PATENT SPECIFICATION

(11) **1 563 850**

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(19) THE PATENT OFFICE LONDON

(54) PHENOXYPHENOXY-ALKANE CARBOXYLIC ACID DERIVATIVES, PROCESS FOR THEIR PREPARATION AND COMPOSITIONS CONTAINING THEM

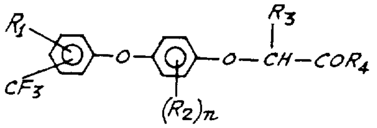
(71) We, HOECHST AKTIENGESELLSCHAFT, a body corporate organised according to the laws of the Federal Republic of Germany, of 6230 Frankfurt/Main 80, Postfach 80 03 20, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to phenoxyphenoxy-alkane carboxylic acid derivatives, to a process for their preparation and to herbicidal compositions containing them.

German Offenlegungsschrift No. 2,433,067 describes 4-phenoxyphenoxy-alkane carboxylic acids and their derivatives carrying a trifluoromethyl group on the terminal phenyl ring. Compounds of this type have a selective herbicidal activity against grass-like weeds.

The present invention is based on the observation that trifluoromethyl-phenoxy-phenoxy-alkane carboxylic acids having additional substituents and their functional derivatives have an outstanding effect as selective herbicides in crop plants.

The present invention therefore provides compounds of the formula

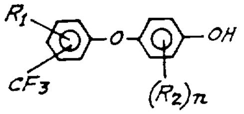


I

in which R_1 is a hydrogen or halogen atom, each R_2 is a halogen atom or a C_1—C_4-alkyl group or a CF_3 group, *n* is 1 or 2, R_3 is a hydrogen atom or a C_1—C_4-alkyl group, and R_4 is a hydroxy, C_1—C_8-alkoxy, C_1—C_8-hydroxyalkoxy, C_2—C_{10}-alkoxy-alkoxy, phenoxy-C_1—C_4-alkoxy, chlorophenoxy-C_1—C_4-alkoxy, halo-C_1—C_4-alkoxy, C_3—C_6-alkenyloxy, C_3—C_6-alkynyloxy, C_3—C_8-cycloalkyloxy, C_3—C_8-cycloalkenyloxy, hydrazino, amino, C_1—C_4-alkylamino, di(C_1—C_4-alkyl)amino, phenylamino, phenoxy, phenylthio (the phenyl group of which may carry one or more substituents selected from halogen atoms and trifluoromethyl, methyl, hydroxy and carbo-(C_1—C_2)-alkoxy groups), or -Ocat, in which cat is the cation of an inorganic or organic base.

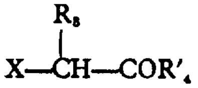
In the compounds of formula I, the CF_3 group on the terminal phenyl ring is preferably in the 4-position. Preferably, R_1 is a chlorine or bromine atom or, especially, a hydrogen atom; R_2 is a bromine atom or, especially, a chlorine atom, advantageously in the 2-position i.e. adjacent to the —O-alkanecarboxylic acid group; R_3 is a methyl group and R_4 is a (C_1—C_8)-alkoxy group, especially a (C_1—C_4)-alkoxy group, or an allyloxy group.

In accordance with the present invention, the compounds of the formula I are prepared by reacting a phenoxyphenol of the formula



II

or a corresponding phenolate, optionally in the presence of an acid-binding agent, with a carboxylic acid derivative of the formula



$$X\!-\!\underset{}{\overset{R_8}{\overset{|}{C}}}H\!-\!COR'_4$$

III

in which X is a halogen atom and R'_4 is a hydroxy or C_1—C_8-alkoxy group and, if desired, transforming the resulting compound of the formula I into another compound of the formula I by esterification, saponification, salification, transesterification, or amidation.

In the formula III, X is preferably a chlorine or bromine atom; preferred halopropionic acids are therefore 2-bromo- and 2-chloropropionic acids.

The reaction is preferably carried out in an organic solvent, for example a ketone such as acetone or diethyl-ketone; a carboxylic acid amide such as dimethyl formamide; a sulfoxide such as dimethyl sulfoxide; or an aromatic hydrocarbon, for example benzene or toluene. When using free phenols of the formula II, the reaction is preferably carried out in the presence of an alkaline compound to bind the hydrogen halide liberated, for example potassium carbonate or a tertiary organic base such as triethylamine.

As soon as the reaction is complete, the resulting halide is separated by filtration or by the addition of water and, after removal of the organic solvent (if any), the ester or other derivative of the carboxylic acid obtained is isolated in known manner.

The compounds obtained can be purified in conventional manner, for example by distillation or recrystallization from an organic solvent or from a mixture of an organic solvent and water.

The various functional derivatives of the formula I can readily be transformed into one another in known manner. Carboxylic acid esters for example can be saponified by heating with alkaline agents, preferably aqueous bases, in the presence of lower alcohols. The alkaline solution can then be acidified whereby the free acid separates in the form of crystals or as an oil.

The free acids of the formula I, obtained by saponification or by reaction with free halopropionic acids (R_4=OH) can be esterified in the usual manner, preferably in the presence of a catalytic amount of an acid catalyst such as sulfuric acid, toluenesulfonic acid, hydrochloric acid, a Lewis acid, for example boron trifluoride, or an acid ion exchanger.

Suitable alcohols for the esterification are, for example, linear or branched aliphatic alcohols having from 1 to 8 carbon atoms, or cyclohexanol.

For esterification, there can be used the acid chlorides, which are readily obtained, for example by reaction of the carboxylic acids of the formula I with thionyl chloride. Reaction of these with the above alcohols yields the corresponding esters.

Other derivatives of the formula I are obtained by reacting the acid chlorides or esters with amines or anilines.

The starting compounds of the formula II can be obtained for example, by first preparing trifluoromethyl-phenoxyphenols according to the process described in DOS No. 2,433,066, which may then be chlorinated or brominated in known manner.

The present invention also provides herbicidal compositions containing as active compound, a phenoxy-phenoxy-carboxylic acid derivatives of the formula I, together with a carrier.

The herbicidal compositions according to the invention contain from 2 to 95% of a compound of the formula I. They can be in the form of emulsifiable concentrates, wettable powders, sprayable solutions, dusts, or granules.

Wettable powders are preparations that can be uniformly dispersed in water and contain, besides the active ingredient, a diluent or an inert substance, a wetting agent, for example polyoxethylated alkylphenols, or polyoxethylated oleyl- or stearylamines, alkyl- or alkyl-phenyl-sulfonates, and dispersing agents, for example the sodium salt of lignin-sulfonic acid, of 2,2'-dinaphthylmethane-6,6'-disulfonic acid, or sodium oleylmethyl-tauride.

Emulsifiable concentrates are obtained by dissolving the active ingredient in an organic solvent, for example butanol, cyclohexanone, dimethylformamide, xylene, or an aromatic hydrocarbon having a higher boiling point, and adding a non-ionic wetting agent (emulsifier), for example a polyoxethylated alkyl-phenol or a polyoxethylated oleyl- or stearyl-amine.

Dusting powders are obtained by grinding the active ingredient with finely divided, solid substances, for example talc, natural clays such as kaolin, bentonite, pyrophillite, or diatomaceous earths.

Spraying solutions, commercially available as aerosol sprays, contain the active ingredient dissolved in an organic solvent, and in addition thereto a propellant, for example a mixture of fluorochlorohydrocarbons.

Granules can be produced by atomizing the active ingredient on to an adsorptive, granulated inert material, or by applying concentrates of the active ingredient to the surface of a support, for example sand, kaolinite or a granulated inert material, with the aid of an adhesive, for example polyvinyl alcohol, the sodium salt of polyacrylic acid, or mineral oils. Alternatively, suitable active ingredients may be made into granules, if desired in admixture with fertilizers, in the manner commonly used for the manufacture of granulated fertilizers.

The commercial herbicidal compositions contain varying concentrations of the active ingredients. In wettable powders the concentration of active ingredient varies, for example, from about 10 to 95%, the remainder being the above formulation additives. Emulsion concentrates contain about 10 to 80% of active ingredient, while dusting powders generally contain 5 to 20% of active ingredient and spraying solutions about 2 to 20%. In the case of granules, the content of active ingredient depends on whether the active ingredient is liquid or solid and on the type of granulation auxiliary or filler used.

For application, the commercial concentrates are optionally diluted in the usual manner, the wettable powder or emulsifiable concentrate, for example with water. Dusts and granulated formulations and sprayable solutions are not diluted further with an inert substance before application. The amount applied varies with the external conditions, such as temperature, humidity and the like. The applied amounts can vary within wide limits, for example in the range of from 0.1 to 10.0 kg per hectare, preferably from 0.3 to 5 kg per hectare.

The active compounds of the invention can be mixed with other herbicides and soil insecticides.

Alternatively, the active compounds of the invention can be mixed with fertilizers whereby a fertilizing and simultaneously a herbicidal effect is obtained.

The following Examples illustrate the invention.

EXAMPLES OF PREPARATION.

General methods.

(A) 0.1 Mol of phenol (II) are dissolved in 50 ml of methylethyl ketone, 0.11 mol of anhydrous potassium carbonate are added and 0.11 mol of halocarboxylic acid ester (III) are added dropwise. The mixture is refluxed for about 16 hours, ice-water is added, the reaction mixture is taken up in methylene chloride, dried over Na_2SO_4, the solvent is distilled off and the crude compound of formula I is crystallized or distilled under reduced pressure.

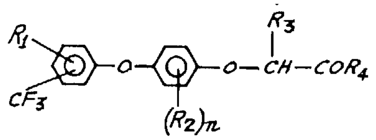
(B) 0.1 Mol of the ester obtained in paragraph A are dissolved in 270 ml of methanol, 24 ml of 45% sodium hydroxide solution are added dropwise and the whole is refluxed for 2 hours. The solvent is then distilled off yielding the acid in the form of the sodium salt. The free acid is obtained by adding dilute hydrochloric acid.

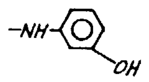
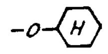
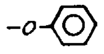
(C) 80 ml of thionyl chloride are added to 0.1 mol of the acid obtained in paragraph B and the mixture is refluxed for 6 hours. The excess thionyl chloride is distilled off and the acid chloride is taken up in toluene.

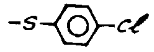
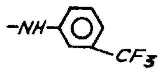
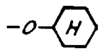
(D) 0.1 Mol of sodium hydroxide dissolved in 50 ml of water are added to 0.1 mol of an alcohol, phenol, mercaptan, or thiophenol dissolved in 50 ml of toluene. At about 25 to 40° C, 0.1 mol of the acid chloride obtained in paragraph C, dissolved in toluene, are added dropwise. After approximately 1 hour, the organic solution is separated, washed with water and dried over potassium carbonate. After distillation of the solvent, the crude compound of formula I is crystallized or purified by distillation.

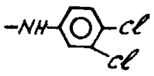
(E) 0.1 Mol of triethylamine are added to 0.1 mol of acid chloride (obtained in paragraph C) dissolved in 50 ml of toluene. At 25 to 40° C, 0.1 mol of an aliphatic amine or aniline are then added dropwise. The mixture is allowed to react for a further hour and then water is added. The toluene phase is separated, washed with water and dried over sodium sulfate. After distillation of the toluene, the amide or anilide is isolated.

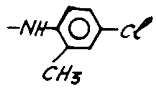
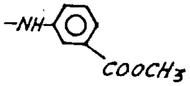
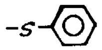
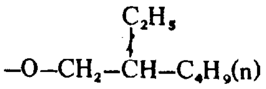
In the following table there are summarized the compounds of formula I which were prepared as described above.

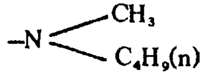
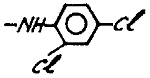
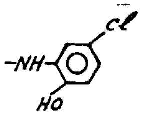
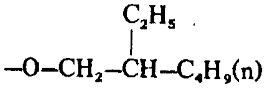
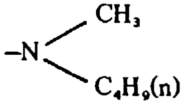
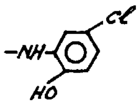


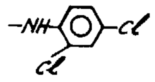
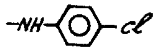
Compound No.		R_1	R_2	R_3	R_4	m.p./b.p./n_D
1	4′-CF_3	H	2-Cl	$-CH_3$	$-OCH_3$	$\text{b.p.}_{0.2}$: 146–148°C
2	,,	,,	,,	,,	$-OC_2H_5$	$\text{b.p.}_{0.2}$: 152–154°C
3	,,	,,	,,	,,	$-OCH(CH_3)_2$	$\text{b.p.}_{0.2}$: 151–153°C
4	,,	,,	,,	,,	$-O-CH_2-CH=CH_2$	$\text{b.p.}_{0.3}$: 164°C
5	,,	,,	,,	,,	$-O-CH_2-CH(CH_3)_2$	$\text{b.p.}_{0.25}$: 163–165°C
6	,,	,,	,,	,,	$-OH$	–
7	3′-CF_3	4′-Cl	3-Cl	H	$-O^-Na^+$	–
8	,,	,,	,,	,,	$-NH_2$	–
9	,,	,,	2-Cl	,,	$-NH-C_4H_9(n)$	–
10	4′-CF_3	2′-Cl	,,	$-CH_3$		–
11	,,	,,	,,	,,		–
12	2′-CF_3	4′-Cl	,,	,,		–

Compound No.		R_1	R_2	R_3	R_4	m.p./b.p./n_D
13	2′-CF_3	4′-Cl	2-Cl	$-CH_3$		–
14	4′-CF_3	H	2,6-Cl	$-CH_3$	$-OCH_3$	b.p.$_{0.15}$: 148–150°C
15	,,	,,	,,	,,	$-OC_2H_5$	b.p.$_{0.1}$: 155–156°C
16	,,	,,	,,	,,	$-OCH(CH_3)_2$	b.p.$_{0.1}$: 153–155°C
17	,,	,,	,,	,,	$-OCH_2-CH(CH_3)_2$	b.p.$_{0.2}$: 170–172°C
18	,,	,,	,,	,,	$-OCH_2-CH_2CL$	–
19	3′-CF_3	4-Cl	,,	H	$-O-CH_2-CCl_3$	–
20	4′-CF_3	H	,,	$-CH_3$	$-N(CH_3)_2$	–
21	,,	,,	,,	,,		–
22	,,	,,	,,	,,	$-NH-NH_2$	–
23	,,	,,	,,	,,	$-NH_2$	–
24	,,	,,	,,	,,		–
25	4′-CF_3	H	2-Br	CH_3	$-OCH_3$	b.p.$_{0.4}$: 156–158°C
26	,,	,,	,,	,,	$-OC_2H_5$	b.p.$_{0.4}$: 166°C

Compound No.		R_1	R_2	R_3	R_4	m.p./b.p./n_D
27	4'-CF_3	H	2-Br	CH_3	$-O-CH(CH_3)_2$	b.p.$_{0.4}$: 164–166°C
28	,,	,,	,,	,,	$-OCH_2-CH=CH_2$	b.p.$_{0.4}$: 165–166°C
29	,,	,,	,,	,,	$-O-CH_2-CH(CH_3)_2$	b.p.$_{0.5}$: 174–176°C
30	,,	,,	,,	,,	$-O-\overset{\overset{CH_3}{\vert}}{C}H-C_2H_5$	b.p.$_{0.35}$: 164–166°C
31	,,	,,	,,	,,	$-O-CH_2-\overset{\overset{C_2H_5}{\vert}}{C}H-C_4H_9(n)$	b.p.$_{0.3}$: 188°C
32	,,	,,	,,	,,	$-OH$	
33	,,	,,	,,	,,	$-O^{-}\overset{+}{H}_2N(CH_3)_2$	–
34	,,	,,	,,	,,	$-NH_2$	
35	,,	,,	,,	,,		–
36	,,	,,	,,	,,	$-OCH_2-CH_2-Cl$	–
37	,,	2'-Cl	3-Br	,,	$-OCH_3$	
38	,,	H	,,	H	$-NH_2'$	
39	,,	H	,,	H	$-OH$	
40	4'-CF_3	H	2,6-Br	$-CH_3$	$-O-CH_3$	–
41	,,	,,	,,	,,	$-OC_2H_5$	–

Compound No.		R_1	R_2	R_3	R_4	m.p./b.p./n_D
42	4′-CF_3	H	2,6-Br	$-CH_3$	$-O-CH_2-CH(CH_3)_2$	—
43	,,	,,	,,	,,	$-O-CH_2-CH_2Cl$	—
44	,,	,,	,,	,,	$-\overset{-}{O}\overset{+}{K}$	
45	,,	,,	3,5-Cl	H		
46	,,	,,	,,	,,	$-NH-CH(CH_3)_2$	
47	,,	2′-Cl	2,6-Br	$-CH_3$	$-OC_2H_5$	
48	,,	,,	,,	,,	$-NH_2$	
49	,,	H	,,	,,		
50	,,	,,	,,	,,		
51	,,	,,	2-Cl	,,	 $-O-CH_2-\underset{}{\overset{C_2H_5}{\overset{\vert}{C}H}}-C_4H_9(n)$	b.p.$_{0.25}$: 184–185°C
52	,,	,,	2-Br	,,	$-N(CH_3)_2$	n_D^{24} : 1.5513

Compound No.		R₁	R₂	R₃	R₄	m.p./b.p./n$_D$
53	4′-CF$_3$	H	2-Br	–CH$_3$	 $-N\begin{smallmatrix}CH_3\\C_4H_9(n)\end{smallmatrix}$	n_D^{26} : 1.5382
54	,,	,,	,,	,,		m.p. : 102–104°C
55	,,	,,	,,	,,		m.p. : 83–85°C
56	,,	,,	,,	,,		m.p. : 203–204°C
57	,,	,,	2,6-Cl	,,	 $-O-CH_2-\overset{\overset{\large C_2H_5}{\vert}}{C}H-C_4H_9(n)$	b.p.$_{0.25}$: 196–197°C
58	,,	,,	,,	,,	–NH$_2$	m.p. : 110–112°C
59	,,	,,	,,	,,	–N(CH$_3$)$_2$	n_D^{25} : 1.5432
60	,,	,,	,,	,,	 $-N\begin{smallmatrix}CH_3\\C_4H_9(n)\end{smallmatrix}$	n_D^{24} : 1.5335
61	,,	,,	,,	,,		m.p. : 191–193°C

Compound No.		R_1	R_2	R_3	R_4	m.p./b.p./n_D
62	4'-CF_3	H	2,6-Cl	$-CH_3$		n_D^{24} : 1.5780
63	4'-CF_3	H	2,6-Cl	$-CH_3$		n_D^{25} : 1.5754
64	4'-CF_3	H	2,6-Cl	$-CH_3$	–OH	Fp. : 108–111 °C

FORMULATION EXAMPLES.

EXAMPLE A:

A wettable powder which is readily dispersible in water is obtained by mixing

25 parts by weight of 2 - [4 - (4' - trifluoromethylphenoxy) - 2 - chloro - phenoxy]-propionic acid isobutyl ester (compound 5 as active ingredient,
64 parts by weight of kaolin-containing quartz as inert substance,
10 parts by weight of the potassium salt of lignin-sulfonic acid,
1 part by weight of sodium oleylmethyl tauride as wetting and dispersing agent,
and grinding the mixture obtained in a disk attrition mill.

EXAMPLE b:

A dusting powder having good herbicidal properties is obtained by mixing

10 parts by weight of 2 - [4 - (4' - trifluoromethylphenoxy) - 2 - chloro - phenoxy]-propionic acid isobutyl ester (compound 5) as active ingredient and
90 parts by weight of talcum as inert substance and grinding the mixture obtained in a cross-beater mill.

EXAMPLE C:

An emulsifiable concentrate consists of

15 parts by weight of 2 - [4 - (4' - trifluoromethylphenoxy) - 2 - chloro - phenoxy]-propionic acid isobutyl ester (compound 5) as active ingredient,
75 parts by weight of cyclohexanone as solvent and
10 parts by weight of oxethylated nonylphenol (10AeO) as emulsifier.

EXAMPLE D:

A granulate consists, for example, of approximately 2—15 parts by weight of 2 - [4 - (4′ - trifluoromethylphenoxy) - 2 - chlorophenoxy] - propionic acid isobutyl ester (compound 5) as active ingredient and inert granulate carrier materials, for example, attapulgite, pumice granulate and quartz sand.

EXAMPLES OF APPLICATION.

EXAMPLE I.

Seeds of various weeds and crop plants were sown in pots. The pots were treated either immediately or about 3 weeks later when the plants had germinated and developed 3 to 4 leaves, with wettable powder formulations suspended in water.

4 Weeks after the treatment the results were evaluated visually according to the scheme of Bolle (cf. Nachrichtenblatt des Deutschen Pflanzenschutzdienstes *16,* 1964, pages 92 to 94), in which the percentage degree of damage to the weeds/crop plants is expressed as an integer, as follows:

number	weeds	crop plants
1	100	0
2	97.5 to <100	0 to 2.5
3	95.0 to < 97.5	> 2.5 to 5.0
4	90.0 to < 95.0	> 5.0 to 10.0
5	85.0 to < 90.0	> 10.0 to 15.0
6	75.0 to < 85.0	>15.0 to 25.0
7	65.0 to < 75.0	> 25.0 to 35.0
8	32.5 to < 65.0	> 35.0 to 67.5
9	0 to < 32.5	> 67.5 to 100

The result indicated in the following Table I shows that at concentrations of 2.5 kg/ha and in part below compounds 1 and 2 control important annual weeds both in pre-emergence and post-emergence application. The listed weeds all belong to the botanic family of graminaceae (grasses). Important crop plants remained undamaged. Compounds 3, 5, and 4 had a similar effect.

TABLE I

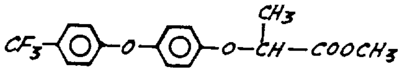
Effect on weeds and crop plants in pre-emergence and post-emergence trials (preem. and postem,), dosage in kg per hectare

types of plants	Compound No. 1				Compound No. 2			
	preem.		postem.		preem.		postem.	
	2.5	0.6	2.5	0.6	2.5	0.6	2.5	0.6
weeds								
Avena fatua	4	6	1	7	4	7	1	8
Alopecurus myosuroides	3	5	3	6	3	4	1	5
Setaria lutescens	1	4	4	8	1	4	4	8
Poa trivialis	1	3	4	7	1	2	2	6
Lolium multiflorum	1	3	3	7	2	3	1	6
Echinochloa crus-galli	2	4	1	6	1	3	1	6
Crop plants								
sugar beet	1	1	1	1	1	1	1	1
rape	1	1	1	1	1	1	1	1
soybean	1	1	1	1	1	1	1	1
pea	1	1	1	1	1	1	1	1
dwarf bean	1	1	2	1	1	1	3	1
horse bean	1	1	1	1	1	1	1	1
cotton	1	1	3	1	1	1	3	1
tomatoe	1	1	1	1	1	1	1	1
tobacco	1	1	1	1	1	1	1	1
carrot	1	1	1	1	1	1	1	1
cabbage	1	1	1	1	1	1	1	1
salad	1	1	1	1	1	1	1	1

EXAMPLE II.

Seeds of Echinochloa crus-galli (barnyard grass) were sown in pots sealed at the bottom. At the same time, 14 day old rice seedlings were planted in pots of the same type. One week later, when the barnyard grass started to germinate, the pots were filled with water so that the water stood 1 cm above the soil surface. Suspensions of the invention compounds were then sprayed on the standing water. The results evaluated 4 weeks after the treatment are indicated in Table II. It can be seen that compounds 2 and 4 kept the barnyard grass under control without doing any noticeable harm to the rice. Similar results were obtained with compounds 1, 3 and 5.

The following compound A (from DT—OS 24 33 067)



$CF_3-C_6H_4-O-C_6H_4-O-CH(CH_3)-COOCH_3$ A

which was used for comparison, controlled Echinochloa almost completely when applied in a concentration of 0.62 kg per hectare, but it did considerable damage to rice.

TABLE II

Effect on Echinochloa and transplanted rice

Compound No.	ha kg/hectare	Echinochloa	rice
2	2.5	1	3
	1.25	1	2
	0.62	3	1
4	2.5	1	4
	1.25	2	2
	0.62	4	1
A	2.5	1	9
	1.25	1	9
	0.62	2	8

EXAMPLE III.

In a pre-emergence trial using some of the compounds of the invention against Setaria, Echinochloa and/or Lolium the following results were obtained:

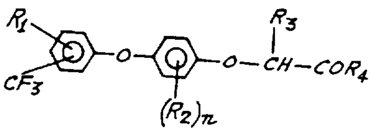
TABLE III

Effect of the compounds of the invention in pre-emergence application.

Compound No.	dose active compound kg/ha	effect on Setaria	Echinochloa	Lolium
1	2.5	1	1	–
	0.6	2	4	–
2	2.5	2	1	–
	0.6	4	3	–
3	2.5	2	3	–
	0.6	5	4	–
4	2.5	1	2	–
	0.6	3	4	–
5	2.5	1	1	–
	0.6	2	4	–
15	2.5	7	–	–
26	1.25	4	–	–
28	2.5	6	–	–
25	5.0	–	–	6
29	5.0	–	–	7
30	5.0	–	–	7

WHAT WE CLAIM IS:—

1. A compound of the formula

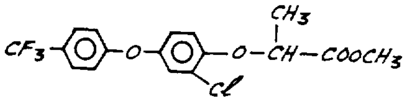


(I)

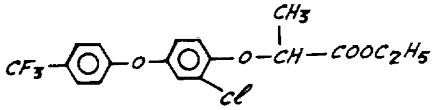
in which R_1 is a hydrogen or halogen atom,
each R_2 is a halogen atom or a C_1—C_4-alkyl group or a CF_3 group,
n is 1 or 2,
R_3 is a hydrogen or C_1—C_4-alkyl, and
R_4 is a hydroxy, C_1—C_8-alkoxy, C_1—C_8-hydroxyalkoxy, C_2—C_{10}-alkoxy-alkoxy, phenoxy-C_1—C_4-alkoxy, chlorophenoxy-C_1—C_4-alkoxy, halo-C_1—C_4-alkoxy, C_3—C_6-alkenyloxy, C_3—C_6-alkynyloxy, C_5—C_8-cycloalkyloxy, C_5—C_8-cycloalkenyloxy, hydrazino, amino, C_1—C_4-alkylamino, di(C_1—C_4-alkyl)amino, phenylamino, phenyloxy, phenylthio (the phenyl group of which may carry one or more substituents selected from halogen atoms and trifluoromethyl, methyl, hydroxy, and carbo-(C_1—C_2)-alkoxy groups), or —Ocat in which cat is the cation of an inorganic or organic base.

2. A compound as claimed in claim 1, wherein R_1 is a hydrogen atom, R_2 is a chlorine or bromine atom, n is 1 to 2, R_3 is a methyl group and R_4 is an alkoxy group having 1 to 8 carbon atoms or an allyloxy group.

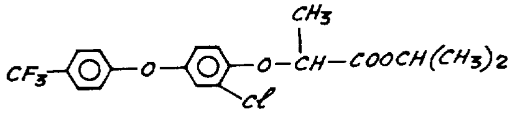
3. The compound of the formula



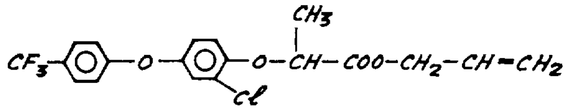
4. The compound of the formula



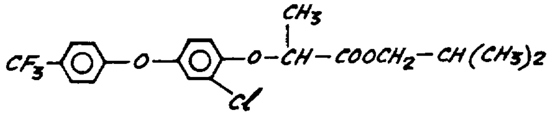
5. The compound of the formula



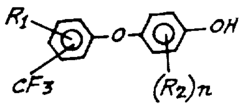
6. The compound of the formula



7. The compound of the formula

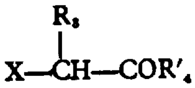


8. A process for preparing a compound as claimed in claim 1, which comprises reacting a phenoxyphenol of the formula



(II)

in which R_1, R_2 and n have the meanings specified in claim 1, with a carboxylic acid derivative of the formula



$$X-\overset{\overset{\displaystyle R_3}{|}}{C}H-COR'_4$$

in which R_3 has the meaning specified in claim 1, X is a halogen atom and R'_4 is hydroxy or C_1—C_8-alkoxy group and, if desired, transforming the resulting compound into another compound as claimed in claim 1 by esterification, saponification, salification, transesterification or amidation.

9. A process as claimed in claim 8 carried out substantially as hereinbefore described.

10. A compound as claimed in claim 1 whenever prepared by a process as claimed in claim 8 or claim 9.

11. A herbicidal composition containing as active ingredient a compound as claimed in claim 1, together with a carrier.

12. A method for combating weeds which comprises applying to the infested area a compound as claimed in claim 1.

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