

PATENT SPECIFICATION

(11) 1 599 121

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 658 65X 662 66X 672 694 695 699 776 805 80Y AA BA
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(54) α -[4-(5-FLUOROMETHYL-2-PYRIDYLOXY)-PHENOXY]ALKANE-CARBOXYLIC ACID DERIVATIVES AND THEIR USE AS HERBICIDES

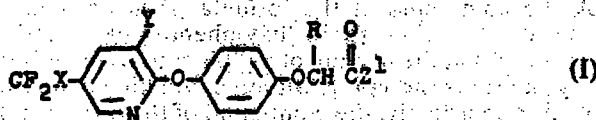
(71) We, ISHIHARA SANGYO KAISHA LTD., of No. 3—11, Edobori 1-chome, Nishi-ku, Osaka-shi, Osaka, Japan, a Japanese Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to α -[4-(5-fluoromethyl-2-pyridyloxy)phenoxy]alkane-carboxylic acid derivatives useful as herbicides for agriculture and horticulture, to herbicidal compositions containing them, and to a method of controlling weeds using them.

In recent years, a number of herbicides have been developed and put to practical use. These herbicides have contributed to a saving of labor and an increased production in agriculture. However, there is still room for improvement, particularly in relation to chemicals which have reduced effects on useful cultivated plants but have a strong herbicidal action on undesirable plants and which are very safe having regard to environmental pollution. For example, certain phenoxyalkane-carboxylic acid derivatives, of which 2,4-dichlorophenoxyacetic acid is representative, have been known for a long time and have superior controlling effects on broad-leaved weeds and still find wide-spread use. However, since these known phenoxyalkane-carboxylic acid derivatives have only a slight activity on graminaceous weeds which are the main noxious weeds, and are phytotoxic to broad-leaved plants which include many crops and cultivated trees, these chemicals have only a limited application.

Further, in recent years, a 4-phenoxy-phenoxy-alkane-carboxylic acids which exhibit a controlling activity on graminaceous weeds but which are not phytotoxic to broad-leaved crops have been proposed as herbicides in, for example, German Patent Application DT-OS 2,223,894 (corresponding to U.S. Patent 3,954,442). Further improvements on these types of herbicidal compounds have been proposed in German Patent Applications DT-OS 2,433,067 and DT-OS 2,546,251 (corresponding to U.S. Patent 4,046,553), but these improvements are of limited value.

The present invention provides 4-(5-fluoromethyl-2-pyridyloxy)phenoxyalkane-carboxylic acids and derivatives thereof of the general formula (I):



wherein X is a fluorine atom or a chlorine atom; Y is a hydrogen atom or a chlorine atom; R is a hydrogen atom, a methyl group or an ethyl group; and Z' is a hydroxy group; a (C₁—C₆)alkoxy group in which the alkyl moiety thereof may be substituted with 1 to 3 halogen atoms; a (C₁—C₄)alkoxy (C₁—C₄)alkoxy group; a

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(C₂—C₄)alkenyloxy group; a (C₂—C₄)alkynyloxy group; a (C₃—C₆)cycloalkoxy group in which the cycloalkyl moiety thereof may be substituted with a (C₁—C₄)alkyl group; a (C₁—C₄)alkoxycarbonyl(C₁—C₄)alkoxy group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; a benzyloxy group; a glycidyloxy group; a (C₁—C₄)alkylthio group; a (C₂—C₄)alkenylthio group; a phenylthio group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; an amino group; a (C₁—C₄)alkylamino group; a (C₁—C₄)alkoxycarbonylmethylamino group; a hydroxycarbonylmethylamino group; an anilino group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms; a pyridine - 2 - yl amino group; an -O-cation; or a halogen atom (e.g., a chlorine atom).

The invention further provides a herbicidal composition comprising a herbicidally effective amount of at least one compound of the above general formula (I) and agriculturally acceptable adjuvants.

Still further, the invention provides a method for controlling weeds comprising applying a herbicidally effective amount of the above-described herbicidal composition to the weeds.

In a preferred aspect the invention resides in a compound of the formula (I) and a herbicidal composition containing the same, wherein X is a fluorine atom; R is a methyl group; and Z' is a hydroxy group; a (C₁—C₄)alkoxy group in which the alkyl moiety thereof may be substituted with 1 to 3 halogen atoms; a (C₁—C₄)alkoxy(C₁—C₄)alkoxy group; a (C₂—C₄)alkenyloxy group; a (C₂—C₄)alkynyloxy group; a (C₃—C₆)cycloalkoxy group in which the cycloalkyl moiety thereof may be substituted with a (C₁—C₄)alkyl group; a (C₁—C₄)alkoxycarbonyl(C₁—C₄)alkoxy group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; a benzyloxy group; a glycidyloxy group; or an -O-cation.

In a further preferred aspect, the invention resides in a compound of the formula (I) and a herbicidal composition containing the same, wherein X is a fluorine atom; Y is a hydrogen atom or a chlorine atom; R is a methyl group; and Z' is a hydroxy group; a (C₁—C₄)alkoxy group; a (C₂—C₄)alkenyloxy group; a (C₃—C₆)cycloalkoxy group; or an -O-cation where the cation is a sodium, potassium, magnesium, calcium, ammonium or organic ammonium cation.

The compounds of the formula (I) of this invention useful as herbicides (hereinafter "herbicidal compound") are novel compounds, and have a unique herbicidal activity which differs from the herbicidal activities of known types of herbicidal compounds. The herbicidal compound of this invention has the following three important characteristics.

(1) The compound of the formula (I) has a strong selective herbicidal activity toward graminaceous plants. On the other hand, since the compound affects broad-leaved plants to only a slight extent, especially those which have grown to some extent, it can be used with high safety on broad-leaved crops or cultivated trees. In other words, the compound of this invention as a reverse selectivity to, and far higher selectivity than, known phenoxyalkanecarboxylic acids.

(2) The compound of the formula (I) has great translocatability in the plant structure. The compound is absorbed by the foliage and roots of a plant, and mainly causes a decay of meristematic cells in the nodes, which leads to withering, collapse and death of the plant. Accordingly, even when applied only to a very limited part of the plant structure, the compound exhibits a strong herbicidal activity, and weeds which have grown considerably are withered and killed due to the activity of the compound of this invention.

(3) The compound of the formula (I) has regrowth controlling activity towards perennial graminaceous weeds and safety on cotton as compared with the known 4-phenoxy- or 4 - (2 - pyridyloxy)phenoxyalkanecarboxylic acids. With respect to the withering and killing of perennial graminaceous weeds which are difficult to control, the compound of the formula (I) has a higher translocatability than 4-phenoxy- or 4 - (2 - pyridyloxy)phenoxyalkanecarboxylic acids and exerts sufficient effects at the portion of the plant to which it is translocated that the plant, including the roots thereof, is withered and killed and the regrowth of the plants is controlled. Accordingly, the compound of the formula (I) is useful in eradication of undesirable plants by a small number of treatments.

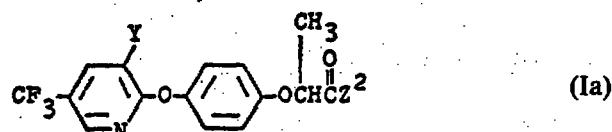
In the above-described definition of the formula (I), suitable examples of halogen atoms which may be employed as a substituent for the (C₁—C₄)alkoxy, phenoxy, phenylthio or anilino groups exemplified as substituents for Z' above include a fluorine atom, a chlorine atom, a bromine atom and an iodine atom with a

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chlorine atom being preferred. Suitable examples of (C₁—C₄)alkyl groups which may also be employed as a substituent for the (C₃—C₆)cycloalkoxy, phenoxy or phenylthio groups exemplified as substituents for Z¹ above include a methyl group, an ethyl group, an n-propyl group, an iso-propyl group, an n-butyl group, an iso-butyl group, a sec-butyl group and a tert-butyl group with a methyl group and an ethyl group being preferred. Suitable examples of cations for the -O-cation which can be used include an alkali metal ion such as sodium ion and potassium ion, an alkaline earth metal ion such as calcium ion and magnesium ion, an ammonium ion, and an organic ammonium ion such as dimethylammonium ion and diethanolammonium ion.

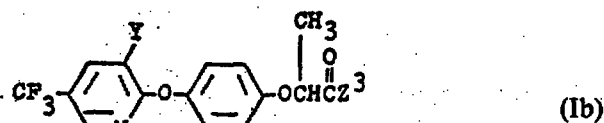
The herbicidal compound of the formula (I) can be used commercially as an active ingredient in herbicidal compositions, as will be seen from the Test Examples given hereinafter.

Of the compounds represented by the formula (I), those compounds of the general formula (Ia) set forth below are preferred:



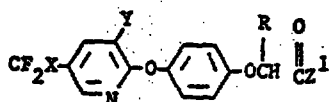
wherein Y is a hydrogen atom or a chlorine atom, and Z² is a hydroxy group, a (C₁—C₄)alkoxy group, a (C₂—C₄)alkenyloxy group, a (C₃—C₆)cycloalkoxy group or an -O-cation.

The compounds represented by the general formula (Ib) are particularly preferred:



wherein Y is a hydrogen atom or a chlorine atom, and Z³ is a hydroxy group, a (C₁—C₄)alkoxy group or an -O-cation.

Typical examples of the compounds of the formula (I) of the present invention are given below.



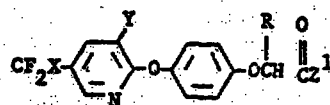
Compound No.	X	Y	R	Z ¹	Physical Constant
1	-F	-H	-H	-OH	mp 123—124°C
2	-F	-H	-CH ₃	-OH	mp 97—100°C
3	-F	-Cl	-CH ₃	-OH	mp 107—109°C
4	-F	-H	-C ₂ H ₅	-OH	mp 95—97°C
5	-Cl	-Cl	-CH ₃	-OH	mp 103—106°C
6	-F	-H	-CH ₃	-OCH ₃	mp 72—74°C
7	-F	-Cl	-CH ₃	-OCH ₃	bp 175—177°C/2 mmHg
8	-F	-H	-H	-OC ₂ H ₅	mp 67—69°C
9	-F	-H	-CH ₃	-OC ₂ H ₅	mp 55—58°C
10	-F	-Cl	-CH ₃	-OC ₂ H ₅	mp 63—65°C
11	-F	-H	-C ₂ H ₅	-OC ₂ H ₅	bp 182—185°C/3 mmHg
12	-Cl	-Cl	-CH ₃	-OC ₂ H ₅	bp 168—170°C/1 mmHg
13	-F	-Cl	-CH ₃	-O-C ₃ H ₇ (n)	n _D ²⁰ 1.5042
14	-F	-Cl	-CH ₃	-O-C ₃ H ₇ (iso)	bp 174—176°C/1 mmHg
15	-Cl	-Cl	-CH ₃	-O-C ₄ H ₉ (n)	bp 205—207°C/2 mmHg
16	-F	-H	-CH ₃	-OCH ₂ CCl ₃	bp 164—167°C/1 mmHg
17	-F	-Cl	-CH ₃	-OCH ₂ CF ₃	bp 184—187°C/1 mmHg
18	-F	-H	-CH ₃	-OCH ₂ CH ₂ OC ₂ H ₅	bp 205—208°C/3 mmHg
19	-F	-H	-CH ₃	-OCH ₂ CH=CH ₂	bp 159—162°C/1 mmHg
					bp 185—187°C/2 mmHg
					bp 198—202°C/3 mmHg

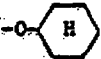
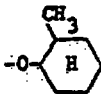
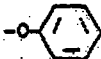
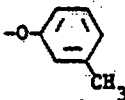
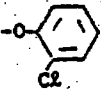
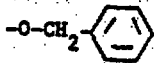
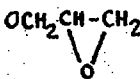
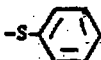
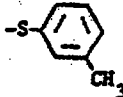
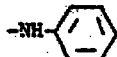
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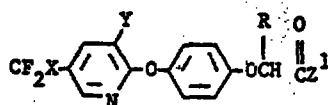
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Compound No.	X	Y	R	Z ¹	Physical Constant		
5	20	-F	-Cl	-CH ₃	-OCH ₂ CH=CH ₂	bp 158—162°C/1 mmHg	5
	21	-F	-H	-CH ₃	-OCH ₂ C≡CH	n _D ²⁰ 1.5212	
	22	-Cl	-Cl	-CH ₃	-OCH ₂ C≡CH	bp 169—172°C/1 mmHg	
	23	-F	-Cl	-CH ₃	-OCH ₂ C≡CH	bp 161—163°C/1 mmHg	
	24	-F	-H	-CH ₃		bp 207—210°C/1 mmHg	
10	25	-F	-Cl	-CH ₃		bp 211—214°C/1 mmHg	10
	26	-F	-H	-CH ₃		bp 180—184°C/2 mmHg	
	27	-F	-H	-CH ₃		bp 205—209°C/2 mmHg	
	28	-F	-Cl	-CH ₃		bp 211—213°C/1 mmHg	
	29	-F	-H	-CH ₃		bp 187—191°C/1 mmHg	
15	30	-F	-H	-CH ₃		n _D ²⁰ 1.5220	15
	31	-F	-H	-CH ₃	-SC ₂ H ₅	N _D ²⁰ 1.5435	
	32	-F	-Cl	-H	-S-C ₃ H ₇ (n)	bp 175—177°C/1 mmHg	
	33	-F	-Cl	-H		bp 201—204°C/1 mmHg	
	34	-F	-H	-CH ₃		bp 232—235°C/3 mmHg	
20	35	-F	-Cl	-CH ₃		bp 224—228°C/1 mmHg	20
	36	-F	-Cl	-CH ₃	-SCH ₂ CH=CH ₂	bp 165—168°C/1 mmHg	
	37	-F	-H	-CH ₃	-NH ₂	mp 163—166°C	
	38	-F	-H	-CH ₃	-NH-C ₄ H ₉ (n)	mp 63—66°C	
	39	-F	-H	-CH ₃	-NHCH ₂ COOC ₂ H ₅	bp 161—166°C/2 mmHg	
25	40	-F	-H	-CH ₃	-NHCH ₂ COOH	mp 87—89°C	25
	41	-F	-H	-CH ₃		mp 139—141°C	

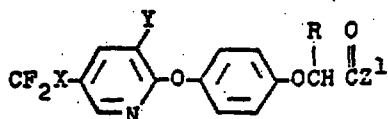


Compound No.	X	Y	R	Z ¹	Physical Constant
42	-F	-Cl	-CH ₃	-NH-	mp 133—135°C
43	-F	-H	-CH ₃	-NH-	mp 95—97°C
44	-F	-H	-CH ₃	-NH-	bp 210—215°C/2 mmHg
45	-F	-H	-CH ₃	-O ⁻ K ⁺	mp 45—50°C
46	-F	-H	-CH ₃	-O ⁻ Na ⁺	mp 70—75°C
47	-F	-Cl	-CH ₃	-O ⁻ Na ⁺	mp 100—105°C
48	-F	-H	-CH ₃	-O ⁻ NH ₄ ⁺	
49	-F	-H	-CH ₃	-O ⁻ NH ₂ (CH ₃) ₂ ⁺	
50	-F	-H	-CH ₃	-Cl	mp 54—57°C
51	-F	-H	-CH ₃	-OCH ₂ COOC ₂ H ₅	bp 181—184°C/2 mmHg
52	-F	-Cl	-CH ₃	-OCHCOOC ₂ H ₅	bp 225—228°C/2 mmHg

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The herbicidal compounds of the present invention of the formula (I):

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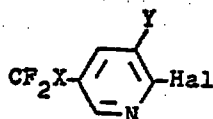
(I)

wherein X, Y, R, and Z¹ are as defined previously, can be produced by either Method A or Method B described below, with Method A being preferred.

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Method A
A 2 - halo - 5 - fluoromethylpyridine of the formula (II):

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(II)

wherein Hal is a halogen atom, X and Y are the same as defined hereinbefore, and a substituted phenol of the formula (III):

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wherein Q is a hydroxy group, a (C₁—C₈)alkoxy group or an

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(III)

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group wherein R is the same as defined hereinbefore and Z⁴ is a hydroxy group, a (C₁—C₈)alkoxy group or an amino group, are first condensed, e.g., using an equimolar amount of the compound of the formula (II) and the compound of the formula (III), in the presence of an alkaline material preferably in an amount of 1 to 1.2 molar times the amount of the compound of the formula (III) to form a substituted pyridyl phenyl ether of the formula (IV):

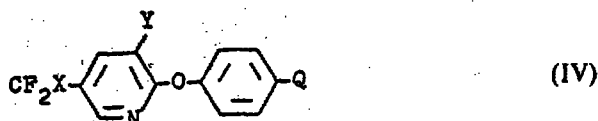
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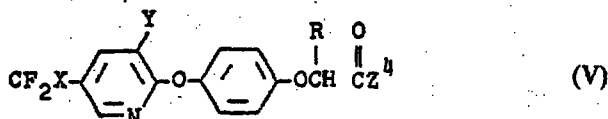


wherein X, Y and Q are the same as defined hereinbefore.

When Q is an



5 group, a compound of the formula (V):

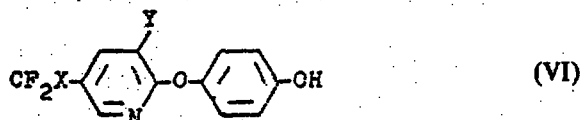


wherein X, Y, R and Z⁴ are the same as defined hereinbefore, is obtained. If desired, the resulting product of the formula (V) can be treated by a conventional method to convert Z⁴ to Z¹ to thereby form the herbicidal compound of the formula (I).

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When Q is a (C₁—C₆)alkoxy group or a hydroxy group, the resulting substituted pyridyl-p-hydroxyphenyl ether of the formula (VI):

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wherein X and Y are the same as defined hereinbefore, and a haloalkanecarboxylic acid or a derivative thereof of the formula (VII):

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wherein Hal, R and Z⁴ are the same as defined hereinbefore, are then condensed, e.g., using an equimolar amount of the compound of the formula (VI) and the compound of the formula (VII), in the presence of an alkaline material preferably in an amount of 1 to 1.2 molar times the compound of the formula (VI), with or without prior dealkylation (i.e., to remove the alkyl moiety of the (C₁—C₆)alkoxy group), to form an object compound of the formula (V) as described above.

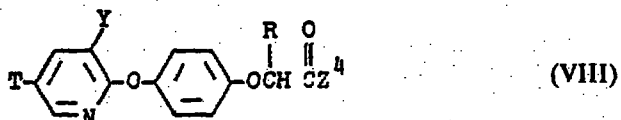
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Method B

Trifluoromethyl iodide is reacted with a compound of the formula (VIII):

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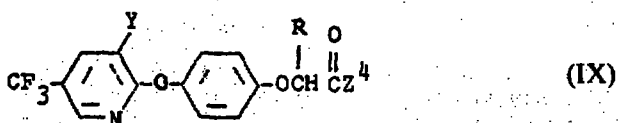


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wherein T is a bromine atom or an iodine atom, and Y, R and Z⁴ are the same as defined hereinbefore, in the presence of copper dust and a polar aprotic solvent, such as pyridine, sulfolane, dimethylformamide or dimethyl sulfoxide, at a temperature of 100 to 200°C for 1 to 24 hours to form a compound of the formula (IX):

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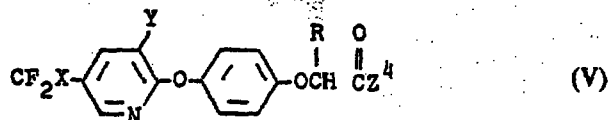
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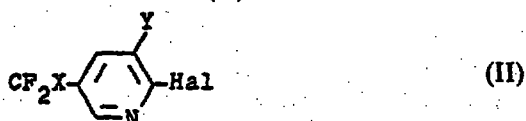
wherein Y, R and Z⁴ are the same as defined hereinbefore. If desired, the substituent Z⁴ of the formula (IX) can be converted into Z¹ in the usual manner to form the herbicidal compound of the formula (I).

The above methods for the production of the compounds of the formula (I) or intermediates used therein are described in greater detail below.

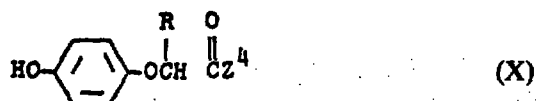
[A-1] The compound of the formula (V):



wherein X, Y, R and Z⁴ are the same as defined hereinbefore, can be prepared by condensing a substituted pyridine of the formula (II):

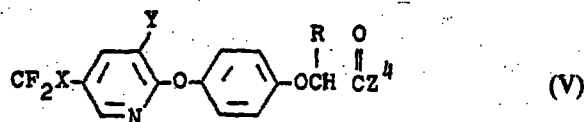


wherein Hal, X and Y are the same as defined hereinbefore, with a p-hydroxyphenoxyalkane carboxylic acid or a derivative thereof of the formula (X):

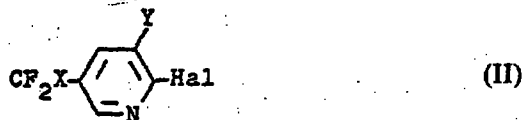


wherein R and Z⁴ are the same as defined hereinbefore, the compound of the formula (II) preferably being used in an amount equimolar to the amount of the compound of the formula (X), in the presence of an alkaline material preferably in an amount of 1 to 1.2 molar times the amount of the compound of the formula (X) at a temperature of at least 50°C, preferably 70 to 180°C, at a pressure of preferably atmospheric pressure for 1 to 20 hours, preferably 1 to 10 hours.

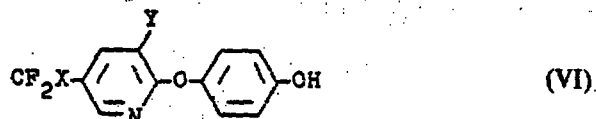
[A-2] The compound of the formula (V):



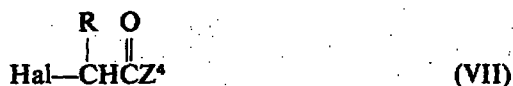
wherein X, Y, R and Z⁴ are the same as defined hereinbefore or a salt thereof, can be prepared by condensing a substituted pyridine of the formula (II):



[compounds obeying formula (II) and processes for their preparation are described and claimed in our co-pending Application No. 10877/78 (Serial No. 1,599,123)] wherein Hal, X and Y are the same as defined hereinbefore, with hydroquinone, the compound of the formula (II) preferably being used in an amount equimolar to the hydroquinone, in the presence of an alkaline material preferably in an amount of 1 to 1.2 molar times the amount of the hydroquinone, at a temperature of at least 50°C, preferably 70 to 180°C, under an inert atmosphere, e.g., of nitrogen for 1 to 20 hours to form a substituted pyridyl-p-hydroxyphenyl ether of the formula (VI):



[compounds obeying formula (VI) and process for their preparation are described and claimed in our co-pending Application No. 10876/78 (Serial No. 1,599,122)] wherein X and Y are the same as defined hereinbefore, and then condensing the compound of the formula (VI) with a haloalkanecarboxylic acid or a derivative thereof of the formula (VII):



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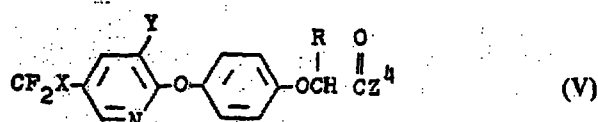
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wherein Hal, R and Z⁴ are the same as defined hereinbefore, the compound of the formula (VI) preferably being used in an amount equimolar to the amount of the compound of the formula (VII) in the presence of an alkaline material preferably in an amount of 1 to 1.2 molar times the amount of the compound of the formula (VI), at a temperature of 40 to 200°C at a pressure of preferably atmospheric pressure for 0.5 to 10 hours.

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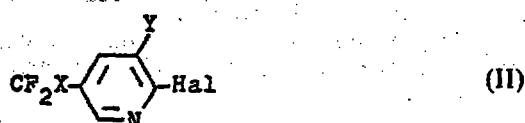
[A-3] The compound of the formula (V):



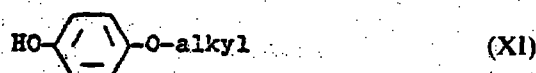
wherein X, Y, R and Z⁴ are the same as defined hereinbefore or a salt thereof, can be prepared by condensing a substituting pyridine of the formula (II):

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wherein Hal, X and Y are the same as defined hereinbefore, with a hydroquinone monoalkyl ether of the formula (XI):



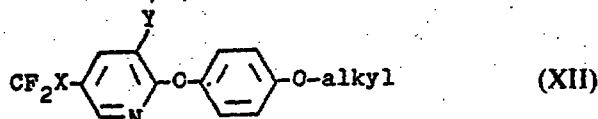
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wherein "alkyl" represents a (C₁—C₆) alkyl group, the compound of the formula (II) preferably being used in an amount equimolar to the amount of the compound of the formula (XI), in the presence of an alkaline material preferably in an amount of 1 to 1.2 molar times the amount of the compound of the formula (XI), at a temperature of at least 50°C, preferably 70 to 180°C, at a pressure of preferably atmospheric pressure for 1 to 20 hours, preferably 1 to 10 hours, to form a substituted pyridyl-p-alkoxyphenyl ether of the formula (XII):

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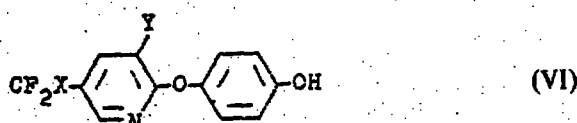
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wherein X, Y and "alkyl" are the same as defined hereinbefore, dealkylating the compound of the formula (XII) to form a substituted pyridyl-p-hydroxyphenyl ether of the formula (VI):

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wherein X and Y are the same as defined hereinbefore, and then condensing the compound of the formula (VI) with a haloalkanecarboxylic acid or a derivative thereof of the formula (VII):



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wherein Hal, R and Z⁴ are the same as defined hereinbefore, the compound of the formula (VI) preferably being used in an amount equimolar to the amount of the compound of the formula (VII) in the presence of an alkaline material preferably in an amount of 1 to 1.2 molar times the amount of the compound of the formula (VI), at a temperature of 40 to 200°C at a pressure of preferably atmospheric pressure for 0.5 to 10 hours.

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Examples of suitable alkaline materials which can be used in all of the condensation reactions described above are alkali metal hydroxides such as sodium hydroxide or potassium hydroxide, and alkali metal carbonates such as sodium

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carbonate or potassium carbonate. In the first condensation, a suitable reaction temperature is at least 50°C, preferably 70 to 180°C, and the reaction time is generally 1 to 20 hours, preferably 1 to 10 hours. A ketone such as methyl ethyl ketone or methyl isobutyl ketone, or a polar aprotic solvent, such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidone, hexamethylphosphoramide or sulfolane, can be used in this reaction as a solvent. In the second condensation, a suitable reaction temperature is 40 to 200°C, and the reaction time is generally 0.5 to 10 hours. In this second condensation, a ketone such as methyl ethyl ketone or methyl isobutyl ketone or toluene can be used as a solvent.

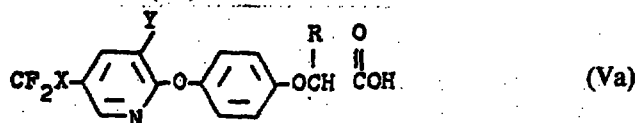
In the dealkylation, the dealkylating agent is used in an amount of 1.5 to 2.0 molar times the amount of the compound of the formula (XII).

When pyridine hydrochloride is used as a dealkylating agent in the dealkylation, the reaction temperature is desirably 50 to 250°C, more desirably 130 to 200°C, the pressure is preferably atmospheric pressure, and the reaction time is most generally 1 to 10 hours. When a hydrohalic acid having a concentration of 40 to 60% by weight such as hydrobromic acid or hydroiodic acid is used as a dealkylating agent, the dealkylating reaction is desirably carried out in the presence of a (C₁—C₄) fatty acid solvent, such as acetic acid or acetic anhydride, in an amount of 1 to 50 times the volume of the compound of the formula (XII) for 1 to 10 hours at a pressure of preferably atmospheric pressure at a temperature of 90 to 150°C.

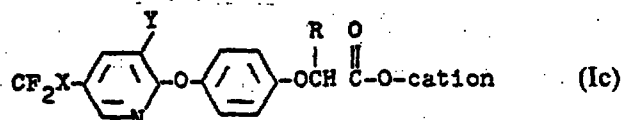
Methods for converting Z⁴ of the formula (V) to Z¹ of the formula (I) are described as follows:

(1) Formation of Salts

A compound of the formula (Va):



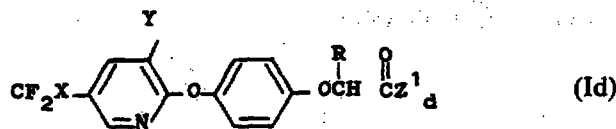
wherein X, Y and R are the same as defined hereinbefore, is neutralized with an alkaline material (e.g., sodium hydroxide, potassium hydroxide or ammonia) to form a compound of the formula (Ic):



wherein X, Y and R are the same as defined hereinbefore.

(2) Formation of Halides

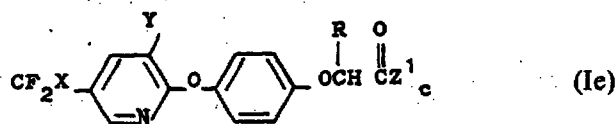
A compound of the formula (Va) is reacted with a halogenating agent (e.g., SOCl₂, PCl₃, PCl₅ or POCl₃) to form a compound of the formula (Id):



wherein X, Y and R are the same as defined hereinbefore and Z_a¹ is a halogen atom.

(3) Formation of Amides

A compound of the formula (V) or (Id) is aminated with an amine of the formula Z_c¹-H (wherein Z_c¹ is an amino group; a (C₁—C₄)alkylamino group; a (C₁—C₄)alkoxycarbonylmethylamino group; a hydroxycarbonylmethylamino group; an anilino group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms; or a pyridine-2-ylamino group) to form a compound of the formula (Ie):



wherein X, Y, R and Z_c¹ are the same as defined hereinbefore.

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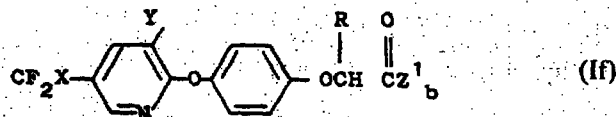
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(4) Formation of Thioesters

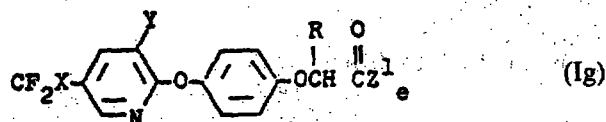
A compound of the formula (Id) is reacted with a mercaptan of the formula Z'_b-H (wherein Z'_b is a (C_1-C_4) alkylthio group; a (C_2-C_4) alkenylthio group; or a phenylthio group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C_1-C_4) alkyl group) to form a compound of the formula (If):



wherein X, Y, R and Z'_b are the same as defined hereinbefore.

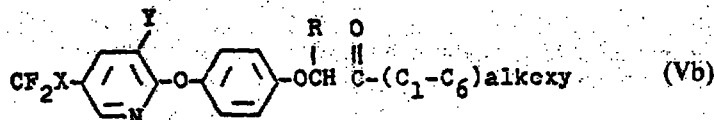
(5) Formation of Esters

(5-1) A compound of the formula (Va) or (Id) is esterified with an alcohol of the formula Z'_e-H (wherein Z'_e is a (C_1-C_6) alkoxy group in which the alkyl moiety thereof may be substituted with 1 to 3 halogen atoms; a (C_1-C_4) alkoxy group; a (C_2-C_4) alkenyl group; a (C_2-C_4) alkynyl group; a (C_3-C_6) cycloalkoxy group in which the cycloalkyl moiety thereof may be substituted with a (C_1-C_4) alkyl group; a (C_1-C_4) alkoxycarbonyl group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C_1-C_4) alkyl group; a benzyloxy group; or a glycidyloxy group) to form a compound of the formula (Ig):



wherein X, Y, R and Z'_e are the same as defined hereinbefore.

(5-2) A compound of the formula (Vb):

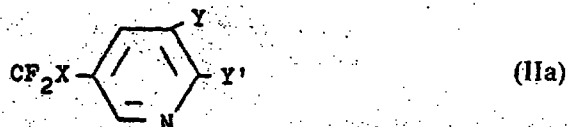


wherein X, Y and R are the same as defined hereinbefore, is ester-interchanged with an alcohol of the formula Z'_e-H as described hereinbefore, in the presence of a Lewis acid catalyst (e.g., BF_3), to form a compound of the formula (Ig).

(6) Formation of Acids

A compound of the formula (Vb) is hydrolyzed (e.g., with an appropriate acid or alkaline material) to form a compound of the formula (Va).

Of the starting material compounds represented by the formula (II), a compound of the formula (IIa):



wherein Y is the same as defined hereinbefore, and Y' is a fluorine atom or a chlorine atom, is produced in, for example, the following manner.

2 - Amino - 5 - methylpyridine [as described in, for example, *Chemical Abstracts*, Vol. 43, 7050i (1949)] is diazotized with or without prior halogenation to form a compound of the formula (IIb):



wherein Y'' is a hydrogen atom, a chlorine atom or a bromine atom, and Y''' is a halogen atom with a fluorine atom, a chlorine atom and a bromine atom being preferred. The compound of the formula (IIb) is then chlorinated under ultraviolet light irradiation to form a compound of the formula (IIc):



wherein Y and Y''' are the same as defined hereinbefore, which is then reacted with a metal fluoride such as antimony trifluoride at a temperature of 100 to 250°C, to form the compound of the formula (IIa) above.

The other starting materials, i.e., hydroquinone, a hydroquinone monoalkyl ether of the formula (XI), a p-hydroxyphenoxyalkanecarboxylic acid of the formula (X) or derivative thereof, a haloalkanecarboxylic acid of the formula (VII) or a derivative thereof, and a compound of the formula (VIII), are described in, for example, U.S. Patent 4,046,553. Further, trifluoromethyl iodide which is also used as one of the starting materials in the present invention is described in, for example, *Org. Reaction*, Vol. 9, p. 358.

Some specific examples of preparing the herbicidal compounds of this invention are shown below. Unless otherwise indicated herein, all parts, percents and ratios are by weight.

Preparation EXAMPLE 1

Preparation of Ethyl α -[4-(5-Trifluoromethyl-2-pyridyloxy)-phenoxy]propionate

[A-1] (a) 40 ml of dimethyl sulfoxide, 4.2 g of hydroquinone, 5.0 g of 2-chloro - 5 - trifluoromethylpyridine and 2.3 g of potassium hydroxide were allowed to react at 150°C for 2 hours in a nitrogen atmosphere while stirring. The reaction product was allowed to cool and poured into an appropriate amount of ice-water. The mixture was then rendered neutral with 30% concentrated hydrochloric acid and extracted with methylene chloride. The extract was washed with water, dried over anhydrous sodium sulfate and the methylene chloride was removed by distillation to obtain 2.5 g of 2 - (4 - hydroxyphenoxy) - 5 - trifluoromethylpyridine having a melting point of 82-84°C.

(b) 40 ml of dimethyl sulfoxide, 5.0 g of hydroquinone monomethyl ether, 5.0 g of 2 - chloro - 5 - trifluoromethylpyridine and 2.3 g of potassium hydroxide were allowed to react at 150°C for 3 hours while stirring. The reaction product was allowed to cool and poured into an appropriate amount of ice-water. The mixture was then extracted with methylene chloride, and the extract was washed with water and dried over anhydrous sodium sulfate. The methylene chloride was then removed by distillation and the resulting residue containing 2 - (4 - methoxyphenoxy) - 5 - trifluoromethylpyridine was mixed with 5.0 g of pyridine hydrochloride. The mixture was allowed to react at 140-160°C for 2 hours while stirring. After allowing the reaction mixture to cool, it was poured into an appropriate amount of ice-water followed by extraction with methylene chloride. The methylene chloride layer was then back extracted with a 5% aqueous solution of sodium hydroxide and the resulting aqueous extract was rendered acidic with 30% concentrated hydrochloric acid to obtain a solid product. The resulting product was recovered by filtration and dried to obtain 2.1 g of 2 - (4 - hydroxyphenoxy) - 5 - trifluoromethylpyridine.

5.1 g of 2 - (4 - hydroxyphenoxy) - 5 - trifluoromethylpyridine obtained as described in (a) or (b) above, and 3.6 g of ethyl α -bromopropionate were dissolved in 50 ml of methyl ethyl ketone, and the solution was allowed to react for 2 hours in the presence of 3.3 g of anhydrous potassium carbonate while refluxing at 80°C. After completion of the reaction, water was added to the reaction product to dissolve any remaining solid, and the mixture was concentrated under reduced pressure to distill out the methyl ethyl ketone. The residue was then extracted with toluene and the extract was washed with water and dried over anhydrous sodium sulfate. The toluene was then removed by distillation to obtain an oily product. The resulting oily product was solidified by cooling, washed with n-hexane and dried to obtain 1.8 g of the desired product having a melting point of 63-65°C.

[A-2] 9.1 g of 2 - chloro - 5 - trifluoromethylpyridine and 21.0 g of ethyl α - (4 - hydroxyphenoxy)propionate were dissolved in 50 ml of dimethyl sulfoxide, and the solution was allowed to react at 150°C for 2 hours in the presence of 13.8 g of anhydrous potassium carbonate while stirring. The reaction product was allowed to cool, poured into ice-water and the resulting solid substance was extracted with toluene. The toluene layer was washed several times with water, dried over anhydrous sodium sulfate and the toluene was removed by distillation to obtain 12.4 g of an oily substance (i).

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The aqueous layer which had been set aside in the above toluene extraction was washed with toluene and rendered acidic with 30% concentrated hydrochloric acid to obtain an oily substance. The resulting oily substance was extracted with methylene chloride, washed thoroughly with water and dried over anhydrous sodium sulfate. The methylene chloride was then removed by distillation to obtain 9.0 g of an oily substance which was then mixed with an excess volume of ethanol. 2 ml of diethyl ether solution of boron trifluoride was added to the mixture followed by refluxing at 80°C for 2 hours. A small amount of water was added to the mixture, and the oil phase obtained after distilling out the ethanol was extracted with methylene chloride. The extract was washed with water and dried over anhydrous sodium sulfate, and the methylene chloride was removed by distillation to obtain 6.0 g of an oily substance (ii).

The oily substances (i) and (ii) obtained above were combined and adsorbed onto a silica gel column followed by elution with toluene. The toluene was distilled off from the resulting eluate to obtain 11.6 g of an oily substance, and the resulting substance was solidified by cooling, washed with n-hexane and dried to obtain 6.5 g of the desired product.

[B] 4.1 g of ethyl α - [4 - (5 - iodo - 2 - pyridyloxy)phenoxy]propionate, 2.45 g of trifluoromethyl iodide, 40 ml of pyridine and 1.62 g of copper powder were mixed in an autoclave, and the mixture was allowed to react at 120—130°C for 12 hours while stirring. After completion of the reaction, the reaction mixture was allowed to cool, and the copper salt precipitated upon addition of diethyl ether was removed by filtration. The resulting ethereal solution was washed successively with water, 15% dilute hydrochloric acid and water, and dried over anhydrous sodium sulfate. Thereafter, the ethereal solution was concentrated, and the resulting oily substance (5 g) was purified by silica gel column chromatography (eluted with methylene chloride) and distilled under reduced pressure to obtain 1.9 g of the desired product having a boiling point of 182—185°C/3 mm Hg.

Preparation EXAMPLE 2

Preparation of α -[4-(5-Trifluoromethyl-2-pyridyloxy)phenoxy]propionic Acid

[A] 16 g of 2 - (4 - hydroxyphenoxy) - 5 - trifluoromethylpyridine was dissolved in 100 ml of toluene and 7 g of sodium hydroxide was then added to the solution at 60°C followed by stirring for 30 minutes. 8.8 g of α -chloropropionic acid was then added dropwise to the mixture at 50—80°C followed by stirring for 1 hour and, thereafter, an additional 7.6 g of sodium hydroxide was added thereto. The resulting mixture was then allowed to react for 1 to 1.5 hours while refluxing at 110°C. Water was added to the resulting reaction product and the mixture was rendered neutral with 10% sulfuric acid. The mixture was then allowed to stand at 70—80°C to separate an organic layer and an aqueous layer. Water and sodium hydroxide were added to the organic layer and the mixture was stirred at 70—80°C to adjust the solution to a pH of 9—10. After removing toluene, the resulting aqueous solution was rendered acidic with 10% sulfuric acid. 100 ml of toluene was added to the solution and the mixture was washed with water, dried over anhydrous sodium sulfate and filtered. The toluene was then removed and the residue was washed with n-hexane to obtain 16.8 g of the desired product having a melting point of 97—100°C.

[B] 3.55 g of ethyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate obtained in preparation Example 1 [B] above was added to a mixture of 4 g of sodium hydroxide, 16 ml of water and 16 ml of ethanol, and the resulting mixture was allowed to react for 2 hours at room temperature while stirring. After completion of the reaction, an appropriate amount of ice was added to the reaction mixture, and the mixture was rendered acidic with 30% concentrated hydrochloric acid. The precipitated crystals were filtered, washed with water and dried to obtain 2.5 g of the desired product.

Preparation EXAMPLE 3

Preparation of Methyl α -[4-(5-Trifluoromethyl-2-pyridyloxy)phenoxy]propionate

[A] 255 g of 2 - (4 - hydroxyphenoxy) - 5 - trifluoromethylpyridine, 199.1 g of methyl α -bromopropionate and 207 g of anhydrous potassium carbonate were allowed to react for 2 hours in 1000 ml of methyl ethyl ketone while heating at a refluxing temperature of 80°C. After allowing the reaction mixture to cool, any inorganic salts were removed by filtration and the methyl ethyl ketone was distilled

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out. The residue was extracted with methylene chloride, and the extract was washed successively with water, a 5% dilute aqueous solution of sodium bicarbonate and water. The extract was dried over anhydrous sodium sulfate, and the methylene chloride was removed by distillation to obtain 346 g of an oily substance which was then cooled rapidly to obtain a solid substance. The resulting solid substance was washed with n-hexane and recrystallized from ethanol to obtain 196 g of the desired product having a melting point of 72–74°C.

[B] 3.27 g of α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionic acid obtained in Preparation Example 2 [B] above was dissolved in 33 ml of methanol, and 0.5 g of a diethyl ether solution of boron trifluoride was added thereto followed by allowing the mixture to react for 3 hours while refluxing at 64°C. After completion of the reaction, a small amount of water was added to the reaction mixture and the resulting mixture was concentrated under reduced pressure followed by extraction with methylene chloride. The extract was washed with water and dried over anhydrous sodium sulfate. The methylene chloride was removed by distillation and the residue was evaporated under reduced pressure to obtain 2.3 g of the desired product as an oily substance having a boiling point of 175–177°C/2 mm Hg. The resulting oily substance solidified upon standing to give a solid product having a melting point of 72–74°C.

Preparation EXAMPLE 4

Preparation of Sodium α - [4 - (5 - Trifluoromethyl - 2 - pyridyloxy) - phenoxy]propionate

3.27 g of α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionic acid was dissolved in a small amount of ethanol and the solution was mixed with 0.8 g of a 50% aqueous solution of sodium hydroxide. The mixture was then allowed to react at room temperature for 30 minutes while stirring, and the reaction mixture was concentrated under reduced pressure. The precipitated crystals were then dried to obtain 3.0 g of the desired product having a melting point of 70–75°C.

Preparation EXAMPLE 5

Preparation of Methyl α - [4 - (3 - Chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate

6 g of 2,3 - dichloro - 5 - trifluoromethylpyridine, 40 ml of dimethyl sulfoxide, 4.2 g of hydroquinone and 2.3 g of potassium hydroxide were allowed to react at 150°C for 2 hours in a nitrogen atmosphere while stirring. The reaction mixture was then allowed to cool and poured into an appropriate amount of ice-water. The mixture was rendered neutral with 30% concentrated hydrochloric acid and extracted with methylene chloride. The extract was washed with water, dried over anhydrous sodium sulfate and the methylene chloride was removed by distillation to obtain 2.7 g of 2 - (4 - hydroxyphenoxy) - 3 - chloro - 5 - trifluoromethylpyridine (m.p. 70–72°C). 5.8 g of the resulting 2 - (4 - hydroxyphenoxy) - 3 - chloro - 5 - trifluoromethylpyridine and 3.3 g of methyl α - bromopropionate were dissolved in 50 ml of methyl ethyl ketone, and the resulting mixture was allowed to react at a refluxing temperature of 80°C for 2 hours in the presence of 3.3 g of anhydrous potassium carbonate. Water was added to the reaction mixture and the mixture was concentrated under reduced pressure to distill out the methyl ethyl ketone. The residue was extracted with toluene and the extract was washed with water, dried over anhydrous sodium sulfate and the toluene was removed by distillation to obtain an oily substance. The resulting oily substance was then solidified by cooling, washed with n-hexane and dried to obtain 2.2 g of the desired product having a melting point of 67–69°C.

[A-2] 4.3 g of 2,3 - dichloro - 5 - trifluoromethylpyridine and 4 g of methyl α - (4 - hydroxyphenoxy)propionate were dissolved in 30 ml of dimethyl sulfoxide, and the resulting solution was allowed to react at 150°C for 2 hours in the presence of 3.3 g of anhydrous potassium carbonate while stirring. After allowing the reaction mixture to cool, it was poured into ice-water and the resulting solid substance was extracted with toluene. The toluene layer was washed several times with water, dried over anhydrous sodium sulfate and the toluene was removed by distillation to obtain 3.5 g of an oily substance (iii).

The aqueous layer which had been set aside was washed with toluene and rendered acidic with 30% concentrated hydrochloric acid to obtain an oily substance. The oily substance was extracted with methylene chloride, and the extract was washed with water and dried over anhydrous sodium sulfate. The methylene chloride was then removed from the extract to obtain 1.5 g of an oily

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substance. The resulting oily substance was mixed with an excess volume of methanol, and 2 ml of a diethyl ether solution of boron trifluoride was added to the solution followed by refluxing at 64°C for 2 hours. A small amount of water was added to the mixture and the methanol was removed by distillation to obtain an oily substance. The oily substance was extracted with methylene chloride, and the extract was washed with water, dried over anhydrous sodium sulfate and the methylene chloride was removed by distillation to obtain 1.2 g of an oily substance (iv).

The combined oily substances (iii) and (iv) were adsorbed onto a silica gel column chromatography and the column was eluted with toluene. The toluene was removed from the eluate to obtain 2.5 g of an oily substance. The resulting oily substance was solidified by cooling and washed with n-hexane and dried to obtain 2.1 g of the desired product.

[B] 3.9 g of methyl α - [4 - (3 - chloro - 5 - iodo - 2 - pyridyloxy)phenoxy]propionate, 2.45 g of trifluoromethyl iodide, 40 ml of pyridine and 1.62 g of copper powder were mixed in an autoclave and the mixture was allowed to react at 140°C for 2 hours with stirring followed by further reacting at 160—170°C for one hour. After allowing the reaction mixture to cool, diethyl ether was added to the reaction mixture and the precipitated copper salts were removed by filtration. The ethereal filtrate was washed successively with water, 10% dilute hydrochloric acid and water, and dried over anhydrous sodium sulfate. The ethereal solution was concentrated to obtain 1.5 g of an oily substance which was then purified by silica gel column chromatography (eluted with methylene chloride), and the solvent was removed from the eluate by distillation to obtain 500 mg of the desired product.

Preparation EXAMPLE 6

Preparation of α -[4-(5-Trifluoromethyl-2-pyridyloxy)phenoxy]propionanilide

4 g of α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionyl chloride prepared from α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionic acid and thionyl chloride in a conventional manner, and 1.3 g of aniline were dissolved in 10 ml of benzene, and 1.2 g of pyridine was added dropwise to the solution while stirring. The mixture was then allowed to react for 3 hours at a refluxing temperature of 80°C, and the reaction product was washed several times with 20 ml of water. The benzene layer was separated, dried over anhydrous sodium sulfate and filtered. The benzene was then removed by distillation to obtain 4.3 g of the desired product having a melting point of 139—141°C.

The herbicidal compound of this invention can be dispersed in water to produce an aqueous dispersion. The herbicidal compound can also be formulated into various forms such as an emulsifiable concentrate, wettable powder, water-miscible solution, dust or granules by optionally incorporating conventional agriculturally acceptable adjuvants, for example, a carrier such as diatomaceous earth, calcium hydroxide, calcium carbonate, talc, white carbon, kaolin, bentonite, or Jeeklite (trade name for kaolinite, produced by Jeeklite Co.), solvents such as n-hexane, toluene, xylene, solvent naphtha, ethanol, dioxane, acetone, isophorone, methyl isobutyl ketone, dimethylformamide, dimethyl sulfoxide or water, or an anionic or nonionic surface active agent such as a sodium alkylsulfate, a sodium alkylbenzenesulfonate, sodium ligninsulfonate, a polyoxyethylene lauryl ether, a polyoxyethylene alkylaryl ether, a polyoxyethylene fatty acid ester, or a polyoxyethylene sorbitan fatty acid ester. A suitable ratio of the compound of this invention to the adjuvant(s) ranges from about 1—90:99—10 by weight, preferably 1—70:99—30 by weight.

The herbicidal composition of this invention can also be mixed or used together with suitable agricultural chemicals such as other herbicides, insecticides or fungicides, or mixed with an agricultural agent such as a fertilizer, a soil conditioner, soil or sand, at the time of formulation or application. Sometimes, such a conjoint use brings about a better effect.

Some typical examples of herbicidal formulations containing the compound of this invention are shown below.

Formulation EXAMPLE 1

20 parts by weight of ethyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate, 60 parts by weight of xylene and 20 parts by

weight of Sorpol 2806B (trade name for a mixture of a polyoxyethylene phenyl phenol derivative, a polyoxyethylene alkylaryl ether, a polyoxyethylene sorbitan alkylate, and an alkylaryl sulfonate produced by Toho Chemical Co., Ltd.), as a surface active agent, were mixed uniformly to form an emulsifiable concentrate.

Formulation EXAMPLE 2

58 parts by weight of bentonite, 30 parts by weight of Jeeklite and 5 parts by weight of sodium ligninsulfonate were mixed and granulated. A solution prepared by diluting 7 parts by weight of allyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate with acetone was sprayed on the granulated components to form granules.

Formulation EXAMPLE 3

40 parts by weight of N - (pyridine - 2 - yl) - α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionamide, 55 parts by weight of Jeeklite, 2 parts by weight of a sodium alkylbenzenesulfonate and 3 parts by weight of a mixture of equal amounts of white carbon and a polyoxyethylene alkylaryl ether were uniformly mixed, and pulverized to form a wettable powder.

Formulation EXAMPLE 4

78 parts by weight of Jeeklite, 15 parts by weight of white carbon, 2 parts by weight of Lavelin S (trade name for a sodium naphthalene sulfonate-formaldehyde condensate, produced by Daiichi Kogyo Seiyaku Co., Ltd.), and 5 parts by weight of Sorpol 5039 (trade name for a sulfate of a polyoxyethylene alkylaryl ether, produced by Toho Chemical Co., Ltd.) were mixed and the mixture obtained was then mixed with methyl α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate in a ratio of 4:1 by weight to form a wettable powder.

Formulation EXAMPLE 5

20 parts by weight of sodium α - [4 - (5 - trifluoromethyl - pyridyloxy)phenoxy]propionate, 5 parts by weight of polyethyleneglycol octylphenyl ether, 2 parts by weight of sodium dodecylbenzenesulfonate, and 73 parts by weight of water were uniformly mixed to form a water-miscible solution.

The unique herbicidal activity of the herbicidal compound of this invention has already been described hereinabove, but will be described in greater detail below.

(1) The compound of this invention can be used to kill graminaceous weeds by pre-emergence soil treatment or foliar treatment during the growth of weeds. In particular, the compound of this invention can be used to kill graminaceous weeds which have grown to a height of about 1 meter by a foliar treatment. Since the compound of this invention is safe to broad-leaved agricultural crops such as soybeans, peanuts and cotton, the compound is suitable for selective weed control in upland farms.

(2) If the method of application, the dosage, and the time of application are appropriately selected, for example, if the weeds which are growing together with plants such as corn are subjected to a foliar treatment with a small amount (5—20 g/100 m²), as the active ingredient, of the compound of this invention after the plant has grown to some degree, the compound of this invention can be applied to fields where graminaceous crops are cultivated. Furthermore, when the dosage of the compound of this invention is excessively increased or the compound of this invention is used together with other herbicides, weeds other than gramineous weeds can be killed.

(3) The compound of this invention has low toxicity to fish.

The herbicidal compound of this invention is most suitably applied to upland farms, especially upland farms where broad-leaved crops are cultivated, and can also be applied to orchards, forests and various non-agricultural lands. The compound of this invention can be applied as a soil treatment or a foliar treatment in upland farm conditions or under flooded conditions. A suitable rate of application varies according to various factors such as the climate condition, the soil condition, the form of the chemical, the time of application, the method of application, or the types of cultivated crops to which it is applied and the main weeds to be controlled. When the compound of this invention is used in the form of a solid preparation (e.g., dust or granules), the amount of the active ingredient is 0.1 to 1,000 g per are (100 m²), preferably 0.5 to 500 g, and more preferably 1 to 250 g, per are.

2.2

The herbicidal activity testing of the compound of this invention and the results obtained are shown below.

Test EXAMPLE 1

Each 1/3,000 are (1/30 m²) flat was charged with soil to provide an upland condition. Predetermined amounts of seeds of edible barnyard grass, radish and soybeans were sown, and covered with soil containing seeds of graminaceous weeds such as large crab-grass (*Digitaria adscendens* HENR.), barnyard grass (*Echinochloa crus-galli* BEAUV.), green foxtail (*Setaria viridis* BEAUV.), etc., to a thickness of about 1 cm. Two days after sowing, an aqueous dispersion of each of the herbicidal compounds shown in Table 1 below was sprayed thereon, and the growth of the weeds was visually evaluated 30 days after the spraying. The results obtained are also shown in Table 1 below. The degree of growth inhibition shown in Table 1 was evaluated on a scale of 10 grades in which 10 indicates that the growth was completely inhibited and 1 indicates no inhibition.

TABLE 1
Degree of Growth Inhibition

Compound No.	Amount of Active Ingredient (g/are)	Edible Barnyard Grass	Radish	Soybeans	Graminaceous Weeds
1	50	8	1	1	10
	25	7	1	1	9
2	50	10	1	1	10
	25	10	1	1	10
3	50	10	1	1	10
	25	10	1	1	10
4	50	10	1	1	10
	25	10	1	1	10
5	50	10	1	1	10
	25	10	1	1	10
6	50	10	1	1	10
	25	10	1	1	10
7	50	10	1	1	10
	25	10	1	1	10
8	50	8	1	1	10
	25	7	1	1	9
9	50	10	1	1	10
	25	10	1	1	10
10	50	10	1	1	10
	25	10	1	1	10
11	50	10	1	1	10
	25	10	1	1	10
12	50	10	1	1	10
	25	10	1	1	10
13	50	10	2	1	10
	25	10	1	1	10
14	50	10	1	1	10
	25	10	1	1	10
15	50	10	1	1	10
	25	10	1	1	10
16	50	10	1	1	10
	25	10	1	1	10
17	50	10	1	1	10
	25	10	1	1	10
18	50	10	1	1	10
	25	10	1	1	10
19	50	10	1	1	10
	25	10	1	1	10
20	50	10	1	1	10
	25	10	1	1	10
21	50	10	1	1	10
	25	10	1	1	10

TABLE 1 (cont.).
Degree of Growth Inhibition

5	Compound No.	Amount of Active Ingredient (g/are)	Edible Barnyard Grass	Radish	Soybeans	Graminaceous Weeds	5
	22	50	10	1	1	10	
		25	10	1	1	10	
	23	50	10	1	1	10	
10		25	10	1	1	10	10
	24	50	10	1	1	10	
		25	10	1	1	10	
	25	50	10	1	1	10	
		25	10	1	1	10	
15	26	50	10	1	1	10	15
		25	10	1	1	10	
	27	50	10	1	1	10	
		25	10	1	1	10	
	28	50	10	1	1	10	
20		25	10	1	1	10	20
	29	50	10	1	1	10	
		25	10	1	1	10	
	30	50	10	1	1	10	
		25	10	1	1	10	
25	31	50	10	1	1	10	25
		25	10	1	1	10	
	34	50	10	1	1	10	
		25	10	1	1	10	
	35	50	10	1	1	10	
30		25	10	1	1	10	30
	36	50	10	1	1	10	
		25	10	1	1	10	
	37	50	10	1	1	10	
		25	10	1	1	10	
35	38	50	10	1	1	10	35
		25	9	1	1	9	
	39	50	10	1	1	10	
		25	10	1	1	10	
40	40	50	10	1	1	10	40
		25	10	1	1	10	
	41	50	10	1	1	10	
		25	10	1	1	10	
	42	50	10	1	1	10	
		25	10	1	1	10	
45	43	50	9	1	1	9	45
		25	8	1	1	8	
	44	50	10	1	1	10	
		25	10	1	1	10	
50	45	50	10	1	1	10	50
		25	10	1	1	10	
	46	50	10	1	1	10	
		25	10	1	1	10	
	47	50	10	1	1	10	
		25	10	1	1	10	
55	48	50	10	1	1	10	55
		25	10	1	1	10	
	49	50	10	1	1	10	
		25	10	1	1	10	
60	50	50	10	1	1	10	60
		25	10	1	1	10	
	51	50	10	1	1	10	
		25	10	1	1	10	
	52	50	10	1	1	10	
		25	10	1	1	10	

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Test EXAMPLE 2

Each 1/3,000 are (1/30 m²) pot was charged with soil to provide an upland condition, and predetermined amounts of seeds of edible barnyard grass and soybeans were sown, and covered with soil to a thickness of about 1 cm. When the edible barnyard grass reached a 2.5-leaf stage, an aqueous dispersion of each of the herbicidal compounds shown in Table 2 below was applied to the foliage in a predetermined amount. Twenty days after the treatment with the compound, the growth of the barnyard grass and soybeans was visually evaluated, and the degree of growth inhibition was evaluated on the same scale as in Test Example 1. The results obtained are shown in Table 2 below.

TABLE 2

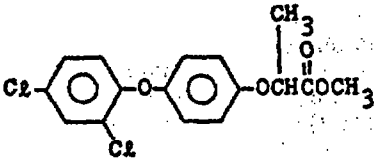
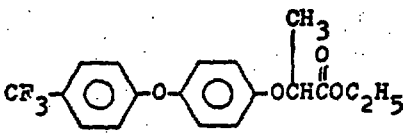
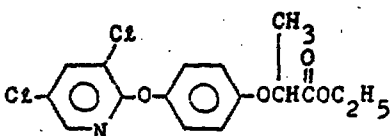
Compound No.	Concentration of Active Ingredient (ppm)	Degree of Growth Inhibition	
		Edible Barnyard Grass	Soybeans
2	400	10	1
	200	10	1
3	400	10	1
	200	10	1
6	400	10	1
	200	10	1
7	400	10	1
	200	10	1
9	400	10	1
	200	10	1
10	400	10	1
	200	10	1
12	400	10	1
	200	10	1
13	400	10	1
	200	10	1
18	400	10	1
	200	10	1
19	400	10	1
	200	10	1
20	400	10	1
	200	10	1
24	400	10	1
	200	10	1
29	400	10	1
	200	10	1
48	400	10	1
	200	10	1

Test EXAMPLE 3

Predetermined amounts of seeds of cotton were sown in each 1/5,000 are (1/50 m²) pot. When the cotton reached a four-leaf stage, a predetermined amount of an aqueous dispersion of each of the compounds shown in Table 3 below was sprayed thereon. Twenty days after the treatment with the dispersion, the growth of the cotton was visually observed to evaluate the degree of phytotoxicity. The degree of phytotoxicity was evaluated in terms of necrosis, wilting of growth and growth inhibition, and the results obtained are shown in Table 3 below. The degree of phytotoxicity shown in Table 3 was evaluated on a scale of 10 grades in which 10 indicates that the cotton was completely withered, and 1 indicates no phytotoxicity showing a similar growth behavior to that in an untreated plot.

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TABLE 3

Test Compound	Amount of Active Ingredient (g/are)	Phytotoxicity		
		Necrosis	Wilting	Growth Inhibition
Compound No. 9	5	1	1	1
	10	1	1	1
	20	2	1	1
	5	3	2	3
	10	6	5	4
	20	7	6	5
	5	3	2	3
	10	4	4	4
	20	7	5	5
	5	2	3	1
	10	4	3	2
	20	4	3	3

(1): Compound of U.S. Patent 3,954,442.

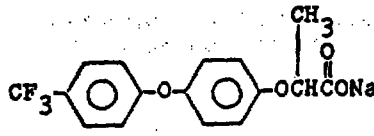
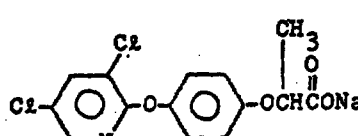
(2): Compound of German Patent Application DT-OS 2,433,067.

(3): Compound of U.S. Patent 4,046,553.

Test EXAMPLE 4

Quackgrass (*Agropyron repens*) obtained by separating a parent plant thereof having a diameter of about 10 cm into two plants was transplanted, one plant in each 1/5000 are (1/50 m²) pot. When the quackgrass reached a 4.5-leaf stage (50—60 plants generated; height of plants: 25—30 cm), a predetermined amount of an aqueous dispersion of each of the compounds shown in Table 4 below was sprayed thereon. Fifty days after the treatment with the dispersion, the degree of regrowth of quackgrass was evaluated. The results obtained are shown in Table 4 below. The degree of regrowth shown in Table 4 was evaluated on a scale of 6 grades in which 5 indicates that regrowth of quackgrass was completely controlled, and 0 indicates that the regrowth was not inhibited and the growth was similar to that in an untreated plot.

TABLE 4

Test Compound	Amount of Active Ingredient (g/are)	Degree of Regrowth Inhibition
Compound No. 46	1.25	5
	5	5
	10	5
	1.25	1
	5	2
	10	3
	1.25	2
	5	3
	10	4

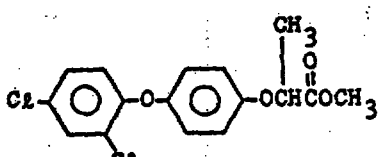
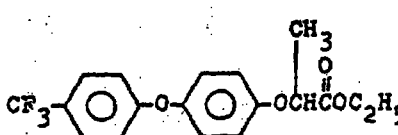
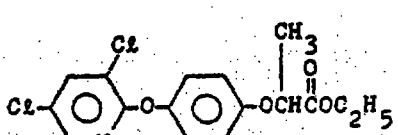
(1): Compound of German Patent Application DT-OS 2,433,067.

(2): Compound of U.S. Patent 4,046,553.

Test EXAMPLE 5

Two subterranean stems (10—20 cm long each) of johnsongrass (*Sorghum halepense* (L.) Pers.) including 4—5 nodes were transplanted in each 1/5,000 are (1/50 m²) pot. When the johnsongrass reached a 4—5 leaf stage, a predetermined amount of an aqueous dispersion of each of the compounds shown in Table 5 below was sprayed thereon. About forty days after the treatment with the dispersion, the number of plants regrown was evaluated. The results obtained are shown in Table 5.

TABLE 5

Test Compound	Amount of Active Ingredient (g/are)	Number of Plants Regrown
Compound No. 9	1.25 2.5 5	0 0 0
	1.25 2.5 5	15 13 13
	1.25 2.5 5	7 6 3
	1.25 2.5 5	3 1 0
Control	—	13

(1): Compound of U.S. Patent 3,954,442.

(2): Compound of German Patent Application DT-OS 2,433,067.

(3): Compound of U.S. Patent 4,046,553.

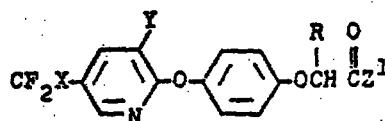
We hereby disclaim n-butyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate, that is a compound of the formula (I) wherein X is —F, Y is —H, R is —CH₃, and Z' is —OC₄H₉(n), a herbicidal composition containing the same as the active ingredient and a method of controlling weeds using such a herbicidal composition, such compound, herbicidal composition and method of controlling weed being claimed in our copending Application No. 8038198 (Serial No. 1,599,126).

Attention is directed under Section 8 of the Patents Act 1949 to our copending Application Nos. 10876/78 and 8038197 (Serial Nos. 1,599,122 and Serial No. 1,599,125).

Subject to the foregoing disclaimer,

WHAT WE CLAIM IS:—

1. A compound having the general formula (I):



(I)

wherein X is a fluorine atom or a chlorine atom; Y is a hydrogen atom or a chlorine atom; R is a hydrogen atom, a methyl group or an ethyl group; and Z' is a hydroxy



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Test EXAMPLE 5

Two subterranean stems (10—20 cm long each) of johnsongrass (*Sorghum halepense* (L.) Pers.) including 4—5 nodes were transplanted in each 1/5,000 are (1/50 m²) pot. When the johnsongrass reached a 4—5 leaf stage, a predetermined amount of an aqueous dispersion of each of the compounds shown in Table 5 below was sprayed thereon. About forty days after the treatment with the dispersion, the number of plants regrown was evaluated. The results obtained are shown in Table 5.

TABLE 5

Test Compound	Amount of Active Ingredient (g/are)	Number of Plants Regrown
Compound No. 9	1.25 2.5 5	0 0 0
	1.25 2.5 5	15 13 13
	1.25 2.5 5	7 6 3
	1.25 2.5 5	3 1 0
Control	—	13

(1): Compound of U.S. Patent 3,954,442.

(2): Compound of German Patent Application DT-OS 2,433,067.

(3): Compound of U.S. Patent 4,046,553.

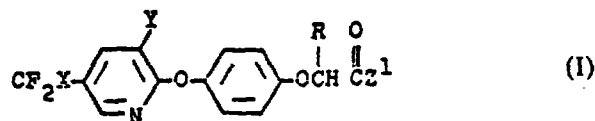
We hereby disclaim n-butyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate, that is a compound of the formula (I) wherein X is —F, Y is —H, R is —CH₃, and Z' is —OC₄H₉(n), a herbicidal composition containing the same as the active ingredient and a method of controlling weeds using such a herbicidal composition, such compound, herbicidal composition and method of controlling weed being claimed in our copending Application No. 8038198 (Serial No. 1,599,126).

Attention is directed under Section 8 of the Patents Act 1949 to our copending Application Nos. 10876/78 and 8038197 (Serial Nos. 1,599,122 and Serial No. 1,599,125).

Subject to the foregoing disclaimer,

WHAT WE CLAIM IS:—

1. A compound having the general formula (I):



wherein X is a fluorine atom or a chlorine atom; Y is a hydrogen atom or a chlorine atom; R is a hydrogen atom, a methyl group or an ethyl group; and Z' is a hydroxy



* C L M S *

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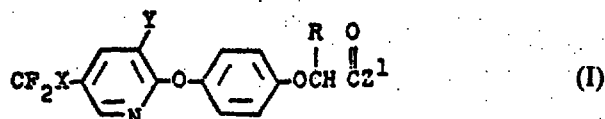
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group; a (C₁—C₆)alkoxy group in which the alkyl moiety thereof may be substituted with 1 to 3 halogen atoms; a (C₁—C₄)alkoxy(C₁—C₄)alkoxy group; a (C₂—C₄)alkenyloxy group; a (C₂—C₄)alkynyloxy group; (C₃—C₆)cycloalkoxy group in which the cycloalkyl moiety thereof may be substituted with a (C₁—C₄)alkyl group; a (C₁—C₄)alkoxycarbonyl(C₁—C₄)alkoxy group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; a benzyloxy group; a glycidyloxy group; a (C₁—C₄)alkylthio group; a (C₂—C₄)alkenylthio group; a phenylthio group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; an amino group; a (C₁—C₄)alkylamino group; a (C₁—C₄)alkoxycarbonylmethylamino group; a hydroxycarbonylmethylamino group; an aniline group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms; a pyridine-2-ylamino group; an -O-cation; or a halogen atom.

2. The compound of Claim 1, wherein X is a fluorine atom; R is a methyl group; and Z¹ is a hydroxy group; a (C₁—C₆)alkoxy group in which the alkyl moiety thereof may be substituted with 1 to 3 halogen atoms; a (C₁—C₄)alkoxy(C₁—C₄)alkoxy group; a (C₂—C₄)alkenyloxy group; a (C₂—C₄)alkynyloxy group; a (C₃—C₆)cycloalkoxy group in which the cycloalkyl moiety thereof may be substituted with a (C₁—C₄)alkyl group; a (C₁—C₄)alkoxycarbonyl(C₁—C₄)alkoxy group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; a benzyloxy group; a glycidyloxy group; or an -O-cation.

3. A compound having the general formula (I):



wherein X is a fluorine atom; Y is a hydrogen atom or a chlorine atom; R is a methyl group; and Z¹ is a hydroxy group, a (C₁—C₆)alkoxy group, a (C₂—C₄)alkenyloxy group, a (C₃—C₆)cycloalkoxy group, or an -O-cation wherein the cation is a sodium, potassium, magnesium, calcium, ammonium or organic ammonium cation.

4. A compound as claimed in Claim 3, wherein Y is hydrogen.

5. A compound as claimed in Claim 3 or Claim 4, wherein Z¹ is a hydroxy group; a (C₁—C₆)alkoxy group; or said -O-cation.

6. A compound as claimed in Claim 3 or Claim 4, wherein said Z¹ is a hydroxy group.

7. A compound as claimed in Claim 3 or Claim 4, wherein Z¹ is a (C₁—C₆)alkoxy group.

8. A compound as claimed in Claim 3 or Claim 4, wherein Z¹ is said -O-cation.

9. α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionic acid.

10. A butyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

11. α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionic acid.

12. sodium α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

13. sodium α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

14. methyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

15. methyl α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

16. ethyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

17. ethyl α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

18. A compound as claimed in Claim 1, substantially as hereinbefore described.

19. A compound as claimed in Claim 3 substantially as hereinbefore described.

20. A herbicidal composition comprising a herbicidally effective amount of at least one compound of Claim 1, as an active ingredient, and an agriculturally acceptable adjuvant.

21. A herbicidal composition as claimed in Claim 20, wherein X is a fluorine atom; R is a methyl group; and Z¹ is a hydroxy group; a (C₁—C₆)alkoxy group in which the alkyl moiety thereof may be substituted with 1 to 3 halogen atoms; a (C₁—C₄)alkoxy(C₁—C₄)alkoxy group; a (C₂—C₄)alkenyloxy group; a (C₂—C₄)alkynyloxy group; a (C₃—C₆)cycloalkoxy group in which the cycloalkyl moiety



thereof may be substituted with a (C₁—C₄)alkyl group; a (C₁—C₄)alkoxycarbonyl(C₁—C₄)alkoxy group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; a benzyloxy group; a glycidyloxy group; or an -O-cation.

22. A herbicidal composition comprising a herbicidally effective amount of at least one compound as claimed in Claim 3, as an active ingredient, and an agriculturally acceptable adjuvant.

23. A herbicidal composition as claimed in Claim 22, wherein Y is hydrogen.

24. A herbicidal composition as claimed in Claim 22 or Claim 23, wherein Z¹ is a hydroxy group; a (C₁—C₄)alkoxy group; or said -O-cation.

25. A herbicidal composition as claimed in Claim 22 or Claim 23, wherein Z¹ is a hydroxy group.

26. A herbicidal composition as claimed in Claim 22 or Claim 23, wherein Z¹ is a (C₁—C₄)alkoxy group.

27. The herbicidal composition as claimed in Claim 22 or Claim 23, wherein Z¹ is said -O-cation.

28. A herbicidal composition as claimed in Claim 22, wherein said compound is α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionic acid.

29. A herbicidal composition as claimed in Claim 22, wherein said compound is a butyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

30. A herbicidal composition as claimed in Claim 22, wherein said compound is α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionic acid.

31. A herbicidal composition as claimed in Claim 22, wherein said compound is sodium α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

32. A herbicidal composition as claimed in Claim 22, wherein said compound is sodium α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

33. A herbicidal composition as claimed in Claim 22, wherein said compound is methyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

34. A herbicidal composition as claimed in Claim 22, wherein said compound is methyl α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

35. A herbicidal composition as claimed in Claim 22, wherein said compound is ethyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

36. A herbicidal composition as claimed in Claim 22, wherein said compound is ethyl α - [4 - (3 - chloro - 5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.

37. A herbicidal composition as claimed in Claim 20, substantially as hereinbefore described with reference to any one of Formulation Examples 1 to 5.

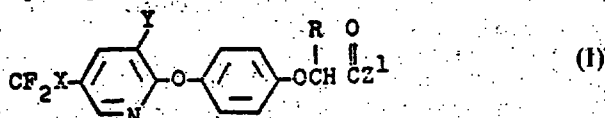
38. A herbicidal composition as claimed in Claim 22, substantially as hereinbefore described with reference to any one of Formulation Examples 1, 2, 4 and 5.

39. A method of controlling weeds comprising applying a herbicidally effective amount of the herbicidal composition as claimed in any one of Claims 20, 21 and 37 to the weeds.

40. A method of controlling weeds comprising applying a herbicidally effective amount of the herbicidal composition as claimed in any one of Claims 22 to 36 and 38 to the weeds.

41. A method as claimed in Claim 39 of controlling weeds substantially as hereinbefore described with reference to any one of Test Examples 1 to 5.

42. A process for preparing a compound having the general formula (I):



wherein X is a fluorine atom or a chlorine atom; Y is a hydrogen atom or a chlorine atom; R is a hydrogen atom, a methyl group or an ethyl group; and Z¹ is a hydroxy group; a (C₁—C₄)alkoxy group; a (C₁—C₄)alkoxy(C₁—C₄)alkoxy group; a (C₂—C₄)alkenyloxy group; a (C₂—C₄)alkynyloxy group; a (C₃—C₆)cycloalkoxy group in which the cycloalkyl moiety thereof may be substituted with a (C₁—C₄)alkyl group; a (C₁—C₄)alkoxycarbonyl(C₁—C₄)alkoxy group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a



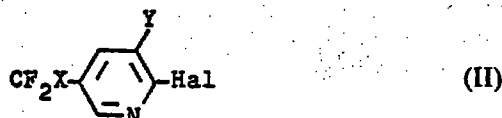
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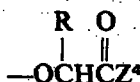
5 (C₁—C₄)alkyl group; a benzyloxy group; a glycidyloxy group; a (C₁—C₄)alkylthio group; a (C₂—C₄)alkenylthio group; a phenylthio group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁—C₄)alkyl group; an amino group; a (C₁—C₄)alkylamino group; a (C₁—C₄)alkoxycarbonylmethylamino group; a hydroxycarbonylmethylamino group; an anilino group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms; a pyridine-2-ylamino group; an -O-cation; or a halogen atom; which comprises first condensing a 2 - halo - 5 - fluoromethylpyridine of the formula (II):



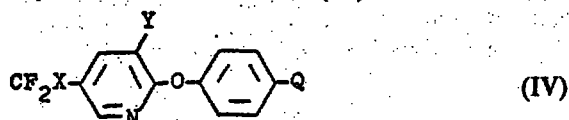
10 wherein Hal is a halogen atom, X and Y are the same as defined hereinbefore, and a substituted phenol of the formula (III):



wherein Q is a hydroxy group, a (C₁—C₉)alkoxy group or an



15 group wherein R is the same as defined hereinbefore and Z⁴ is a hydroxy group, a (C₁—C₉)alkoxy group or an amino group, in the presence of an alkaline material to form a substituted pyridyl phenyl ether of the formula (IV):



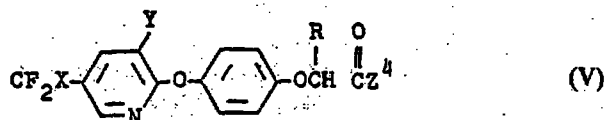
20 wherein X, Y and Q are the same as defined hereinbefore, and, when Q is other than an



group, condensing the substituted pyridyl phenyl ether having the formula (IV) and a haloalkanecarboxylic acid or a derivative thereof of the formula (VII):

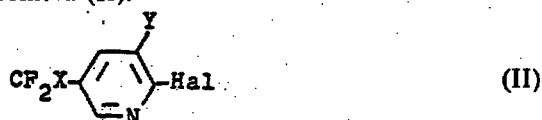


25 wherein Hal, R and Z⁴ are the same as defined hereinbefore in the presence of an alkaline material, to thereby form a compound having the formula (V):



30 wherein X, Y, R and Z⁴ are the same as defined hereinbefore, and if necessary, converting the Z⁴ moiety of the compound of the formula (V) to Z¹ wherein Z¹ is the same as defined hereinbefore, by a conventional method for neutralization, halogenation, amination, thioesterification, esterification or ester-interchange reaction.

43. The process of Claim 42 which comprises condensing a 2 - halo - 5 - fluoromethylpyridine of the formula (II):



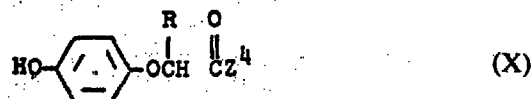


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wherein Hal, X and Y are the same as defined in Claim 42, with a p-hydroxyphenoxyalkanecarboxylic acid or a derivative thereof of the formula (X):

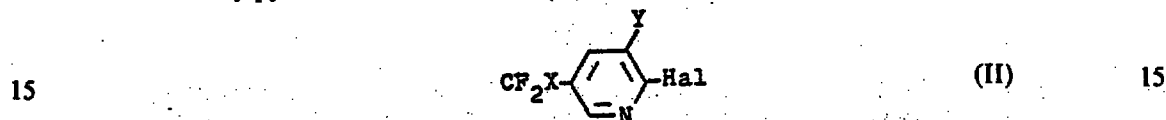


5 wherein R and Z⁴ are the same as defined in Claim 42, in the presence of an alkaline material at a temperature of at least 50°C for 1 to 20 hours to form a compound having the formula (V): 5

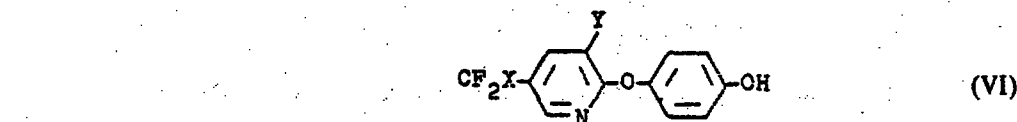


10 wherein X, Y, R and Z⁴ are the same as defined in Claim 42, and if necessary, converting the Z⁴ moiety of the compound of the formula (V) to Z¹ wherein Z¹ is the same as defined in Claim 42, by a conventional method for neutralization, halogenation, amination, thioesterification, esterification or ester-interchange reaction. 10

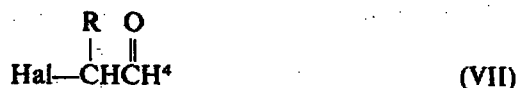
44. The process of Claim 42 which comprises condensing a 2-halo-5-fluoromethylpyridine of the formula (II):



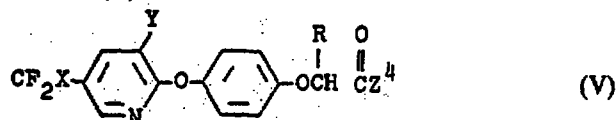
wherein Hal, X and Y are the same as defined in Claim 42 with hydroquinone in the presence of an alkaline material at a temperature of at least 50°C for 1 to 20 hours to form a substituted pyridyl-p-hydroxyphenyl ether of the formula (VI):



20 wherein X and Y are the same as defined in Claim 42, and then condensing the compound of the formula (VI) with a haloalkanecarboxylic acid or a derivative thereof of the formula (VII): 20

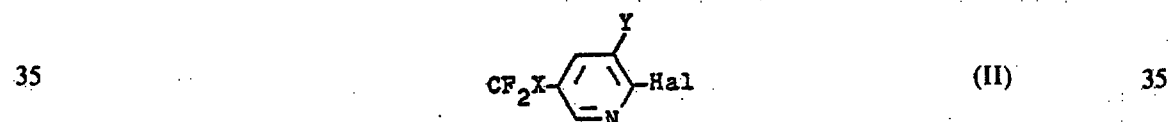


25 wherein Hal, R and Z⁴ are the same as defined in Claim 42, in the presence of an alkaline material at a temperature of 40 to 200°C for 0.5 to 10 hours to form a compound having the formula (V): 25

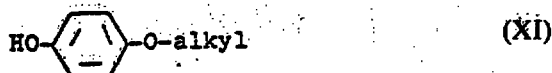


30 wherein X, Y, R and Z⁴ are the same as defined in Claim 42, and if necessary, converting the Z⁴ moiety of the compound of the formula (V) to Z¹ wherein Z¹ is the same as defined in Claim 42 by a conventional method for neutralization, halogenation, amination, thioesterification, esterification or ester-interchange reaction. 30

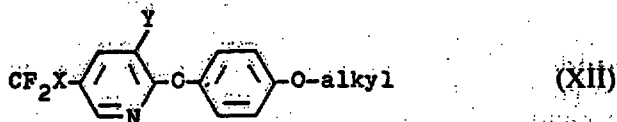
45. The process of Claim 42 which comprises condensing a 2-halo-5-fluoromethylpyridine of the formula (II):



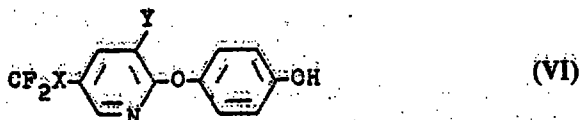
wherein Hal, X and Y are the same as defined in Claim 42 with a hydroquinone monoalkyl ether of the formula (XI):



5 wherein "alkyl" represents a (C₁-C₆)alkyl group; in the presence of an alkaline material at a temperature of at least 50°C for 1 to 20 hours to form a substituted pyridyl - p - alkoxyphenyl ether of the formula (XII): 5



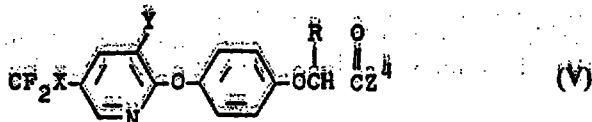
10 wherein "alkyl" is the same as defined above, and X and Y are the same as defined in Claim 42 dealkylating the compound of the formula (XII) to form a substituted pyridyl - p - hydroxyphenyl ether of the formula (VI): 10



wherein X and Y are the same as defined in Claim 42 and then condensing the compound of the formula (VI) with a haloalkanecarboxylic acid or a derivative thereof of the formula (VII):



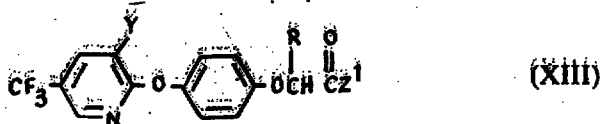
wherein Hal, R and Z⁴ are the same as defined in Claim 42 in the presence of an alkaline material at a temperature of 40 to 200°C for 0.5 to 10 hours to form a compound having the formula (V):



20 wherein X, Y, R and Z⁴ are the same as defined in Claim 42, and if necessary, converting the Z⁴ moiety of the compound of the formula (V) to Z¹ wherein Z¹ is the same as defined in Claim 42 by a conventional method for neutralization, halogenation, amination, thioesterification, esterification or ester-interchange reaction: 20

25 46. The process of Claim 42, wherein said alkaline material in the first and second condensation is an alkali metal hydroxy or an alkali metal carbonate: 25

47. A process for preparing a compound having the general formula (XIII):



30 wherein Y is a hydrogen atom or a chlorine atom; R is a hydrogen atom, a methyl group or an ethyl group; and Z¹ is a hydroxy group; a (C₁-C₆)alkoxy group in which the alkyl moiety thereof may be substituted with 1 to 3 halogen atoms; a (C₁-C₆)alkoxy(C₁-C₆)alkoxy group; a (C₂-C₆)alkenyloxy group; a (C₂-C₆)alkynyloxy group; a (C₃-C₆)cycloalkoxy group in which the cycloalkyl moiety thereof may be substituted with a (C₁-C₆)alkyl group; a (C₁-C₆)alkoxycarbonyl(C₁-C₆)alkoxy group; a phenoxy group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁-C₆)alkyl group; a benzyloxy group; a glycidyloxy group; a (C₁-C₆)alkylthio group; a (C₂-C₆)alkenylthio group; a phenylthio group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms or a (C₁-C₆)alkyl group; an amino group; a (C₁-C₆)alkylamino group; a (C₁-C₆)alkoxycarbonylmethylamino group; a 40

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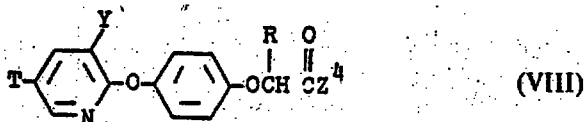
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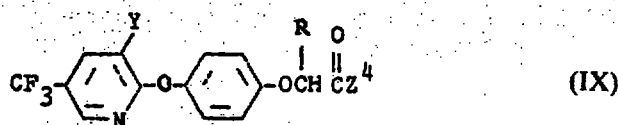
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hydroxycarbonylmethylamino group; an anilino group in which the aryl moiety thereof may be substituted with 1 to 3 halogen atoms; a pyridine-2-ylamino group; an -O-cation; or a halogen atom; which comprises reacting trifluoromethyl iodide with a compound of the formula (VIII):



wherein T is a bromine atom or an iodine atom, and Y and R are the same as defined hereinbefore and Z⁴ is a hydroxy group, a (C₁—C₆)alkoxy group or an amino group, in the presence of copper dust and a polar aprotic solvent at a temperature of 100 to 200°C for 1 to 24 hours to form a compound having the formula (IX):

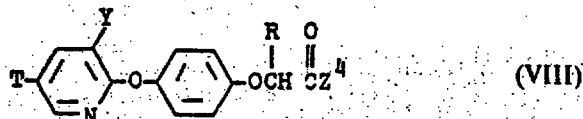


wherein Y, R and Z⁴ are the same as defined hereinbefore, and if necessary, converting the Z⁴ moiety of the compound of the formula (IX) to Z' wherein Z' is the same as defined hereinbefore, by a conventional method for neutralization, halogenation, amination, thioesterification, esterification or ester-interchange reaction.

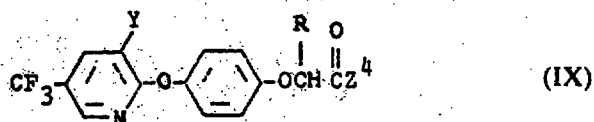
48. A process for preparing a compound having the general formula (XIII):



wherein Y is a hydrogen atom or a chlorine atom; R is a methyl group; and Z' is a hydroxy group; a (C₁—C₆)alkoxy group; a (C₂—C₆)alkenyloxy group; a (C₃—C₆)cycloalkoxy group; or an -O-cation where the cation is a sodium, potassium, magnesium, calcium, ammonium or organic ammonium cation, which comprises reacting trifluoromethyl iodide with a compound of the formula (VIII):



wherein T is a bromine atom or an iodine atom, Y and R are the same as defined hereinbefore, and Z⁴ is a hydroxy group or a (C₁—C₆)alkoxy group in the presence of copper dust and a polar aprotic solvent at a temperature of 100 to 200°C for 1 to 24 hours to form a compound having the formula (IX):



wherein Y, R and Z⁴ are the same as defined hereinbefore, and if necessary, converting the Z⁴ moiety of the compound of the formula (IX) to Z' wherein Z' is the same as defined hereinbefore, by a conventional method.

49. A process as claimed in Claim 42 or Claim 47 substantially as hereinbefore described with reference to any one of the Preparation Examples.

50. A process as claimed in Claim 48 substantially as hereinbefore described with reference to any one of the Preparation Examples 1[B], 2[B], 3[B], 4 and 5[B].

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51. An α - [4 - (5 - fluoromethyl - 2 - pyridyloxy)phenoxy]alkanecarboxylic acid derivative prepared by a process as claimed in any one of Claims 42 to 47 or 49.

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52. An α - [4 - (5 - fluoromethyl - 2 - pyridyloxy)phenoxy]alkanecarboxylic acid derivative prepared by a process as claimed in Claim 48 or Claim 50.

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