PATENT SPECIFICATION

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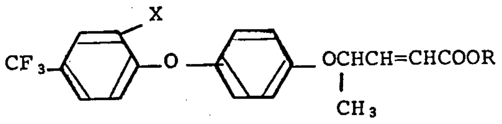
(54) PHENOXYPHENOXY CROTONIC ACID DERIVATIVES AND HERBICIDAL COMPOSITION

(71) We, KUMIAI CHEMICAL INDUSTRY CO., LTD., a Japanese Company of 4—26, Ikenohata 1-chome, Taitoh-ku, Tokyo, Japan, 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:—

The present invention relates to trifluoromethylphenoxy phenoxy crotonic acid derivatives having the formula



(I)

wherein X represents hydrogen or a halogen atom and R represents an alkyl, haloalkyl, alkenyl, haloalkenyl or alkynyl group; to processes for their preparation and to herbicidal compositions comprising the same.

Recently, many herbicides have been proposed and used to reduce the need for agricultural labour.

There is however still a need for improved herbicides which have no adverse effect on crops while being effective against noxious weeds in small doses of the active ingredient and which are safe to use without causing environmental pollution.

The inventors have synthesized various phenoxyphenoxy crotonic acid derivatives so as to find satisfactory herbicides and have studied the herbicidal effects thereof.

In the compounds of formula I, X preferably represents a hydrogen atom. R is preferably an alkyl group of 1 to 4 carbon atoms, especially an ethyl group.

The novel trifluoromethylphenoxy phenoxy crotonic acid derivatives having the formula (I) of the present invention have superior herbidical activity against gramineous weeds such as barnyard grass, crab grass and Johnson grass in comparison with the compounds described in Japanese Unexamined Patent Publication No. 33637/1977 such as methyl 2-[4-trifluoromethylphenoxy)phenoxy]-crotonate, ethyl 2-[4-(4-trifluoromethyl-2-chlorophenoxy)phenoxy]crotonate, ethyl α-[4(4-trifluoromethylphenoxy)phenoxy]valerylate and ethyl α-[4-(4-trifluoromethyl-2-chlorophenoxy)phenoxy]valerylate. The novel compounds of the present invention have superior residual activity in soil in a soil treatment in comparison with the α-[4-(4-trifluoromethylphenoxy)phenoxy]propionic acid derivatives disclosed in Japanese Unexamined Patent Publication No. 12924/1976.

The novel compounds of the present invention also have excellent effects such as a long suppression of weeds in later emergence; a long suppression of recovery following an incomplete suppression of weeds in a foliage treatment; growth control of grown weeds and excellent stability of activity under varying conditions caused by rain-fall, atmospheric moisture and high temperature.

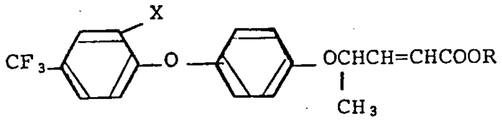
The novel compounds of the present invention have a methyl group at the γ-position of the trifluoromethylphenoxy phenoxy crotonic acid compounds, whereby the special herbicidal effect, especially the significant herbicidal effect against gramineous weeds such as Johnson grass, Foxtail Backgrass, barnyard grass and crab grass are imparted.

The novel compounds of the present invention have significant selectivity without phytoxicity to broad leaf crop plants such as radish, soybean, pea-nut, cotton, flax, beet, pimento and sunflower, but completely control gramineous weeds such as barnyard grass, crab grass, Johnson grass, wild sorghum, quack grass, Dent Foxtail and paspalum grass.

The novel compounds of the present invention can be applied as herbicides by desirable methods in all seasons, by soil treatment and by foliage treatment in the post-emergence and pre-emergence stages.

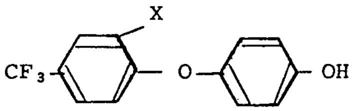
The novel compounds have significant herbicidal effect in foliage treatment, for example, completely controlling Johnson grass in the 5 leaf-stage or later.

The trifluoromethylphenoxy phenoxy crotonic acid derivatives having the formula



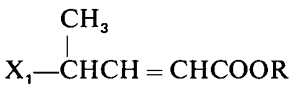
(I)

wherein X and R are as defined above can be produced in high yield by reacting a trifluoromethylphenoxy phenol derivative having the formula



(II)

wherein X is as defined above with γ-halogen-γ-methylcrotonic acid derivative having the formula



$$X_1\text{—}\overset{\overset{\displaystyle CH_3}{|}}{C}HCH=CHCOOR \qquad \text{(III)}$$

wherein X_1 represents a halogen atom and R is as defined above in a reaction medium in the presence of a base at 0 to 150°C for 1 to 20 hours and, where R is a hydrogen atom, converting the acid product to the corresponding ester.

Suitable bases include alkali metal hydroxides such as sodium hydroxide or potassium hydroxide; alkali metal carbonates such as sodium carbonate, potassium carbonate, sodium bicarbonate; alcoholates such as sodium ethylate and tertiary amines such as triethyl amine, dimethyl aniline or pyridine.

Suitable reaction media include water, acetone, methylethyl ketone, methanol, ethanol, isopropanol, butanol, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, benzene, toluene, xylene, chlorobenzene, chloroform, carbon tetrachloride and dichloroethane.

Examples of the preparation of the compounds by this process are described hereunder:—

Preparation 1

Ethyl γ-methyl-γ[4-(4'-trifluoromethylphenoxy) phenoxy]crotonate

To 70 ml of ethanol was added 0.9 g (0.039 mole) of sodium (metal) to prepare sodium ethylate and 8.9 g (0.035 mole) of 4-(4'-trifluoromethylphenoxy)phenol was added to the sodium ethylate. 8.0 g (0.039 mole) of ethyl γ-bromo-γ-methyl crotonate was added. The mixture was refluxed for 4 hours. The reaction mixture was extracted with toluene and the toluene phase was successively washed with water, dilute hydrochloric acid and water and dried with anhydrous sodium sulfate and the solution was concentrated by distilling off toluene. The residue was purifed by vacuum distillation to give 10.8 g (yield: 81.5%) of pale yellow viscous liquid having a boiling point of 173°C/0.01 mmHg and n_D^{20} 1.5175.

Preparation 2

Isopropyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonate

In 150 ml dimethylformamide were dissolved 25.4 g (0.1 mole) of 4-(4-trifluoromethylphenoxy)phenol, 19.3 g (0.14 mole) of sodium carbonate and 27.0 g (0.1 mole) of isopropyl γ-bromo-γ- methyl crotonate and the mixture was stirred at 100°C for 6 hours.

After cooling the reaction mixture, it was poured into water and the reaction product was extracted with dichloromethane and successively washed with water, dilute hydrochloric acid and water and dried with anhydrous sodium sulfate, and then the solution was concentrated by distilling off dichloromethane.

The residue was purified by vacuum distillation to give 33.6 g (yield: 85%) of pale yellow liquid having a boiling point of 158°C/0.015 mmHg and a refractive index of n_D^{20} 1.5134.

Preparation 3

Allyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy crotonate

In 300 ml of anhydrous toluene were dissolved 25.4 g (0.1 mole) of 4-(4′-trifluoromethylphenoxy)phenol and 8.8 g (0.11 mole) of pyridine. The solution was cooled in ice water and 21 g (0.12 mole) of allyl γ-chloro-γ-methyl crotonate was added. The mixture was heated at room temperature for 2 hours and then at 40°C for 2 hours and then washed with water, dried with anhydrous sodium sulfate and concentrated by distilling off toluene.

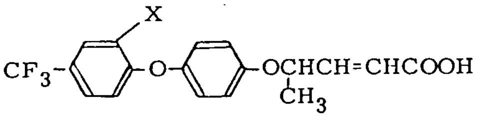
The residue was purified by vacuum distillation to give 34.9 g (yield 89%) of pale yellow liquid having a boiling point of 172 to 174°C/0.015 mmHg and a refractive index of n_D^{20} 1.5218.

In accordance with said process, but using the following starting compounds instead of allyl γ-chloro-γ-methyl crotonate and reacting them with 4-[4′-trifluoromethylphenoxy)phenol in ethanol in the presence of potassium carbonate, the following corresponding products were obtained.

Starting compound	Products
methyl γ-bromo-γ-methyl crotonate	methyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
ethyl γ-bromo-γ-methyl crotonate	ethyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
propyl γ-bromo-γ-methyl crotonate	propyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
butyl γ-bromo-γ-methyl crotonate	butyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
allyl γ-bromo-γ-methyl crotonate	allyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
chloroethyl γ-bromo-γ-methyl crotonate	chloroethyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
propargyl γ-bromo-γ-methyl crotonate	propargyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate

In accordance with said process but reacting ethyl γ-bromo-γ-methyl crotonate with 4-(2′-chloro-4′-trifluoromethylphenoxy)phenol in ethanol in the presence of potassium carbonate, ethyl γ-methyl-γ-[4-(2′-chloro-4′-trifluoromethylphenoxy)phenoxy]crotonate was obtained.

The trifluoromethylphenoxy phenoxy crotonic acid derivatives having the formula (I) can be also produced by reacting a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



(VI)

wherein X represents a hydrogen or halogen atom, with an alcohol having the formula

ROH

wherein R represents an alkyl, haloalkyl, alkenyl, haloalkenyl or alkynyl group, in the presence of a dehydrating agent such as sulfuric acid, hydrochloric acid; an aromatic sulfonic acid such as benzenesulfonic acid, toluenesulfonic acid or β-naphthalenesulfonic acid; an anhydrous sulfate such as anhydrous copper sulfate or anhydrous iron sulfate; phosphorus oxychloride, phosphoric acid anhydride, boron trifluoride or an acidic ion-exchanger at 20 to 150°C or under reflux for 1 to 20 hours.

Examples of the preparation of the compounds by this process are described hereunder:—

Preparation 4

Methyl γ-methyl-γ-[4(4′-trifluoromethylphenoxy)phenoxy]crotonate:

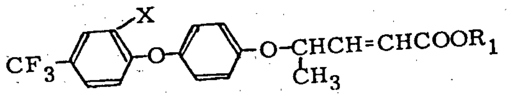
A mixture of 70.0 g (0.2 mole) of γ-methyl-γ-[4(4′-trifluoromethylphenoxy)-phenoxy] crotonic acid, 200 ml of methanol and 10 g of conc. sulfuric acid was refluxed for 4 hours and then concentrated by distilling off about 1/2 of the methanol. 300 ml of water was added to dilute the residue and the resulting oily product was extracted with ether. The ether phase was dried with anhydrous sodium sulfate and ether was distilled off. The residual oily product was purified by vacuum distillation to give 65.9 g (yield: 90.0%) of pale yellow viscous liquid having a boiling point of 157 to 162°C/0.015 mmHg and a refractive index of n_D^{20} 1.5238.

In accordance with said process but reacting γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonic acid with methanol, ethanol, propanol, butanol, allyl alcohol or propargyl alcohol in the presence of paratoluenesulfonic acid as a catalyst, the following products were obtained.

Alcohol	Product
methanol	methyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
ethanol	ethyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
propanol	propyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
butanol	butyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
allyl alcohol	allyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate
propargyl alcohol	propargyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy) phenoxy] crotonate

In accordance with said process but reacting γ-methyl-γ-[4-(2′ chloro-4′-trifluoromethylphenoxy)phenoxy]crotonic acid with ethanol in the presence of paratoluenesulfonic acid as a catalyst, ethyl γ-methyl-γ-[4-(2′-chloro-4′-trifluoromethylphenoxy)phenoxy]crotonate was obtained.

The trifluoromethylphenoxy phenoxy crotonic acid derivatives having the formula (1) can be also converted to other compounds having the fomula of the invention by reacting a trilfuoromethylphenoxy phenoxy crotonic acid derivative having the formula



(1^{-1})

wherein R_1 represents an alkyl, haloalkyl, alkenyl, haloalkenyl or alkynyl group with an alcohol having the formula

$$R_2OH$$

wherein R_2 is different from R_1 and represents an alkyl, haloalkyl, alkenyl, haloalkenyl, or alkynyl group, at 0 to 150°C for 1 to 20 hours. The reaction may be carried out in the presence of a catalyst comprising an acid such as sulfuric acid or paratoluenesulfonic acid; an alcoholate such as sodium ethylate or potassium butyrate; pyridine or a basic ion exchange resin.

Examples of the preparation of the compounds by this process will be described hereunder:—

Preparation 5

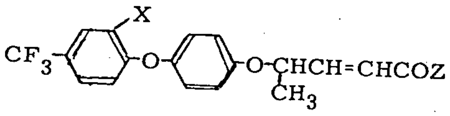
Isopropyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonate:

To 70 ml of isopropyl alcohol were added 19.0 g (0.05 mole) of ethyl γ-methyl-γ[4-(4′-trifluoromethylphenoxy)phenoxy] crotonate and 3 g of sulfuric acid. The mixture was refluxed for 15 hours and concentrated by distilling off about 50 ml of isopropyl alcohol 150 ml of water was added, the resulting oil was extracted with ether and the ether phase was washed with water and dried with anhydrous sodium sulfate and ether distilled off.

The residual oily product was purified by vacuum distillation to give 14.2 g (yield: 72.3%) of pale yellow viscous liquid having a boiling point of 158°/0.015 mmHg and a refractive index of n_D^{20} 1.5134.

In accordance with said process but reacting ethyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate with butyl alcohol instead of butyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate was obtained.

The trifluoromethylphenoxy phenoxy crotonic acid derivatives having the formula (I) can be produced by reacting trifluoromethylphenoxy phenoxy crotonic acid halide having the formula



(VIII)

wherein X represents hydrogen or halogen atom; and Z represents a halogen atom, with an alcohol having the formula

$$ROH \qquad (V)$$

wherein R represents an alkyl, haloalkyl, alkenyl, haloalkenyl or alkynyl group in the absence or in the presence of a base as a dehydrohalogenation agent in a reaction medium or excess of the alcohol having the formula ROH or without a reaction medium, at −10 to 150°C for 1 to 20 hours.

Suitable dehydrohalogenation agents are inorganic or organic bases including alkali metal hydroxides such as sodium hydroxide or potassium hydroxide; alkali metal carbonates such as sodium carbonate, potassium carbonate or sodium bicarbonate; alcoholates such as sodium ethylate; and tertiary amines such as triethyl amine, dimethyl aniline or pyridine.

Suitable reaction media include acetone, methyl ethyl ketone, dimethylformamide, dimethylsulfoxide, tetrahydrofuran, benzene, toluene, xylene, chlorobenzene, chloroform, carbon tetrachloride and dichloroethane.

Examples of the preparation of the compounds by this process are described hereunder.

Preparation 6

Ethyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate:

To 200 ml of anhydrous ethyl alcohol was added 37 g (0.1 mole) of γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonic acid chloride. The mixture was kept at room temperature for 1 day and then, ethyl alcohol was distilled off.

The residue was purified by a vacuum distillation to give 34.9 g (yield: 92.5%) of pale orange liquid having a boiling point of 173°C/0.0-1 mmHg and a refractive index of n_D^{20} 1.5175.

Preparation 7

η-Butyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate

To 250 ml of n-butyl alcohol was added 40.6 g (0.1 mole) of γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonic acid bromide. The mixture was gradually heated to 60°C and kept at 60°C for 5 hours and n-butyl alcohol was distilled off.

The residue was purified by a vacuum distillation to give 36.1 g (yield: 88.8%) of a pale yellow viscous liquid having a boiling point of 180 to 182°C/0.02 mmHg and a refractive index of n_D^{20} 1.5137.

Preparation 8

Methyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate:

A mixture of 74 g (0.02 mole) of γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)-phenoxy]crotonic acid and 30 ml of thionyl chloride was refluxed for 6 hours. Excess thionyl chloride was distilled off and 50 ml of methanol was added to the residual acid chloride. The mixture was refluxed for 5 hours and methanol was distilled off.

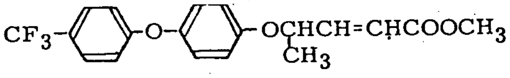
The residue was purified by vacuum distillation to give 6.4 g (yield: 87.3%) of pale yellow liquid having a boiling point of 157 to 162°C/0.015 mmHg and a refractive index of n_D^{20} 1.5238.

In accordance with said process but reacting γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonic acid with thionyl chloride, distilling off excess thionyl chloride and reacting propyl alcohol, butyl alcohol, allyl alcohol, propargyl alcohol, or chloroethyl alcohol instead of methanol, the following corresponding products were obtained.

Alcohol	Product
propyl aocohol	propyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy) phenoxy] crotonate
butyl alcohol	butyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy) phenoxy] crotonate
allyl alcohol	allyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy) phenoxy] crotonate
propargyl alcohol	propargyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy) phenoxy] crotonate
chloroethyl alcohol	chloroethyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy) phenoxy] crotonate

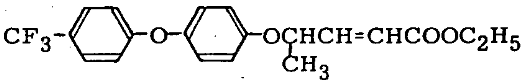
Typical compounds obtained by said processes are exemplified below. The compound numerals are referred in the following description.

Compound No. 1:
Methyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate.



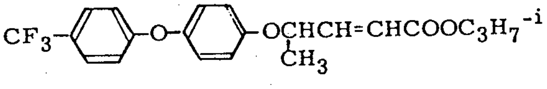
b.p.: 157 to 162°C/0.015 mmHg;
n_D^{20}: 1.5238

Compound No. 2:
Ethyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate



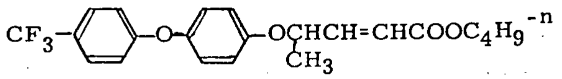
b.p.: 173°C/0.01 mmHg;
n_D^{20}: 1.5175

Compound No. 3:
Isopropyl γ-methyl-γ-[4-(4'-trifluoromethylphenoxy)phenoxy]crotonate.



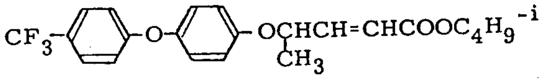
b.p.: 158°C/0.015 mmHg;
n_D^{20}: 1.5134

Compound No. 4:
n-Butyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonate.



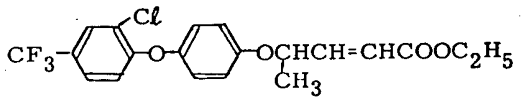
b.p.: 180 to 182°C/0.02 mm Hg;
n_D^{20}: 1.5137

Compound No. 5:
Isobutyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonate.



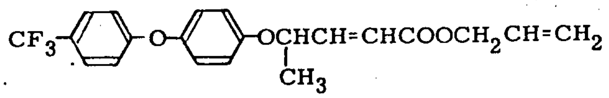
b.p.: 172 to 174°C/0.007 mmHg;
n_D^{20}: 1.5100

Compound No. 6:
Ethyl γ-methyl-γ-[4-(4′-trifluoromethyl-2-chlorophenoxy)phenoxy]crotonate.



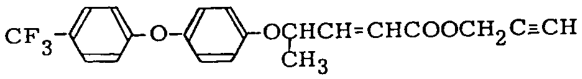
b.p.: 175 to 185°C/0.007 mmHg;
n_D^{20}: 1.5283

Compound No. 7:
Allyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonate.



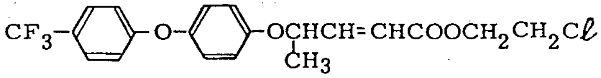
b.p.: 172 to 174°C/0.015 mmHg;
n_D^{20}: 1.5218

Compound No. 8:
Propargyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonate.



b.p.: 180 to 181°C/0.015 mmHg;
n_D^{20}: 1.5310

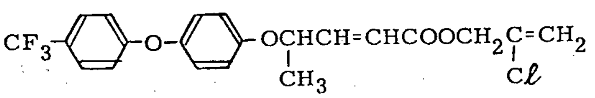
Compound No. 9:
2-chloroethyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonate.



b.p.: 192°C/0.007 mmHg;
n_D^{20}: 1.5284

Compound No. 10:

2-chloroallyl γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy)crotonate.



b.p.: 190 to 193°C/0.01 mmHg;
n_D^{20}: 1.5310

The following compounds are also effective as herbicides: γ-methyl-γ-[4-(4′-trifluoromethylphenoxy)phenoxy]crotonic acid n-propyl ester, sec-butyl ester, tert-butyl ester, n-amyl ester, i-amyl ester, n-hexyl ester, n-octyl ester, vinyl ester, 2-methylallyl ester, butenyl ester, 2-propylallyl ester, 2-hexenyl ester, 2-bromoethyl ester, trichloroethyl ester, 1-chloro-2-propyl ester, 1,3-dichloro-2-propyl ester and 3-bromopropyl ester.

γ-methyl-γ-[4-(4′-trifluoromethyl-2-chlorophenoxy)phenoxy]crotonic acid or γ-methyl-γ-[4-(4′-trifluoromethyl-2-bromophenoxy)phenoxy]crotonic acid methyl ester, ethyl ester, n-propyl ester, i-propyl ester, n-butyl ester, isobutyl ester, sec-butyl ester, tert-butyl ester, amyl ester, allyl ester, propargyl ester, chloroethyl ester, bromoethyl ester, trichloroethyl ester, 1-chloro-2-propyl ester or 1,3-dichloro-2-propyl ester.

The novel compounds of the present invention produced by said syntheses have significant herbicidal effect and non-phytotoxicity to many crop plants and can be applied to up-land paddy fields, orchards, forests and non-cultivated ground by soil treatment or foliage treatment, selecting suitable methods of application and suitable doses of the active ingredient.

The dose of the active compound of the present invention is dependent upon weather conditions, soil conditions, the form of the composition, the season of the application, the method of the application, the crop plants being treated and the kinds of weeds, and is usually in a range of 0.01 to 10 kg, preferably 0.1 to 5 kg and especially 0.5 to 3 kg per hectare in the soil treatment and a concentration of 10 to 10,000 ppm, preferably 100 to 5,000 ppm and especially 250 to 3,000 ppm of the active ingredient in the foliage treatment.

The compound of the present invention can be used in a pure form and also in the form of compositions such as granules, wettable powders dusts, emulsifiable concentrates, fine power, flowable compositions and suspensions to give superior effects.

In the preparation of the herbicidal compositions, the compound of the present invention can be uniformly mixed with or dissolved in suitable adjuvants, for example a solid carrier such as talc, bentonite, clay, kaolin, diatomaceous earth, silica gel, vermiculite, lime, siliceous sand, ammonium sulfate or urea; liquid carriers such as alcohols, dioxane, acetone, cyclohexanone, methyl naphthalene or dimethylformamide; a surfactant as an emulsifier dispersing agent or wetting agent such as alkyl sulfate, alkylsulfonate, polyoxyethyleneglycol ethers, polyoxyethylenealkylaryl ethers such as polyoxyethylenenonylphenol ether or polyoxyethylenesoritane monoalkylate; carboxymethyl cellulose; gum arabic and other adjuvants.

The amounts of the active ingredients, adjuvants and additives in the herbicidal compositions of the present invention are further illustrated below:—

Wettable powder:

Active ingredient: 5 to 95 wt.%, preferably 20 to 50 wt.%
Surfactant: 1 to 20 wt.% preferably 5 to 10 wt.%
Solid carrier: 5 to 85 wt.%, preferably 40 to 70 wt.%

The active ingredient is admixed with the solid carrier and the surfactant and the mixture is pulverized.

Emulsifiable concentrate:

Active ingredient: 5 to 95 wt.%, preferably 20 to 70 wt.%
Surfactant: 1 to 40 wt.%, preferably 5 to 20 wt.%
Liquid carrier: 5 to 90 wt.%, preferably 30 to 60 wt.%

The active ingredient is dissolved in the liquid carrier and the surfactant is admixed.

Dust:

Active ingredient: 0.5 to 10 wt.%, preferably 1 to 5 wt.%
Solid carrier: 99.5 to 90 wt.%, preferably 99 to 95 wt.%

The active ingredient is mixed with fine solid carrier and the mixture is pulverized.

Granule:
Active ingredient: 0.5 to 40 wt.% preferably 2 to 10 wt.%
Solid carrier: 99.5 to 60 wt.% preferably 98 to 90 wt.%

The active ingredient is sprayed or otherwise coated on the solid carrier to form the granules.

Other herbicides can be incorporated in the herbicidal composition of the present invention.

Suitable additional herbicides include; carboxylic acid type compounds such as 2,3,6-trichlorobenzoic acid and salts thereof, 2,3,5,6-tetrachlorobenzoic acid and salts thereof, 2-methoxy-3,5,6-trichlorobenzoic acid and salts thereof, 2-methoxy-3,6-dichlorobenzoic acid and salts thereof, 2-methyl-3,6-dichlorobenzoic acid and salts thereof, 2,3-dichloro-6-methylbenzoic acid and salts thereof, 2,4-dichlorophenoxyacetic acid and salts and esters thereof, 2,4,5-trichlorophenoxyacetic acid and salts and esters thereof, 2-methyl-4-chlorophenoxyacetic acid and salts and esters thereof, α-(2,4,5-trichlorophenoxy)propionic acid and salts and esters thereof, 2-(2,4-dichlorophenoxy)butyric acid and salts and esters thereof, 4-(2-methyl-4-chlorophenoxy)butyric acid and salts and esters thereof, 2,3,6-trichlorophenylacetic acid and salts thereof, 3,6-endoxohexahydrophthalic acid, dimethyl 2,3,5,6-tetrachloroterephthalate, trichloroacetic acid and salts thereof, 2,2-dichloropropionic acid and salts thereof and 2,3-dichloroisobutyric acid and salts thereof; and carbamic acid type compounds such as ethyl N,N-di(n-propyl)-thiolcarbamate, propyl N,N -di(n-propyl)thiolcarbamate, ethyl N-ethyl-N-(n-butyl)thiol-carbamate, propyl N-ethyl-N-(n-butyl)thiolcarbamate, 2-chloroallyl N,N-diethyl dithiocarbamate, N-methyl dithiocarbamate, S-ethyl hexahydro-1H-azepine-1-carbothioate, S-4-chlorobenzyl N,N-diethyl thiolcarbamate, S-benzyl N,N-di-sec-butyl thiocarbamate, isopropyl N-phenyl carbamate, isopropyl N-(m-chlorophenyl)carbamate, 4-chloro-2-butyl N-(m-chlorophenyl)carbamate, methyl N-(3,4-dichlorophenyl)carbamate and methyl sulfanyl carbamate; phenol type compounds such as dinitro-O-(sec-butyl)phenol and salts thereof and pentachlorophenol and salts thereof; urea type compounds such as 3-(3,4-dichlorophenyl)-1,1-dimethyl urea, 3-phenyl-1,1-dimethyl urea, 3-(3,4-dichlorophenyl)-3-methoxy-1,1-dimethyl urea, 3-(4-chlorophenyl)-3-methoxy-1,1-dimethylurea, 3-(3,4-dichlorophenyl)-1-n-butyl-1-methylurea, 3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea, 3-(4-chlorophenyl)-1-methoxy-1-methylurea, 3-(3,4-dichlorophenyl)-1,1,3-trimethylurea, 3-(3,4-dichlorophenyl)-1,1-diethylurea, 1-(2-methylcyclohexyl)-3-phenylurea, 1-(5-t-butyl-1,3,4-triadiazol-2-yl)-1,3-dimethylurea, 3-(3-chloro-4-methylphenyl)-1,1-dimethylurea, 3-(3-chloro-4-methoxyphenyl)-1,1-dimethylurea and dichloralurea; triazine type compounds such as 2-chloro-4,6-bis(ethylamino)-s-triazine, 2-chloro-4-ethylamino-6-isopropyl-amino-s-triazine, 2-chloro-4,6-bis(methoxypropylamino)-s-triazine, 2-methoxy-4,6-bis(isopropylamino)-s-triazine, 2-methyl-mercapto-4,6-bis(isopropylamino)-s-triazine, 2-methylmercapto-4, 6-bis(ethylamino)-s-triazine, 2-methylmercapto-4-ethylamino-6-isopropylamino-s-triazine, 2-chloro-4,6-bis(isopropylamino)-s-triazine, 2-methoxy-4,6-bis(ethylamino)-s-triazine, 2-methoxy-4-ethylamino-6-isopropylamino-s-triazine, 2-methylmercapto-4-(2-methoxyethylamino)-6-isopropylamino-s-triazine, 2-(4-chloro-6-ethylamino-s-triazine-2-yl)amino-2-methyl.propionitrile, 4-amino-6-t-butyl-3-methylthio-1,2,4-triazine-5-(4H)-one, and 3-cyclohexyl-6-dimethylamino-1-methyl-s-triazine-2,4-(1H, 3H) dione;
ether type compounds such as 2,4-dichloro-4′-nitrodiphenyl ether, 2,4,6-trichloro-4′-nitrodiphenyl ether, 2,4-dichloro-6-fluoro-4′-nitrodiphenyl ether, 3-methyl-4′-nitrodiphenyl. ether, 3,5-dimethyl-4′-nitrodiphenyl ether, 2,4′-dinitro-4-trifluoromethyl diphenyl ether, 2,4-dichloro-3′-methoxy-4′-nitrodiphenyl ether, 2-chloro-4-trifluoromethyl-4′-nitrodiphenyl ether, 2-chloro-4-trifluoromethyl-3′-ethoxy-4′-

nitrodiphenyl ether, 2-chloro-4-trifluoromethyl-3′-carbethoxy-4′-nitrodiphenyl ether and 2-chloro-4-trifluoromethyl-3′-(1-carbethoxy)ethoxy-4′-nitrodiphenyl ether;

anilide type compounds such as N-(3,4-dichlorophenyl)propionamide, N-(3,4-dichlorophenyl)methacrylamide, N-(3-chloro-4-methylphenyl)-2-methylpentamide, N-(3,4-dichlorophenyl)-trimethyl acetamide, N-(3,4-dichlorophenyl)-α,α-dimethyl valeramide, N-isoprophyl-N-phenylchloroacetamide, N-n-butoxymethyl-N-(2,6-diethylphenyl)chloroacetamide and N-n-methoxymethyl-N-(2,6-diethylphenyl)chloroacetamide;

uracil type compounds such as 5-bromo-3-sec-butyl-6-methyluracil, 5-bromo-3-cyclohexyl-1,6-dimethyluracil, 3-cyclohexyl-5,6-trimethyleneuracil, 5-bromo-3-isopropyl-6-methyluracil, and 3-tert.-butyl-5-chloro-6-methyluracil;

nitrile type compounds such as 2,6-dichlorobenzonitrile, diphenylacetonitrile, 3,5-dibromo-4-hydroxybenzonitrile, and 3,5-diiodo-4-hydroxybenzonitrile;

others such as 2-chloro-N,N-diallylacetamide, N-(1,1-dimethyl-2-propyl)-3,5-dichlorobenzamide, maleic acid hydrazide, 3-amino-1,2,4-triazole, mono-sodium methane arsonate, di-sodium methane arsonate, N,N-dimethyl-α,α-diphenyl acetamide, N,N-di(n-propyl)-2,6-dinitro-4-trifluoromethyl aniline, N,N-di(n-propyl)-2,6-dinitro-4-methyl aniline, N,N-di(n-propyl)-2,6-dinitro-4-methylsulfonyl aniline, O-(2,4-dichlorophenyl)-O-methylisopropyl phosphoramide thioate, 4-amino-3,5,6-trichloropiclinic acid, 2,3-dichloro-1,4-naphthoquinone, dimethoxycarbonyl disulfide, 3-isopropyl-1H-2,1,3-benzothiadiazine-4(3H)-one-2,2-dioxide, 6,7-dihydrodipyridol [1,2-a : 2′ 1′-c) pyrazinium salt, 1,1′-dimethyl-4,4′-bipyridinium salt, 3,4,5,6-tetrahydro-3,5-dimethyl-2-thio-2H-1,3,5-thiadiazine, 1,2-dimethyl-3,5-diphenylpyrazolinium methyl sulfate, N-sec-butyl-2,6-dinitro-3,4-xylidine, N-sec.-butyl-4-t-butyl-2,6-dinitroaniline, N^3, N^3-diethyl-2,4-dinitro-6-trifluoromethyl-1,3-phenylenediamine, 1,1,1-trifluoro-(4′-phenylsulfonyl)-methane sulfono-O-toluidine, 2-(1-naphthoxy)-N,N-diethyl propionamide, 2-t-butyl-4-(2,4-dichloro-5-isopropoxyphenyl)-1,3,4-oxadiazoline-5-one, 4-chloro-5-methylamino-2-(α,α,α-trifluoro-m-tolyl)-3(2H)-pyridazinone, N-cyclopropylmethyl-α,α,α-trifluoro-2,6-dinitro-N-propyl-p-toluidine and N-phosphonomethyl glycine.

When the additional herbicides described are mixed with the compound of the present invention, the ratio of the compounds and the dose of the compounds is selected depending upon the respective selectivities and herbicidal effects of the compounds on the crop plants and their effect on the noxious weeds treated with them.

Examples of the preparations of the herbicidal compositions are illustrated below. However, the kinds and amounts of adjuvants used are not limited and can be varied according to the usual considerations.

Composition No. 1: Wettable powder:

Compound No. 1	30 wt.%
Sodium higher alcohol sulfate	5 wt.%
Clay	65 wt.%

These components were uniformly mixed and pulverized to prepare a wettable powder.

Composition No. 2: Emulsifiable concentrate:

Compound No. 2	25 wt.%
Polyoxyethylenealkylaryl ether	10 wt.%
Calcium dinaphthylmethanesulfonate	5 wt.%
Xylene	60 wt.%

These components were uniformly mixed to prepare an emulsifiable concentrate.

Composition No. 3: Granules:

Compound No. 3	3 wt.%
Bentonite	40 wt.%
Clay	50 wt.%
Sodium lignin sulfonate	7 wt.%

These components were uniformly mixed and pulverized, then kneaded with water and granulated and dried to prepare granulates.

Composition No. 4: Dust:

Compound No. 4	2 wt.%
Clay	98 wt.%

The compounds were mixed and pulverized to prepare a dust:

The herbicidal compositions are produced by combining the active ingredient with the adjuvants as follows.

Wettable powder:

Active ingredient:	5 to 95 wt.% preferably 20 to 50 wt.%
Surfactant:	1 to 20 wt.% preferably 5 to 10 wt.%
Solid carrier:	5 to 85 wt.% preferably 40 to 70 wt.%

The components are mixed and pulverized.

Emulsifiable concentrate:

Active ingredient:	5 to 95 wt.% preferably 20 to 70 wt.%
Surfactant:	1 to 40 wt.% preferably 5 to 20 wt.%
Liquid carrier:	5 to 90 wt.% preferably 30 to 60 wt.%

The active ingredient is dissolved in the liquid carrier with the surfactant.

Dust:

Active ingredient:	0.5 to 10 wt.% preferably 1 to 5 wt.%
Solid carrier:	99.5 to 90 wt.% preferably 99 to 95 wt.%

The active ingredient is pulverized with fine solid carrier.

Granules:

Active ingredient:	0.5 to 40 wt.% preferably 2 to 10 wt.%
Solid carrier:	99.5 to 60 wt.% preferably 98 to 90 wt.%

The active ingredient is sprayed on the solid carrier to absorb it, or otherwise coated on the solid carrier.

The herbicidal activity of the compounds of the present invention will be further illustrated by the following experimental tests.

Experiment 1:

Test for crop plants and up-land weeds in pre-emergence (pre-germination) soil treatment.

Pots of 600 cm^2 were filled with up-land soil and seeds of wheat, barley, soybean, radish, barnyard grass and crab grass were sown in a depth of 0.5 cm. Each emulsifiable concentrate, prepared in accordance with the method of Composition No. 2, was diluted with water to give the specific concentration of the compound for the application of 1 Klit./ha. and the diluted solution was uniformly sprayed on the soil surface.

Twenty days after the treatment, the herbicidal effect and the phytotoxicity of the crop plants were observed and rated as follows:

Herbicidal effect or phytotoxicity:

10: Complete growth suppression is found;
9: Growth suppression of from 90 to 100%;
8: Growth suppression of from 80 to 90%;
7: Growth suppression of from 70 to 80%;
6 Growth suppression of from 60 to 70%;
5 Growth suppression of from 50 to 60%;
4: Growth suppression of from 40 to 50%;
3: Growth suppression of from 30 to 40%;
2: Growth suppression of from 20 to 30%;
1: Growth suppression of from 0 to 20%;
0: No herbicidal effect.

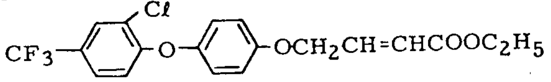
Wh.:	Wheat	Bar.:	Barley
So.:	Soybean	Ra.:	Radish
B.G.:	Barnyard Grass	Cr.G.:	Crab Grass

TABLE 1

Result of Test in pre-emergence soil treatment (pot test)

Compound (active ingredient Kg/ha.)	Dose	Wh.	Bar.	So.	Ra.	B.G.	Cr.G.
Compound No. 1	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 2	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 3	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 4	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 5	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 6	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 7	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 8	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 9	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 10	0.5 0.25	0 0	0 0	0 0	0 0	10 10	10 10
Reference Compound (A)	0.5 0.25	0 0	0 0	0 0	0 0	5 1	6 3

Reference Compound A



Experiment 2

Test for crop plants and up-land weeds in pre-emergence soil treatment.

Polyethylene pots of 2,000 cm^2 were each filled with up-land soil and seeds of rice, maize, wheat, soybean, cotton, radish, barnyard grass, crab grass, Dent Foxtail, Johnson grass and *Chenopodium album L.* (25 seeds for each plant) were sown in a depth of 0.5 cm.

Each emulsifiable concentrate, prepared in accordance with the method of Composition No. 2, was diluted with water to give 0.25, 0.125 and 0.625 Kg/ha. of the active ingredient, and the diluted solution was uniformly sprayed on the surface of the soil at a rate of 20.0 ml per pot.

Twenty days after the treatment, the herbicidal effect and the phytotoxicity of the crop plants were observed and rated as described above.

Ric.:	Rice
Mai.:	Maize
Wh.:	Wheat
So.:	Soybean
Cot.:	Cotton
Ra.:	Radish
B.G.:	Barnyard Grass
Cr.G.:	Crab Grass
F.B.	Dent Foxtail
J.G.	Johnson Grass
Ch.:	Chenopodium album L.

TABLE 2

Result of Test in pre-emergence soil treatment (pot test)

Compound (active ingredient Kg/ha.)	Dose	Ric.	Mai.	Wh.	So.	Cot.	Ra.	B.G.	Cr.G.	F.B.	J.G.	Ch.
Compound No. 1	0.25	8	6	0	0	0	0	10	10	10	10	0
	0.125	7	1	0	0	0	0	10	10	10	10	0
	0.0625	2	0	0	0	0	0	9	10	10	10	0
Compound No. 2	0.25	8	7	0	0	0	0	10	10	10	10	0
	0.125	6	2	0	0	0	0	10	10	10	10	0
	0.0625	3	0	0	0	0	0	9	10	10	10	0
Compound No. 3	0.25	6	4	0	0	0	0	10	10	10	10	0
	0.125	3	0	0	0	0	0	10	10	10	10	0
	0.0625	0	0	0	0	0	0	9	10	10	10	0
Compound No. 4	0.25	4	3	0	0	0	0	10	10	10	10	0
	0.125	2	0	0	0	0	0	10	10	10	10	0
	0.0615	0	0	0	0	0	0	8	10	10	10	0
Compound No. 5	0.25	6	2	0	0	0	0	10	10	10	10	0
	0.125	4	1	0	0	0	0	10	10	10	10	0
	0.0625	1	0	0	0	0	0	8	10	10	10	0
Compound No. 6	0.25	3	3	0	0	0	0	10	10	10	10	0
	0.125	1	0	0	0	0	0	10	10	10	10	0
	0.0625	0	0	0	0	0	0	8	6	8	8	0
Compound No. 7	0.25	6	1	0	0	0	0	10	10	10	10	0
	0.125	3	0	0	0	0	0	10	10	10	10	0
	0.0625	1	0	0	0	0	0	8	10	10	10	0
Compound No. 8	0.25	5	3	0	0	0	0	10	10	10	10	0
	0.125	2	0	0	0	0	0	10	10	10	10	0
	0.0625	0	0	0	0	0	0	9	10	10	9	0
Compound No. 9	0.25	2	0	0	0	0	0	10	10	10	10	0
	0.125	1	0	0	0	0	0	10	10	10	10	0
	0.0625	0	0	0	0	0	0	9	10	10	10	0
Compound No. 10	0.025	6	2	0	0	0	0	10	10	10	10	0
	0.125	3	0	0	0	0	0	10	10	10	10	0
	0.0625	0	0	0	0	0	0	8	10	10	10	0

TABLE 2 (Continued)

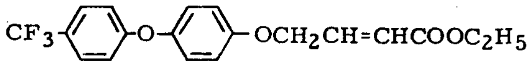
Result of Test in pre-emergence soil treatment (pot test)

Compound (active ingredient Kg./ha.)	Dose	Ric.	Mai.	Wh.	So.	Cot.	Ra.	B.G.	Cr.G.	F.B.	J.G.	Ch.
Reference Compound (A)	0.25	0	0	0	0	0	0	2	3	2	0	0
	0.125	0	0	0	0	0	0	0	0	0	0	0
	0.0625	0	0	0	0	0	0	0	0	0	0	0
Reference Compound (B)	0.25	0	0	0	0	0	0	1	2	1	0	0
	0.125	0	0	0	0	0	0	0	0	0	0	0
	0.0625	0	0	0	0	0	0	0	0	0	0	0
Reference Compound (C)	0.25	0	0	0	0	0	0	4	5	2	1	0
	0.125	0	0	0	0	0	0	1	2	0	0	0
	0.0625	0	0	0	0	0	0	0	0	0	0	0
Reference Compound (D)	0.25	0	0	0	0	0	0	3	4	2	1	0
	0.125	0	0	0	0	0	0	0	0	0	0	0
	0.0625	0	0	0	0	0	0	0	0	0	0	0

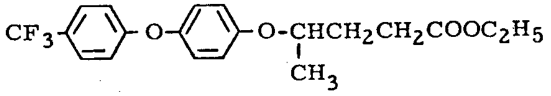
Note:

Reference Compound (A): The compound shown in Experiment 1.

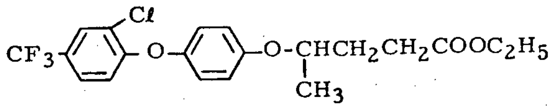
Reference Compound (B):



Reference Compound (C):



Reference Compound (D):



Experiment 3

Test for crop plants and up-land weeds in (post-emergence germination) foliage treatment.

Each pot of 600 cm² was filled with up-land soil and seeds of corn, barley, soybean, radish, barnyard grass and crab grass were sown.

Each emulsifiable concentrate, prepared in accordance with the method of Composition No. 2, was diluted with water to give the specific concentration of the compound and the diluted solution was uniformly sprayed at a rate of 1 kl/ha, when the gramineous weeds were grown to 2 to 2.5 leaf stage and the broad-leaf weeds were grown to the first divergence stage.

Fifteen days from the treatment, the herbicidal effect and the phytotoxicity of the crop plants were observed and rated as described above.

Wh.:	Wheat
Bar.:	Barley
So.:	Soybean
Ra.:	Radish
B.G.:	Barnyard Grass
Cr.G.:	Crab Grass

TABLE 3

Result of Test in Foliage Treatment (pot test)

Compound	Concentration (ppm)	Wh.	Bar.	So.	Ra.	B.G.	Cr.G.
Compound No. 1	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 2	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 3	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 4	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 5	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 6	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 7	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 8	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 9	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Compound No. 10	500 250	0 0	0 0	0 0	0 0	10 10	10 10
Reference Compound (A)	500 250	0 0	0 0	0 0	0 0	4 1	5 2
Reference Compound (B)	500 250	0 0	0 0	0 0	0 0	3 1	4 1
Referecne Compound (C)	500 250	0 0	0 0	0 0	0 0	3 1	3 2
Reference Compound (D)	500 250	0 0	0 0	0 0	0 0	2 0	2 1

Notes to Table 3
Reference Compounds (A), (B), (C), (D).
The compounds shown in Experiment 2.

Experiment 4

Test for crop plants and up-land weeds in post-emergence foliage treatment.

Each polyethylene pot of 2,000 cm^2 was filled with up-land soil and seeds of rice, maize, wheat, soybean, cotton, radish, barnyard grass, crab grass, Dent Foxtail, Johnson grass and *Chenopodium album L.* (25 seeds for each plant) were sown.

Each emulsifiable concentrate prepared in accordance with the method of Composition No. 2 was diluted with water to give the concentration of 125, 62.5 and 31.25 ppm and the diluted solution was uniformly sprayed at a rate of 20.0 ml per pot, when the plants were grown to 2 to 4 leaf stages.

Ten days from the treatment, the herbicidal effect and the phytotoxicity of the crop plants were observed and rated as described above.

Ric.:	Rice
Mai.:	Wheat
Wh.:	Wheat
So.:	Soybean
Cot.:	Cotton
Ra.:	Radish
B.G.:	Barnyard Grass
Cr.G.:	Crab Grass
F.B.:	Dent Foxtail
J.G.:	Johnson Grass
Ch.:	Chenopodium album L.

TABLE 4

Result of Test in post-emergence foliage treatment (pot test)

Compound	Concentration (ppm)	Ric.	Mai.	Wh.	So.	Cot.	Ra.	B.G.	Cr.G.	F.B.	J.G.	Ch.
Compound No. 1	125	8	4	0	0	0	0	10	10	10	10	0
	62.5	2	2	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	9	10	10	10	0
Compound No. 2	125	8	5	0	0	0	0	10	10	10	10	0
	62.5	3	2	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	10	9	10	9	0
Compound No. 3	125	3	2	0	0	0	0	10	10	10	10	0
	62.5	0	0	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	10	10	10	10	0
Compound No. 4	125	0	2	0	0	0	0	10	10	10	10	0
	62.5	0	0	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	8	9	10	10	0
Compound No. 5	125	4	2	0	0	0	0	10	10	10	10	0
	62.5	0	1	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	8	9	9	10	0
Compound No. 6	125	0	4	0	0	0	0	10	10	10	10	0
	62.5	0	2	0	0	0	0	8	7	8	10	0
	31.25	0	0	0	0	0	0	4	5	7	8	0
Compound No. 7	125	4	1	0	0	0	0	10	10	10	10	0
	62.5	2	0	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	10	9	10	10	0
Compound No. 8	125	6	4	0	0	0	0	10	10	10	10	0
	62.5	2	1	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	10	8	10	8	0
Compound No. 9	125	3	0	0	0	0	0	10	10	10	10	0
	62.5	0	0	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	10	9	9	10	0
Compound No. 10	125	5	4	0	0	0	0	10	10	10	10	0
	62.5	1	0	0	0	0	0	10	10	10	10	0
	31.25	0	0	0	0	0	0	10	8	10	8	0

TABLE 4 (Continued)

Result of Test in post-emergence foliage treatment (pot test)

Compound Concentration (ppm)	Ric.	Mai.	Wh.	So.	Cot.	Ra.	B.G.	Cr.G.	F.B.	J.G.	Ch.
Reference 125	0	0	0	0	0	0	0	0	0	0	0
Compound 62.5	0	0	0	0	0	0	0	0	0	0	0
(A) 31.25	0	0	0	0	0	0	0	0	0	0	0
Reference 125	0	0	0	0	0	0	0	0	0	0	0
Compound 62.5	0	0	0	0	0	0	0	0	0	0	0
(B) 31.25	0	0	0	0	0	0	0	0	0	0	0
Reference 125	0	0	0	0	0	0	1	2	0	0	0
Compound 62.5	0	0	0	0	0	0	0	1	0	0	0
(C) 31.25	0	0	0	0	0	0	0	0	0	0	0
Reference 125	0	0	0	0	0	0	1	0	0	0	0
Compound 62.5	0	0	0	0	0	0	0	0	0	0	0
(D) 31.25	0	0	0	0	0	0	0	0	0	0	0

Reference compounds (A), (B), (C), (D).

The compounds shown in Experiment 2.

Rain endurance test:

Weeds

	Barnyard grass:	3.8 to 4 leaf stage 21 to 25 cm
	Crab grass:	3 to 3.5 leaf stage 5 to 10 cm

Active ingredient:
In accordance with the preparation No. 2, an emulsifiable concentrate was prepared by using compound No. 2.

Rain falling condition:
The pots were subjected to artificial rain for periods of 20 minutes each at 30 min. 3 hours, 6 hours or 24 hours after the treatment, in a total amount of 5 mm per twenty minute period.

Test methods:
A solution of the active ingredient at the specific concentration was uniformly sprayed at a rate of 100 liter/10a. Then, the artificial rain was applied under the above conditions by an artificial rainfall apparatus.

Observation:
The herbicidal degrees were observed at 15 days after the treatment and compared with those of the sections not subjected to rainfall.

Test results:
The herbicidal effect index was 5 in the case of rainfall at 30 minutes after the treatment with 500 ppm of the solution to barnyard grass whereas the herbicidal effect index was 5 in the cases of no rainfall and rainfalling at 3 hours or more after

the treatment with 500 ppm of the solution to barnyard grass.

The herbicidal effect index was 2.5 in all cases, with or without rainfall, after the treatment with 100 ppm of the solution to crab grass.

The herbicidal effect index was 4 in the case of rainfall at 30 minutes after the treatment with 100 ppm of the solution to barnyard grass whereas the herbicidal effect index was 4.5, with or without rainfall at 3 hours or more after the treatment with 100 ppm of the solution to barnyard grass.

The rain endurance of the active ingredient was significantly high.

The herbicidal effect tests of the compounds no. 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 were carried out on a up-land field in which (Johnson grass) and Bermuda grass and other gramineous weeds such as crab grass and barnyard grass were naturally grown, on the 21st day after sowing soybean seeds, by spraying a solution of each active ingredient at a ratio of 500 liter/ha. The leaft stages of weeds and soybean were as follows.

Soybean	2 leaf-stage
Johnson grass:	2. 5—4 leaf-stage
Bermuda grass:	5—6 leaf stage
Crab grass:	3. 5—5 leaf-stage
Barnyard grass:	3. 5—4 leaf-stage

The herbicidal effects were excellent without any phytotoxicity to soybean.

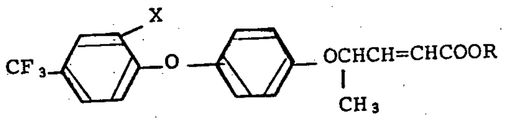
The herbicidal effect tests of the compounds no. 1, 2, 3 and 6 were carried out on an up-land in which Torpedo grass and paspalum grass and other gramineous weeds such as paspalum conjugatum Berg, crab grass and barnyard grass were naturally grown, on 21 days after sowing cotton seeds by spraying each solution of each active ingredient at a ratio of 500 liter/ha. The leaf stages of weeds and cotton were as follows.

Cotton:	2 leaf-stage
Torpedo grass:	3. 5—4 leaf-stage
Paspalum grass:	3—4 leaf-stage
Barnyard grass:	3. 5—4 leaf-stage

The herbicidal effects were excellent without any phytotoxicity to cotton.

WHAT WE CLAIM IS:—

1. A trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



(I)

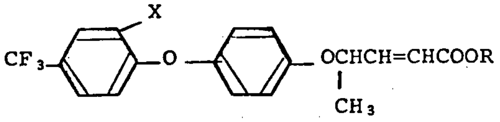
wherein X represents hydrogen or halogen atom, and R represents an alkyl, haloalkyl, alkenyl, haloalkenyl or alkynyl group.

2. A trifluoromethylphenoxy phenoxy crotonic acid derivative according to Claim 1 wherein X represents a hydrogen atom.

3. A trifluoromethylphenoxy phenoxy crotonic acid derivative according to Claim 2 wherein R represents an alkyl group having 1 to 4 carbon atoms.

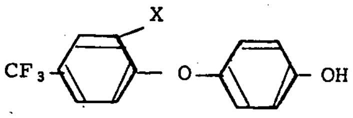
4. A trifluoromethylphenoxy phenoxy crotonic acid derivative according to Claim 3 wherein R represents an ethyl group.

5. A process for producing a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



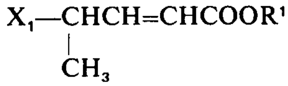
(I)

wherein X and R are as defined in claim 1, which comprises reacting a trifluoromethylphenoxy phenol derivative having the formula



(II)

wherein X is as defined in claim 1
with a γ-halogenocrotonic acid derivative having the formula

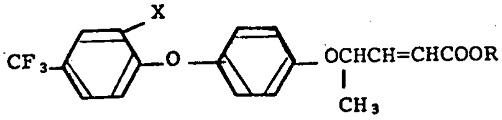


$$X_1\text{—}\underset{\displaystyle CH_3}{\underset{|}{C}}HCH{=}CHCOOR^1 \qquad \text{(III)}$$

(III)

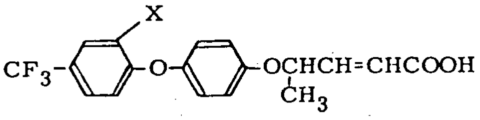
wherein X_1 is a halogen atom and R^1 is a hydrogen atom or agroup R as defined in claim 1, in the presence of a base at 0 to 150°C for 1 to 20 hours, and converting an acid form to the corresponding ester form when R is a hydrogen atom.

6. A process for producing a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



(I)

wherein X and R are as defined in claim 1, which comprises reacting a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



(VI)

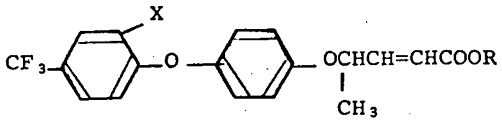
wherein X is as defined in claim 1, with an alcohol having the formula

ROH (V)

wherein R is as defined above, in the presence of a dehydrating agent at 20 to 150°C or under reflux for 1 to 20 hours.

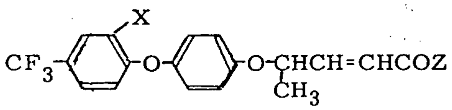
7. A process according to claim 6 wherein the dehydrating agent is selected from sulphuric acid hydrochloric acid, aromatic sulfonic acid, anhydrous sulfates, phosphorus oxychloride, phosphoric acid anhydride, boron trifluoride and acidic ion exchangers.

8. A process for producing a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



(I)

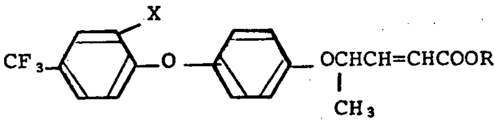
wherein X and R are as defined in claim 1, which comprises reacting a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



(VIII)

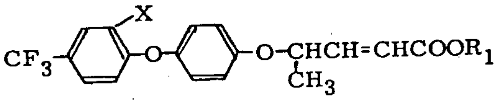
wherein Z represents a halogen atom and X is as defined above with an alcohol having the formula ROH wherein R is as defined above, in the presence of a base as a dehydrohalogenatom agent, at −10 to 150°C for 1 to 20 hours.

9. A process for producing a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



(I)

wherein X and R are as defined in claim 1 which comprises reacting a trifluoromethylphenoxy phenoxy crotonic acid derivative having the formula



I'

wherein R_1 is different from R in formula (I) and represents an alkyl, haloalkyl, alkenyl, haloalkenyl or alkynyl group, with an alcohol having the formula R_2OH wherein R_2 is different from R_1 and represents an alkyl, haloalkyl, alkenyl, haloalkenyl or alkynyl group, at 0 to 150°C for from 1 to 20 hours.

10. Any one of the compounds numbered 1 to 10 herein.

11. A process according to claim 5 substantially as herein described with reference to Preparations 1 to 3.

12. A process according to claim 6 substantially as herein described with reference to Preparations 4 to 8.

13. A trifluoromethylphenoxy phenoxy crotonic acid derivative made by a process according to any one of claims 5 to 9, claim 11 or claim 12.

14. A herbicidal composition which comprises a trifluoromethylphenoxy phenoxy crotonic acid derivative according to any one of claims 1 to 4, claim 10 or claim 13 and an adjuvant.

15. A herbicidal composition according to claim 14 substantially as herein described with reference to any one of compositions 1 to 4 or Experiments 1 to 4.

16. A process for destroying weeds comprises treating soil or foliage with a herbicidal composition according to claim 14 or claim 15.

17. A process according to claim 16 in which the herbicidal composition is applied at an effective rate of the active ingredient of 0.01 to 10 Kg per ha. in a soil treatment.

18. A process according to claim 16 in which the herbicidal composition is applied in solution at an effective rate of the active ingredient of 10 to 10,000 ppm in a foliage treatment.

19. A process according to claim 16 substantially as herein described with reference to any one of Experiments 1 to 4.

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