectare in a volume equivalent to 900 litres per hectare in the soil spray and foliar spray test, and at a dosage of level equivalent to 10 kilograms of active material per hectare in a volume equivalent to approximately 3,000 litres per hectare
30 in the soil drench tests.

In the pre-emergence tests untreated sown soil and in the post-emergence tests untreated soil bearing seedling plants were used as controls.

35 The herbicidal effects of the test compounds were assessed visually twelve days after spraying the

foliage and the soil, and thirteen days after drenching the soil and were recorded on a 0-9 scale.

A rating 0 indicates growth as untreated control, a rating 9 indicates death (i.e. 100% effectiveness).

- 5 An increase of 1 unit on the linear scale approximates to a 10% increase in the level of effect.

The results of the tests are set out in the following Table 3 in which the compounds are identified by reference to the preceding examples. In
10 the Table, a blank space indicates a 0 rating, and an asterisk indicates that no result was obtained.

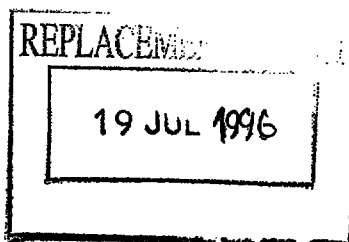


TABLE 3

Compound																									
Ex. No.	Soil drench 10 kg/ha									Dosage kg/ha	Foliar spray						Pre-emergence								
	Mz	R	BG	O	L	M	SB	S	Mz		R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
2	6	6	8	7	3	9	9	4	5	9	7	9	9	9	9	8	8	8	9	9	8	9	9	7	
									1	6	5	9	7	8	9	9	8	6	9	8	6	9	9	7	
3	3	3	7	6	5	9	7	3	5	8	8	9	8	9	9	8	7	6	9	9	7	9	9	5	
									1	6	6	8	7	7	9	9	8	6	5	9	6	4	9	3	
4	1	1	5	4	5	8	6	3	5	6	6	8	7	8	9	9	8	6	5	9	8	7	9	2	
									1	5	4	8	7	7	9	9	8	5	4	9	7	6	9	1	
5									5	7	2	8	7	6	9	9	8		6	4	1	9	8	3	
									1	3		6	4	5	9	9	7		1			7	6		
6	2		5	3	3	7	6	1	5	7	6	8	6	8	9	9	7	2	4	9	2	3	9	8	2
									1	5	3	6	3	7	8	8	6	1	2	8		1	8	8	

TABLE 3 (cont'd)

Compound of		Soil drench 10 kg/ha				Dosage		Foliar spray				Pre-emergence					
Ex. No.	Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S
7	6	3	6	5	2	7	9	4	5	7	6	9	6	8	9	9	3
									1	5	2	7	4	7	9	9	9
8	5	5	6	4	5	7	7	2	5	5	4	9	7	8	9	9	5
									1	3	2	7	5	8	9	9	8
9	6	5	7	3	4	8	8	5	5	7	5	9	7	8	9	9	4
									1	6	5	9	6	8	9	9	2
10									3	5	5	3	6	4	6	9	4
									1	4	*	*		5	7	*	2
11	4		4		4	4	2		5	7	3	8	5	6	9	9	4
									1	6	2	7	4	5	8	9	5

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TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage	Foliar spray				Pre-emergence							
	Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S
12	5		5	1	4	*	9	1	5	8	5	9	6	8	9	9	5
									1	7	4	9	5	8	9	9	2
13									5	5	3	8	5	6	9	9	5
									1	2		7	2	5	8	9	6
14									5	5	3	7	5	5	7	8	5
									1	3	1	3	2	3	6	6	3
15	4		3	2	1	2	2	1	5	5	4	8	7	7	9	9	2
									1	3	2	5	4	6	8	9	5
16	2		4	2	3	3	4		5	4	5	8	5	7	8	9	6
									1	2	2	6	2	6	7	7	4

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TABLE 3 (cont'd)

Compound of																	
Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha	Foliar spray				Pre-emergence							
	Mz	R	BG	O		L	M	SB	S	Mz	R	BG	O	L	M	SB	S
17			1	1	5	6	3	4	2	6	8	9	6	2			
					1	2	2	1	1	4	7	7	5				1
18	3	3	5	1	3	5	6	5	6	6	4	7	9	9	7	1	4
								1	4	2	3	2	6	8	9	7	2
19	4	3	5	4	5	6	6	3	5	7	6	9	6	8	9	8	*
									1	6	5	6	5	8	9	7	*
20			3	2	1	3	4		5	7	6	8	7	8	9	7	*
									1	5	4	6	4	7	9	6	*
21			2		2	2			5	6	4	7	5	7	9	7	1
									1	4	2	6	3	5	9	9	*

TABLE 3 (cont'd)

[illegible]

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TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha	Foliar spray				Pre-emergence							
	Mz	R	BG	O		L	M	SB	S	Mz	R	BG	O	L	M	SB	S
27	6	6	6	6	5	8	7	8	8	9	9	9	9	9	9	9	8
					1	6	5	7	6	8	9	9	7	6	5	9	8
28					5	4	4	4	6	3	5	9	9	7		2	1
					1	3	2	2	5	2	4	8	8	5		1	
29	5		4	2	5	7	7	5	4	3	7	4	7	9	7	3	9
					1	3	1	4	2	5	9	9	6	3	1	6	1
30	5	2	2		4	7	5	2	5	7	3	6	9	9	7	2	9
									1	5	3	5	2	4	9	5	4
31	4		2			4			5	2	1	9	5	5	9	6	4
					1				4	2	4	2	3	8	8	4	

TABLE 3 (cont'd)

Compound of		Soil drench 10 kg/ha				Dosage kg/ha				Foliar spray				Pre-emergence			
Ex. No.		Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
32		6	3	6	2	7	4	5	5	3	9	5	6	9	9	7	5
								1	3		7	4	3	9	9	5	2
33		7	*	*	*	3	7	3	3	5	7	4	9	6	8	9	8
								1	5	3	7	4	7	9	9	7	4
34		6	6	8	7	6	8	7	2	5	8	8	8	8	9	9	8
										1	8	8	8	8	9	9	8
35		6	6	8	5	5	6	9	5	5	8	6	9	9	8	9	8
										1	5	3	8	5	7	8	9
36		*	*	*	*	*	*	*	*	5	9	8	9	9	8	9	8
										1	7	6	8	6	8	9	8

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TABLE 3 (cont'd)

Compound of Ex. No.		Soil drench 10 kg/ha						Dosage		Foliar spray						Pre-emergence										
		Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
37										5	7	4	9	6	6	9	9	7							5	
										1	3	2	6	2	5	8	8	5							3	
38		2		4	1	2	4	1		5	6	1	7	3	7	7	8	7	4	1	7	1	4	7	8	4
										1	4	1	5	1	5	7	7	6	1		2		1	5	4	
39		1		1	1	5	6	3		5	8	3	7	5	7	9	8	7	4		8	3	5	8	8	7
										1	5		6	2	6	8	7	6	1		6		1	7	5	3
40		4	3	6	5	4	7	4	2	5	7	4	7	5	7	8	8	7	4	1	8	4	5	8	9	4
										1	4		6	2	6	8	8	6	1		7	3	3	7	8	
41										5	4		4	2	5	9	7	5					4	2		
										1	2		2		2	8	6	5						1		

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TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha				Foliar spray				Pre-emergence			
	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
42									5	5	4		4	8	6	4
									1		1		1	6	2	1
43									5	5	8	3	2	6	7	4
									1	3	2			3	1	
44	2				3	2	1		5	2	1	6	2	4	9	8
									1	1		5	1	3	8	7
																6
45	1				1				5		3	2	4	8	8	6
									1		1	1	2	8	7	5
																2
																5
46	5	3	2	3	3	5	2		5	4	4	8	5	7	9	9
									1	1	2	7	4	6	8	8
																7
																4
																1
																8
																2
																4
																9
																5
																4
																4

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TABLE 3 (cont'd)

Compound of		Soil drench 10 kg/ha				Dosage		Foliar spray				Pre-emergence					
Ex. No.	Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S
47	4				4		1		5	3	1	7	4	6	9	8	7
									1	1		4	2	3	8	7	6
48	5	2	8	6	4	6	8	5	5	6	7	9	8	8	9	9	7
									1	*	*	*	*	*	*	*	*
49	2		8	6	4	7	7	3	5	6	7	9	7	8	9	9	7
									1	5	4	9	6	7	9	9	7
50	1		5		1	3	7	3	5	3		9	3	6	8	9	6
									1	2		8	1	4	7	8	6
51	3		4	3	4	4	3		5	6	5	8	6	7	9	9	9
									1	5	2	7	5	6	9	9	8
															</		

TABLE 3 (cont'd)

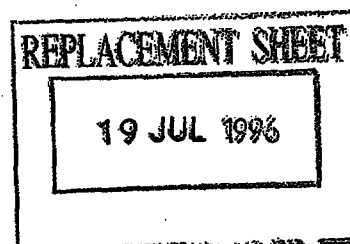
Compound of Ex. No.		Soil drench 10 kg/ha						Dosage kg/ha	Foliar spray						Pre-emergence									
		Mz	R	BG	O	L	M		SB	S	Mz	R	BG	O	L	M	SB	S	BG	O	L	M	SB	S
52					3	4	7		5	7	3	9	5	7	9	9	7	1		3	2	2	7	4
								1	4	4	2	4	4	7	9	9	6		1	1		4	2	
53		3		5	2	1	3	5	5	5	5	9	6	7	9	9	8	5	9	5	5	8	8	
								1	4	4	2	8	5	6	8	9	7		5			7	7	
54		6	3	7	4	3	6	5	5	7	6	9	6	7	9	9	8	6	5	9	7	6	9	1
								1	5	5	2	8	2	5	9	9	7	3	9	2	2	7	8	
55		3		4		2	3	2	5	5	3	9	6	6	9	9	7	4	9	2	3	8	8	
								1	4	4		8	4	5	9	9	7	1	3			7	5	
56		6	4	5	4	3	6	5	4	5	7	4	9	6	7	9	9	7	6	4	9	7	9	4
								1	5	5	1	9	3	7	9	9	7	5	9	6	6	8	9	

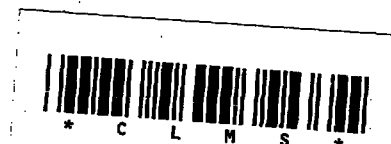
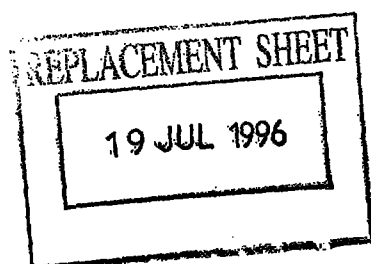
TABLE 3 (cont'd)

Compound of Ex. No.	Soil drench 10 kg/ha				Dosage kg/ha				Foliar spray				Pre-emergence			
	Mz	R	BG	O	L	M	SB	S	Mz	R	BG	O	L	M	SB	S
57					3	2		5	5	2	3	2	5	9	8	7
								1	3		2		4	8	8	5
58	6	4	5	4	4	6	7	4	5	7	5	8	5	8	9	9
								1	4	3	6	3	6	9	8	6
59								5	5	2	5	2	6	9	8	6
								1	2		2	1	4	8	8	5
60					3			5	6	5	6	2	5	9	9	6
								1	3	2	3		5	8	9	6
61								5	5	2	7	2	6	9	9	4
								1	3		3		3	7	7	3

TABLE 3 (cont'd)

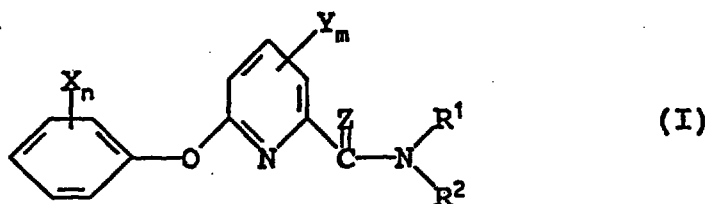
Compound of Ex. No.	Soil drench 10 kg/ha				Dosage				Foliar spray				Pre-emergence									
	Mz	R	BG	O	L	M	SB	S	kg/ha	Mz	R	BG	O	L	M	SB	S					
63	4	2	4	4	2	4	3		5	5	6	8	6	6	8	2	8	6	4	8	9	4
									1	3	3	8	4	4	8	8		5	4	2	7	4





CLAIMS

1. A compound of the general formula I



wherein

- 5 n is an integer from 1 to 5 and the or each X
 independently represents a hydrogen or
 halogen atom, an alkyl or alkoxy group
 optionally substituted by one or more of the
 same or different substituents selected from
10 halogen atoms and cyano, hydroxy and alkoxy
 groups, or a cyano, nitro, alkenyloxy,
 alkynyloxy, alkylthio, haloalkylthio,
 alkenylthio or alkynylthio group;
 m is 0 or an integer from 1 to 3 and the or
 each Y independently represents a halogen
15 atom or an alkyl or haloalkyl group;
 Z represents an oxygen atom or a sulphur atom;
 and

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5 R^1 and R^2 each, independently, represents a
hydrogen atom, an alkyl group optionally
substituted by one or more of the same or
different substituents selected from halogen
atoms or hydroxy, cyano, alkoxy, alkylthio,
alkoxycarbonyl, or mono- or di-alkylamino
groups, an alkenyl, alkynyl, cycloalkyl, or
optionally substituted cycloalkylalkyl
group, or a hydroxy, alkoxy, alkenyloxy,
10 alkynyloxy, alkoxycarbonyl, amino, mono- or
di-alkylamino, alkoxycarbonylamino group, an
arylamino group optionally substituted by a
halogen atom, or a dialkylcarbamoyl group;

or

15 R^1 and R^2 together represent an alkylene chain
which is optionally interrupted by an oxygen
or sulphur atom or by a group -NR- in which
R represents a hydrogen atom or an alkyl
group.

20 2. A compound as claimed in claim 1, wherein n is 1
or 2 and the or each X independently represents a
hydrogen, fluorine, chlorine or bromine atom or a
nitro, ethyl, methoxy or trifluoromethyl group.

25 3. A compound as claimed in claim 2, wherein n is 1
and X represents a 3-trifluoromethyl or 3-methoxy
group or a 3-chlorine atom.

30 4. A compound as claimed in any one of claims 1 to
3, wherein either
 R^1 represents a hydrogen atom or a C_{1-4} alkyl or
 C_{2-4} alkenyl group, while R^2 represents a
hydrogen atom or an unsubstituted C_{1-8} alkyl
group, a C_{1-4} alkyl group substituted by
fluorine, hydroxy, cyano, C_{1-2} alkoxy, (C_{1-2}
alkoxy)carbonyl or mono- or di-(C_{1-2} alkyl)amino,
35 a C_{3-6} cycloalkyl group, a C_{2-4} alkenyl group, a

This Sheet Has Been Replaced



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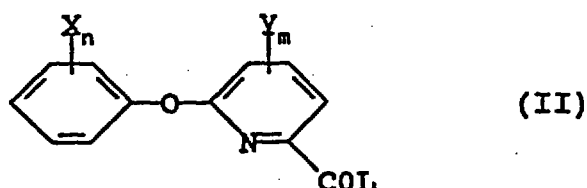
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- 5 C₂₋₄ alkynyl group, a C₁₋₄ alkoxy group, a (C₁₋₄ alkyl)amino group, a C₂₋₄ alkenyloxy group, a (C₁₋₂ alkoxy)carbonyl group, a (C₁₋₂ alkoxy) carbonylamino group, a di(C₁₋₂ alkyl) carbamoyl group, an arylamino group in which the aryl group is optionally halo-substituted, or a halo-substituted (C₃₋₆ cycloalkyl)C₁₋₄ alkyl group;
- or
- 10 R¹ and R² together represent a group -(CH₂)₄-, -(CH₂)₂O(CH₂)₂- or -(CH₂)₂NR(CH₂)₂- in which R is a C₁₋₂ alkyl group.
5. A compound as claimed in claim 4, wherein either R¹ represents a hydrogen atom while R² represents
- 15 an unsubstituted C₁₋₅ alkyl group, a C₁₋₂ alkyl group substituted by fluorine or methoxy, a C₃₋₆ cycloalkyl group, a C₃ alkenyl group, a C₃ alkynyl group, a C₁₋₂ alkoxy group, a C₃ alkenyloxy group or a chloro-substituted cyclopropylmethyl group, or R¹ represents a C₁₋₃
- 20 alkyl group while R² represents the same C₁₋₃ alkyl group or a chloro-substituted cyclopropylmethyl group.
6. A compound as claimed in claim 5, wherein R¹
- 25 represents a hydrogen atom and R² represents an ethyl, propyl, cyclopropyl or cyclobutyl group.
7. A process for the preparation of a compound of general formula I as claimed in claim 1, which comprises preparing a compound of general formula
- 30 I in which Z represents an oxygen atom, by
- a) reacting a compound of the general



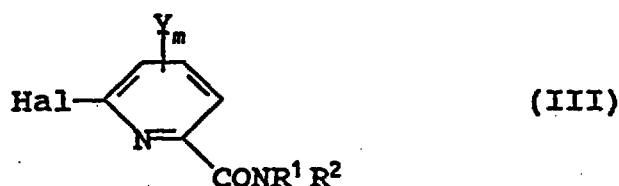
- 50 -

formula II

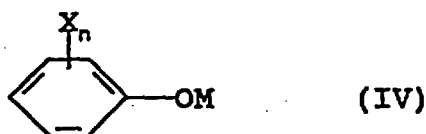


in which X_n and Y_m are as defined in claim 1, and L represents a leaving group, with an amine of the general formula NHR^1R^2 , in which R^1 and R^2 are as defined in claim 1; or

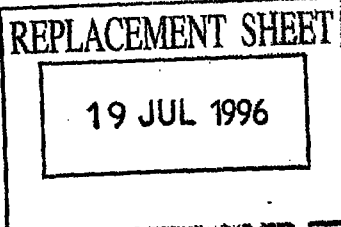
b) reacting a compound of the general formula III



in which Y_m , R^1 and R^2 are as defined in claim 1, and Hal represents a halogen atom with a compound of the general formula IV



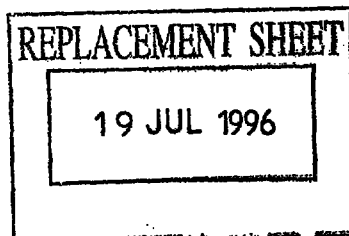
in which X_n is as defined in claim 1 and M represents an alkali metal atom; and optionally converting the product into a compound of general formula I in which Z represents a sulphur atom.

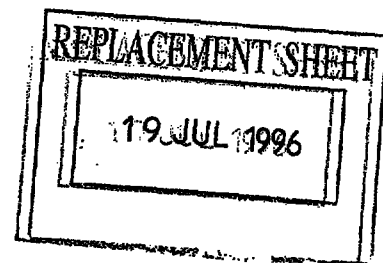




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8. A herbicidal composition which comprises a compound as claimed in anyone of claims 1 to 6, together with a carrier.
- 5 9. A method of combating undesired plant growth at a locus, which comprises treating the locus with a compound as claimed in any one of claims 1 to 6, or with a composition as claimed in claim 8.
- 10 10. The use of a compound as claimed in any one of claims 1 to 7, or a composition as claimed in claim 8, as a herbicide.

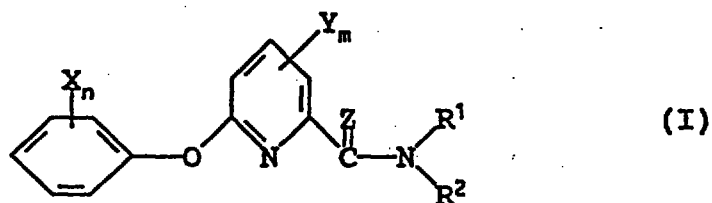




ABSTRACT

HERBICIDAL CARBOXAMIDE DERIVATIVES

Compounds of the formula



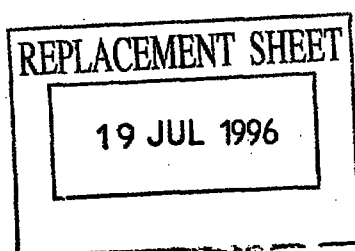
wherein

- 5 n is 1 to 5 and the/each X is hydrogen, halogen, cyano, nitro, optionally substituted alkyl or alkoxy alkenyloxy, alkynyloxy, haloalkylthio, alkenylthio or alkynylthio;
- m is 0 or 1 to 3 and the/each Y is halogen, alkyl or haloalkyl;
- 10 Z is oxygen or sulphur;
- and
- R¹ and R² each, independently, is hydrogen, alkyl optionally substituted by halogen, hydroxy, cyano, alkoxy, alkylthio, alkoxycarbonyl, or
- 15 mono- or di-alkylamino, alkenyl, alkynyl, hydroxy, alkoxy, alkenyloxy, alkynyloxy, alkoxycarbonyl, amino, mono- or di-alkylamino,

alkoxycarbonylamino, arylamino, dialkylcarbamoyl, cycloalkyl, or optionally substituted cycloalkylalkyl;

- or
5 R^1 and R^2 together form an alkylene chain optionally interrupted by oxygen, sulphur or -NR-, R being hydrogen or alkyl;

are herbicides.

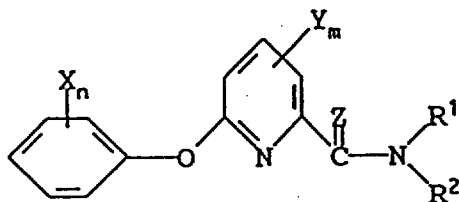


U.S. Patent Specification No. 4 251 263 is concerned with the N-alkyl amides of Gutman, and related N-alkenyl and N-alkynyl amides. The compound documented as being the most active of the aliphatic amides prepared and tested is N-(1,1-dimethylprop-2-ynyl)-2-(3-trifluoromethylphenoxy)-3-pyridine carboxamide, which gives 85% control preemergence and only 57% control postemergence on specified narrow- and broad-leaved species.

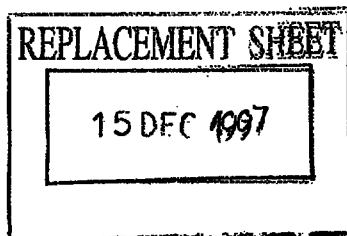
EP-A-0447004 discloses certain herbicidally active 2-phenoxy-6-pyridine carboxamide derivatives which bear an optionally substituted phenyl or benzyl group on the nitrogen atom of the amide moiety.

Suprisingly, it has now been found that 2-phenoxy-6-pyridine carboxamide compounds with aliphatic (both straight chain and alicyclic) and other substitution of the amide nitrogen atom have unexpectedly high levels of herbicidal activity against representative narrow- and broad-leaved test species in pre- and/or post-emergence application; certain examples exhibiting 90 to 100% effectiveness against test species both pre- and post-emergence.

The present invention accordingly provides a compound of the general formula I



(I)



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wherein

- n is an integer from 1 to 5 and the or each X independently represents a hydrogen or halogen atom, a C₁₋₁₂ alkyl or C₁₋₁₂ alkoxy group optionally substituted by one or more of the same or different substituents selected from halogen atoms and cyano, hydroxy and C₁₋₁₂ alkoxy groups, or a cyano, nitro, C₂₋₁₂ alkenyloxy, C₂₋₁₂ alkynyloxy, C₁₋₁₂ alkylthio, C₁₋₁₂ haloalkylthio, C₂₋₁₂ alkenylthio or C₂₋₁₂ alkynylthio group;
- m is 0 or an integer from 1 to 3 and the or each Y independently represents a halogen atom or a C₁₋₁₂ alkyl or C₁₋₁₂ haloalkyl group;
- Z represents an oxygen atom or a sulphur atom;
- and
- R¹ and R² each, independently, represents a hydrogen atom, a C₁₋₁₂ alkyl group optionally substituted by one or more of the same or different substituents selected from halogen atoms or hydroxy, cyano, C₁₋₁₂ alkoxy, C₁₋₁₂ alkylthio, C₁₋₁₂ alkoxycarbonyl, or mono- or di-C₁₋₁₂ alkylamino groups, a C₂₋₁₂ alkenyl, C₂₋₁₂ alkynyl, C₃₋₈ cycloalkyl, or optionally halo-substituted C₃₋₈ cycloalkyl-C₁₋₁₂ alkyl group, or a hydroxy, C₁₋₁₂ alkoxy, C₂₋₁₂ alkenyloxy, C₂₋₁₂ alkynyloxy, C₁₋₁₂ alkoxycarbonyl, amino, mono- or di-C₁₋₁₂ alkylamino, C₁₋₁₂ alkoxycarbonylamino group, a phenylamino group optionally substituted by a halogen atom or a di-C₁₋₁₂ alkylcarbamoyl group;

or

R¹ and R² together represent a C₃₋₆ alkylene chain which is optionally interrupted by an oxygen or sulphur atom or by a group -NR- in which R represents a hydrogen atom or a C₁₋₁₂ alkyl group.

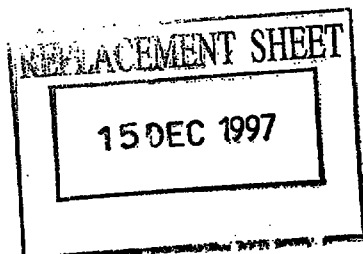
REPLACEMENT SHEET

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When any of the substituents X, Y, R¹ and R² represents or contains an alkyl, alkenyl or alkynyl substituent group, this may be linear or branched and preferably has up to 8, especially up to 5, carbon atoms. Thus, for example, an alkyl group R² may be butyl, e.g. i-butyl, n-butyl, sec-butyl or tert-butyl. Where a cycloalkyl substituent group is present, this preferably has from 3 to 6 carbon atom ring atoms. An alkylene chain preferably has 4 or 5 chain members. A halogen atom suitably denotes a fluorine, chlorine,

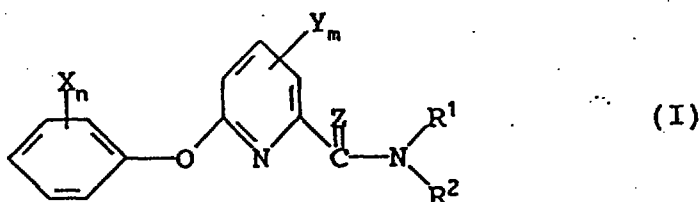


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CLAIMS

1. A compound of the general formula I



wherein

- n - is an integer from 1 to 5 and the or each X independently represents a hydrogen or halogen atom, a C₁₋₁₂ alkyl or C₁₋₁₂ alkoxy group optionally substituted by one or more of the same or different substituents selected from halogen atoms and cyano, hydroxy and C₁₋₁₂ alkoxy groups, or a cyano, nitro, C₂₋₁₂ alkenyloxy, C₂₋₁₂ alkynyloxy, C₁₋₁₂ alkylthio, C₁₋₁₂ haloalkylthio, C₂₋₁₂ alkenylthio or C₂₋₁₂ alkynylthio group;
- m is 0 or an integer from 1 to 3 and the or each Y independently represents a halogen atom or a C₁₋₁₂ alkyl or C₁₋₁₂ haloalkyl group;
- Z represents an oxygen atom or a sulphur atom;
- and
- R¹ and R² each, independently, represents a hydrogen atom, a C₁₋₁₂ alkyl group optionally substituted by one or more of the same or different substituents selected from halogen atoms or hydroxy, cyano, C₁₋₁₂ alkoxy, C₁₋₁₂ alkylthio, C₁₋₁₂ alkoxycarbonyl, or mono- or di-C₁₋₁₂ alkylamino groups, a C₂₋₁₂ alkenyl, C₂₋₁₂ alkynyl, C₃₋₈ cycloalkyl, or optionally halo-substituted C₃₋₈ cycloalkyl-C₁₋₁₂ alkyl group, or a hydroxy, C₁₋₁₂ alkoxy, C₂₋₁₂ alkenyloxy, C₂₋₁₂ alkynyloxy, C₁₋₁₂ alkoxycarbonyl, amino, mono- or di-C₁₋₁₂ alkylamino, C₁₋₁₂ alkoxycarbonylamino group, a phenylamino group optionally substituted by a halogen atom or a di-C₁₋₁₂ alkylcarbamoyl group;

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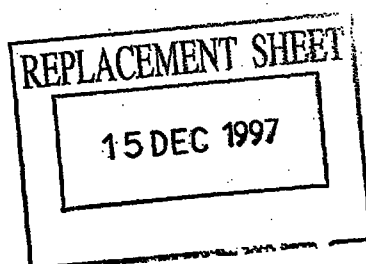


or

R^1 and R^2 together represent a C_{3-6} alkylene chain which is optionally interrupted by an oxygen or sulphur atom or by a group $-NR-$ in which R represents a hydrogen atom or a C_{1-12} alkyl group.

2. A compound as claimed in claim 1, wherein n is 1 or 2 and the or each X independently represents a hydrogen, fluorine, chlorine or bromine atom or a nitro, ethyl, methoxy or trifluoromethyl group.
3. A compound as claimed in claim 2, wherein n is 1 and X represents a 3-trifluoromethyl or 3-methoxy group or a 3-chlorine atom.
4. A compound as claimed in any one of claims 1 to 3, wherein either R^1 represents a hydrogen atom or a C_{1-4} alkyl or C_{2-4} alkenyl group, while R^2 represents a hydrogen atom or an unsubstituted C_{1-8} alkyl group, a C_{1-4} alkyl group substituted by fluorine, hydroxy, cyano, C_{1-2} alkoxy, (C_{1-2} alkoxy)carbonyl or mono- or di-(C_{1-2} alkyl)amino, a C_{3-6} cycloalkyl group, a C_{2-4} alkenyl group, a

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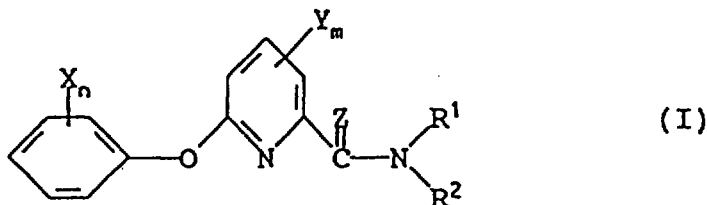
- 2 -

U.S. Patent Specification No. 4 251 263 is concerned with the N-alkyl amides of Gutman, and related N-alkenyl and N-alkynyl amides. The compound documented as being the most active of the aliphatic amides prepared and tested is N-(1,1-dimethylprop-2-ynyl)-2-(3-trifluoromethylphenoxy)-3-pyridine carboxamide, which gives 85% control preemergence and only 57% control postemergence on specified narrow- and broad-leaved species.

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REPLACEMENT SHEETS		SG
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☒	Claim(s): paged 11 to paged 11	48
☐	Drawing(s): paged to paged	
☐	Abstract: paged to paged	
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wherein

n is an integer from 1 to 5 and the or each X independently represents a hydrogen or halogen atom, a C₁₋₁₂ alkyl or C₁₋₁₂ alkoxy group optionally substituted by one or more of the same or different substituents selected from halogen atoms and cyano, hydroxy and C₁₋₁₂ alkoxy groups, or a cyano, nitro, C₂₋₁₂ alkenyloxy, C₂₋₁₂ alkynyloxy, C₁₋₁₂ alkylthio, C₁₋₁₂ haloalkylthio, C₂₋₁₂ alkenylthio or C₂₋₁₂ alkynylthio group;

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Z represents an oxygen atom or a sulphur atom;

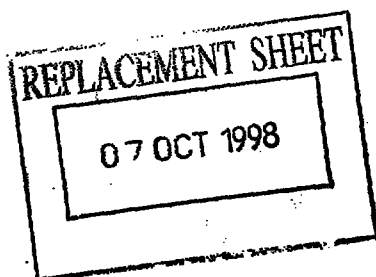
and

R¹ and R² each, independently, represents a hydrogen atom, a C₁₋₁₂ alkyl group optionally substituted by one or more of the same or different substituents selected from halogen atoms or hydroxy, cyano, C₁₋₁₂ alkoxy, C₁₋₁₂ alkylthio, C₁₋₁₂ alkoxycarbonyl, or mono- or di-C₁₋₁₂ alkylamino groups, a C₂₋₁₂ alkenyl, C₂₋₁₂ alkynyl, C₃₋₈ cycloalkyl, or optionally halo-substituted C₃₋₈ cycloalkyl-C₁₋₁₂ alkyl group, or a hydroxy, C₁₋₁₂ alkoxy, C₂₋₁₂ alkenyloxy, C₂₋₁₂ alkynyloxy, C₁₋₁₂ alkoxycarbonyl, amino, mono- or di-C₁₋₁₂ alkylamino, C₁₋₁₂ alkoxycarbonylamino group, a phenylamino group optionally substituted by a halogen atom or a di-C₁₋₁₂ alkylcarbonyl group;

or

R¹ and R² together represent a C₃₋₆ alkylene chain which is optionally interrupted by an oxygen or sulphur atom or by a group -NR- in which R represents a hydrogen atom or a C₁₋₁₂ alkyl group.

When any of the substituents X, Y, R¹ and R² represents or contains an alkyl, alkenyl or alkynyl substituent group, this may be linear or branched and preferably has up to 8, especially up to 5, carbon atoms. Thus, for example, an alkyl group R² may be butyl, e.g. i-butyl, n-butyl, sec-butyl or tert-butyl. Where a cycloalkyl substituent group is present, this preferably has from 3 to 6 carbon atom ring atoms. An alkylene chain preferably has 4 or 5 chain members. A halogen atom suitably denotes a fluorine, chlorine,



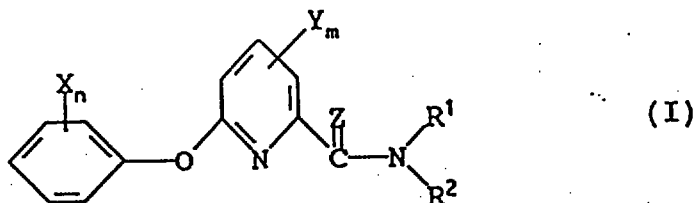
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- 47 -

CLAIMS

1. A compound of the general formula I



wherein

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- m is 0 or an integer from 1 to 3 and the or each Y independently represents a halogen atom or a C₁₋₁₂ alkyl or C₁₋₁₂ haloalkyl group;
- Z represents an oxygen atom or a sulphur atom;
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or

R^1 and R^2 together represent a C_{3-6} alkylene chain which is optionally interrupted by an oxygen or sulphur atom or by a group $-NR-$ in which R represents a hydrogen atom or a C_{1-12} alkyl group.

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3. A compound as claimed in claim 2, wherein n is 1 and X represents a 3-trifluoromethyl or 3-methoxy group or a 3-chlorine atom.
4. A compound as claimed in any one of claims 1 to 3, wherein either R^1 represents a hydrogen atom or a C_{1-4} alkyl or C_{2-4} alkenyl group, while R^2 represents a hydrogen atom or an unsubstituted C_{1-8} alkyl group, a C_{1-4} alkyl group substituted by fluorine, hydroxy, cyano, C_{1-2} alkoxy, (C_{1-2} alkoxy)carbonyl or mono- or di-(C_{1-2} alkyl)amino, a C_{3-6} cycloalkyl group, a C_{2-4} alkenyl group, a

