(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 000 483**
A1

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 78100291.0

(22) Date of filing: 30.06.78

(51) Int.Cl.^{2}: **C 07 D 213/64**, C 07 D 213/70,
A 01 N 9/22, //C07D213/61

(30) Priority: **22.07.77 US 817943**

(43) Date of publication of application:
07.02.79 Bulletin 79/3

(84) Designated contracting states:
BE DE FR GB NL SE

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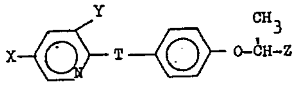
(54) Trifluoromethyl pyridinyl(oxy/thio)phenoxy propanoic acids and propanols and derivatives thereof and methods of herbicidal use.

(57) A trifluoromethylpyridyl (oxy/thio) phenoxypropionic compound corresponding to the formula



wherein T is oxygen or sulfur;
X is C1, Br, or CF_3;
Y is H, C1, Br, or CF_3, provided at least one of X and Y is CF_3;

Z is –C–OR, –CNR$_1$R$_2$, –C–O$^\ominus$M$^\oplus$, –CN, –CH$_2$OR$_3$, –CH$_2$OCR$_4$, or –CSR$_5$;
M is $^\oplus$NHR$_1$R$_1$R$_1$, Na, K, Mg, or Ca;
R is H, C1-8 alkyl, benzyl, chlorobenzyl, or C3-6 alkoxyalkyl;
R$_1$ is H, C1-4 alkyl, or C2-3 hydoxyalkyl;
R$_2$ is R$_1$ or –OCH$_3$;
R$_3$ is H or C1-4 alkyl;
R$_4$ is C1-7 alkyl; and
R$_5$ is C1-4 alkyl.

Preparation starting from a trichloromethyl substituted pyridine.

The compounds are useful as herbicides, particularly for control of grassy weeds.

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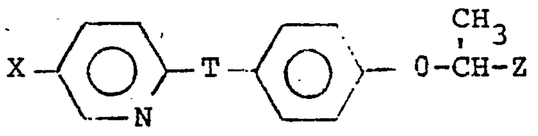
TRIFLUOROMETHYL PYRIDINYL(OXY/THIO)PHENOXY PROPANOIC ACIDS AND PROPANOLS AND DERIVATIVES THEREOF AND METHODS OF HERBICIDAL USE

The invention relates (a) to novel pyridyloxy(thio)-phenoxy propanoic acids, salts and esters thereof and pyridyl(oxy/thio)phenoxy propanols and esters and ethers thereof, and propionitriles, (b) to herbicidal compositions of such compounds and (c) to methods of using such compounds for the control of undesired plant growth. The compounds are particularly useful for control of grassy weeds.

The present invention provides a trifluoromethyl-pyridyl(oxythio)phenoxypropionic compound corresponding to the formula



wherein T is oxygen or sulfur;

X is Cl, Br, or CF_3;

Y is H, Cl, Br, or CF_3, provided at least one of X and Y is CF_3;

Z is $-\overset{O}{\overset{\|}{C}}-OR$, $-\overset{O}{\overset{\|}{C}}NR_1R_2$, $-\overset{O}{\overset{\|}{C}}-O^{\ominus}M^{\oplus}$, $-CN$, $-CH_2OR_3$, $-CH_2O\overset{O}{\overset{\|}{C}}R_4$, or $-\overset{O}{\overset{\|}{C}}SR_5$;

M is $^{\oplus}NHR_1R_1R_1$, Na, K, Mg, or Ca;
R is H, C_{1-8} alkyl, benzyl, chlorobenzyl, or
C_{3-6} alkoxyalkyl;
R_1 is H, C_{1-4} alkyl, or C_{2-3} hydroxyalkyl;
R_2 is R_1 or $-OCH_3$;
R_3 is H or C_{1-4} alkyl;
R_4 is C_{1-7} alkyl; and
R_5 is C_{1-4} alkyl.

The compounds of the above formula, hereinafter referred to for convenience as "active ingredients", have been found to be especially active as herbicides for the control of undesired vegetation, for example, grassy or graminaceous weeds. Accordingly, the present invention also encompasses compositions containing one or more active ingredients as well as preemergent and postemergent methods of controlling undesired plant growth, especially in the presence of valuable crops. Such methods comprise applying a herbicidally-effective amount of one or more active ingredients to the locus of the undesired plants, that is, the seeds, foliage, rhizomes, stems and roots or other parts of the growing plants or soil in which the plants are growing or may be found.

The compounds of the present invention are generally oils or crystalline solids at ambient temperatures which are soluble in many organic solvents commonly employed as herbicidal carriers. The active ingredients of the above formula wherein T is oxygen, X is CF_3, Y is Cl or H, and Z is $-\overset{O}{\overset{\|}{C}}-OR$ wherein R is C_1-C_8 alkyl constitute preferred embodiments of the present invention. The active ingredients of the above formula wherein T is oxygen, X is CF_3, Y is Cl, Br, CF_3 or hydrogen, Z is $-\overset{O}{\overset{\|}{C}}NR_1R_2$ constitute additional preferred embodiments. Yet additional preferred embodiments are the present compounds wherein T is sulfur, X is CF_3, Y is Cl, and Z is $-\overset{O}{\overset{\|}{C}}-OR$ wherein R is H or C_1-C_8 alkyl.

The compounds of the present invention wherein T is oxygen can be readily prepared by the reaction of 2-(4-hydroxyphenoxy)propanoic acid or an ester thereof with a substituted pyridine having the requisite substitution in the 3- and/or 5-ring positions in addition to 2-halo substitution. The pyridine compound used as starting material can be prepared from a 2-halopyridine compound, generally the 2-chloro substituted compound, having trichloromethyl substitution in either or both of the 3- and 5-ring positions in addition to any desired chloro or bromo substitution at the 3- or 5-positions, if not occupied by a CCl_3 group, by reacting the pyridine compound with a fluorinating material such as antimoney trifluoride whereupon the trichloromethyl group or groups are converted to trifluoromethyl groups.

The compounds of the present invention wherein T is sulfur similarly can be prepared by the reaction of 2-(4-mercaptophenoxy)propanoic acid or an ester thereof with an appropriate substituted pyridine in substantially the same manner as described above.

The reaction between such a substituted pyridine and the said hydroxy- or mercapto-phenoxy propanoic acid can be readily carried out in a polar solvent such as dimethyl sulfoxide to which has been added a small amount of aqueous or powdered sodium hydroxide. Reaction is usually carried out at a temperature in the range of about 70 to about 125°C over a period of about 1 to 3 hours under ambient atmospheric pressure. The reaction mixture is then allowed to cool and is poured into a quantity of cold water and acidified with hydrochloric acid, whereupon the product precipitates and is separated and purified as may be required.

The propanoate esters of the present invention may be prepared in substantially the same manner as set forth above for the propanoic acids, using the requisite ester of 2-(4-hydroxyphenoxy)propanoic acid or 2-(4-mercaptophenoxy)-propanoic acid to react with the appropriately substituted 2-halopyridine. Or, if desired, the appropriate propanoic acid of the invention is esterified by first converting to the acid chloride with thionyl chloride and then reacting the acid chloride with the appropriate alcohol, or, mercaptan, such as ethyl mercaptan, propyl mercaptan, or butyl mercaptan, according to generally accepted procedures or the classic method of reacting an alcohol and an acid in the presence of a little sulfuric acid may be followed.

The propanoic acid compounds of the invention after conversion to the acid chloride may also be reacted with (a) ammonia to form the simple amide, (b) with an alkyl amine to form an N-alkyl amide or N,N-dialkyl amide, or (c) with a methoxy amine to form the methoxy amide.

The simple amide serves as preferred starting material for the manufacture of the nitriles, which are obtained upon reaction of the amide with phosphorous oxychloride.

The propanoate metal salts are prepared from the propanoic acid form of the compound by simply reacting the carboxylic acid with the requisite inorganic base, such as NaOH, KOH, $Ca(OH)_2$ or $Mg(OH)_2$. The amine salts are prepared by reacting the propanoic acid compound with the requisite amine, for example, triethanolamine or trimethylamine.

The compounds which are substituted propanols are prepared preferably from one of the above-described esters of the propanoic acid form of the compound, such as the methyl ester, by reaction of the ester with sodium borohydride in a polar solvent medium such as methanol, reaction being carried out initially at a temperature below about 30°C during an initial period of 1 to 2 hours after which the temperature is brought to about 50 to 60°C and the solvent then stripped off. The reaction product is then admixed with water and extracted with a water-immiscible organic solvent. Removal of the solvent leaves an oily product.

Esterification of such alcohol is carried out according to methods generally known in the art in which, e.g., an acid chloride is reacted with the alcohol in solvent medium in the presence of a hydrogen chloride acceptor, such as triethylamine. The hydrochloride salt is filtered off and the solvent stripped, leaving an oily product.

Ethers of the alcohols of the invention are prepared by reacting the alcohol with, e.g., sodium hydride in a polar solvent such as dimethyl formamide at a temperature of about 35 to 60°C, after which an alkyl bromide is added to the reaction mixture and heated to 75 to 100°C for one to two hours. The solvent medium is then stripped off under reduced pressure and the crude product is poured into cold water and final product taken up with water immiscible solvent such as heptane. The solvent, on being stripped off, leaves an oily product.

In an alternate process for making the present propanoic acid compounds, a salt, e.g., the sodium salt, of 4-methoxyphenol, or of 4-mercaptophenol, is dissolved in a solvent such as dimethyl sulfoxide and the requisite trifluoromethyl-substituted 2-chloropyridine is added to the solution of the methoxy phenol and reacted in the presence of aqueous sodium hydroxide at a temperature in the range of about 70 to 130°C and over a time interval of about 30 to 45 minutes. The reaction mixture is then cooled and poured over ice. The solid product is filtered off, washed with water, taken up in a solvent mixture and reprecipitated therefrom. The methoxy group, if present, is then cleaved off the phenyl ring by refluxing the compound in 48% by weight HBr for about an hour and after purification, precipitated from acidic solution and recovered, as by filtration, and dried. The 4-(trifluoromethyl-substituted 2-pyridyloxy)phenol, or 4-(trifluoromethyl-substituted 2-pyridylthio)phenol, is then dissolved in a solvent such as dimethyl sulfoxide, anhydrous powdered sodium hydroxide is added thereto and reacted therewith for a few minutes at about 75 to 85°C. Then an ester, such as the ethyl ester of 2-bromopropanoic acid is added to the reaction mixture and stirred for a time, such as about half an hour, at approximately 100°C or up to about 2 hours in the case of the sulfur bridged compound. The reaction mixture is then allowed to cool and poured over ice or simply into cold water whereupon an oily layer separates which can be recovered by taking up in a water-immiscible solvent and subsequently stripping the solvent off leaving an oily product. The product so obtained will be the alkyl ester of the propanoic acid compound. In carrying out the several reactions of this alternate process, the reactants are usually mixed with a carrier medium, such as, for example, methyl ethyl ketone, methyl isobutyl ketone or an aprotic polar solvent such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, N-methylpyrrolidone, hexamethylphosphoramide, or sulfolane. The first step condensation is generally carried out at a temperature of at least 50°C, preferably about 70 to about 150°C and during a reaction period of about 1 to about 20 hours, preferably about 1 to about 10 hours. The second condensation reaction is carried out under similar reaction conditions except that the reaction is usually accomplished in a shorter period of [illegible] about 0.5 to 10 hours, typically using one of the [illegible] solvents such as dimethylsulfoxide as reaction [illegible] dealkylation step, where employed, is carried out using a suitable dealkylation agent, a hydro acid such as [illegible] bromic acid or hydriodic acid employed as a concentrated aqueous solution of about 40 to about 60 percent [illegible] concentration. Reaction is carried out at reflux temperature which usually falls in the range of about 75 to about [illegible] but preferably is about 100°C to 140°C. The [illegible] reaction is generally completed in about 1 to about [illegible]

The active ingredients of the above formula [illegible] Z is $-CH_2OOCR$ are readily prepared from the requisite [illegible] panoic acid compound, prepared as described above [illegible] by esterification with a primary alcohol [illegible] available, such as methanol, and in the presence [illegible] amount of sulfuric acid, after which the ester [illegible] the alcohol by reaction with sodium borohydride [illegible] medium and at close to ambient room temperature. [illegible] removal of excess primary alcohol the product [illegible] from the reaction mixture with a water-immiscible [illegible] solvent mixture such as methylene chloride-hepta[illegible] the solvent is stripped off and removed under [illegible] pressure leaving the product which is usually [illegible]

The so-produced substituted propano[illegible] if desired, by reacting it with the acid [illegible] esterifying acid in solvent medium, such as [illegible] taining an HCl acceptor such as triethyl[illegible] proceeds steadily over about [illegible] temperature in the range of [illegible] precipitated trialkylamine [illegible] the solvent medium stripped off. [illegible] is preferably washed with water and then [illegible] heptane, dried, and the heptane distilled off leaving an oily product.

The substituted propionitriles of the invention are prepared using the propanoic acid compound as the starting material. The carboxylic acid is reacted with thionyl chloride to form the acid chloride which is in turn reacted with NH_4OH to produce the amide. The amide is reacted with $POCl_3$ to form the nitrile.

The following examples illustrate the present invention.

<u>Preparation of Intermediate</u>

2-Chloro-5-(trichloromethyl)pyridine (23.0 grams; 0.1 mole) was mixed with antimony trifluoride (22.3 g; 0.125 mole) and then chlorine gas (9.0 g; 0.126 mole) was passed into the stirred mixture over a period of 8 minutes during which time the temperature rose from ambient to 100°C. The reaction mixture was stirred for an additional 20 minutes before adding 25 milliliters of concentrated HCl plus 27 milliliters of water and steam distilling off any unreacted starting material and volatile chlorides and fluorides. Thereafter, pentane was added to the reaction vessel to take up the solid product which was subsequently recovered by distilling off the solvent.

The crystalline product obtained had a melting temperature of 30-1°C and upon analysis was found to contain 39.5[illegible] carbon; 1.78% hydrogen; 7.72% nitrogen; and 19.42% [illegible] theoretical composition for 2-chloro-5-[illegible]yl)pyridine is 39.69% carbon; 1.66% hydrogen; [illegible]; and 19.53% chlorine.

The following substituted pyridines are prepared in [illegible]

Ring Substituents On Pyridine

2	3	5	Physical Property
Cl	CF_3	CF_3	B.P. 94-96°C @ 109 mm Hg
Cl	Cl	CF_3	B.P. 50-51°C @ 21 mm Hg
Cl	CF_3	Cl	$n_D^{25°}$ = 1.4825

Example 1

2-(4-Hydroxyphenoxy)propanoic acid (2.35 g; 0.0129 mole) was dissolved in dimethylsulfoxide (16 ml) and then a solution of sodium hydroxide (1.06 g; 0.026 mole) in 3.5 ml of water was added. This mixture was stirred and heated to about 60°C over a 20-minute period in order to insure formation of the disodium salt. Next, a solution of 2-chloro-3,5-bis(trifluoromethyl)pyridine (2.73 g; 0.0129 mole) in [illegible] ml of dimethylsulfoxide was added over a 3-minute period and the mixture then warmed to 110°C in 35 minutes. The mixture was then heated at 105-110°C for an additional 45 minutes, allowed to cool for 30 minutes, and then poured into cold water. The resulting crude, gummy product was taken up in hot toluene, treated with activated charcoal, and filtered. The toluene was then flashed off and the product was mixed with cold pentane resulting in the separation of a crystalline product having a melting temperature of 80.5-83°C. The product was found on analysis to contain 48.87% carbon; 3.14% hydrogen; and 3.59% nitrogen. The theoretical composition for 2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)phenoxy]propanoic acid is 48.62% carbon; 2.80% hydrogen; [illegible] 3.54% nitrogen.

In a manner similar to the foregoing [illegible] using the requisite starting materials, the following compounds of the invention were prepared:

Ring Substituents On Pyridine		Melting Temperature, °C	Elemental Analysis, % By Weight*			
3	5		C	H	N	Cl
Cl	CF_3	105.5-107	49.73 (49.81)	3.25 (3.06)	3.78 (3.87)	9.66 (9.80)
--	CF_3	97 -100	54.91 (55.05)	3.77 (3.70)	4.27 (4.28)	--
CF_3	Cl	115 -118	49.79 (49.81)	3.21 (3.06)	3.99 (3.87)	9.77 (9.80)

*Theoretical composition shown in parenthesis

Example 2

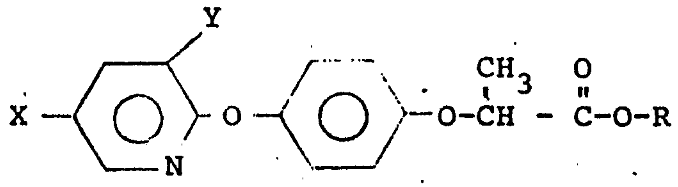
2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)phenoxy]-propanoic acid (16.0 g; 0.0405 mole) was refluxed with [illegible] ml of thionyl chloride for 26 minutes and then the unreacted thionyl chloride was distilled off. The resulting acid chloride was put into 40 ml of methanol. Triethylamine (5.2 g; 0.0514 mole) was put into 75 ml of methanol. The acid chloride solution was then added and the reaction mixture was refluxed for 30 minutes. The methanol was removed by distillation and the crude product was washed with water and taken up in heptane. The heptane was removed and 15 grams of amber oil was obtained which had a refractive index of 1.4832 at 25°C.

The product had the following elemental analysis:

	C	H	N
Calculated	49.88	3.20	3.42
Found	49.97	3.20	3.52

These results confirm the obtention of methyl 2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)phenoxy]propanoate.

Other compounds of the present invention were similarly prepared by employing procedures analogous to those set forth in the above example. Such other active ingredients include the following compounds:



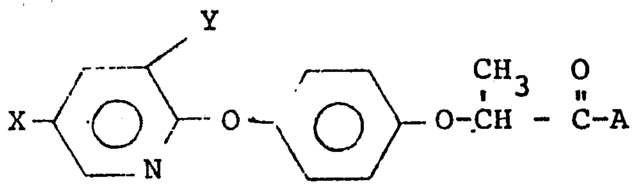
X	Y	R	Refractive Index @ 25°C	Elemental Analysis, % By Weight*			
				C	H	N	Cl
CF_3	CF_3	$-(CH_2)_7CH_3$	1.4743	55.65 (56.80)	5.02 (5.36)	2.96 (2.76)	--
Cl	CF_3	$-(CH_2)_3CH_3$	1.5076	54.49 (54.62)	4.69 (4.58)	3.41 (3.35)	8.60 (8.49)
CF_3	Cl	$-(CH_2)_3CH_3$	1.5080	54.61 (54.62)	4.65 (4.58)	3.34 (3.35)	8.47 (8.49)
CF_3	H		1.5432	49.94 (51.07)	2.76 (2.68)	7.25 (7.44)	
CF_3	Cl	$-(CH_2)_2OC_4H_9$-n	1.5061				

*Theoretical composition shown in parenthesis

Example 3

To 5.0 g (0.0138 mole) of 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propanoic acid was added 30 ml of $SOCl_2$ and the mixture heated at reflux for about 20 minutes, after which unreacted $SOCl_2$ was removed on a still under water aspirator vacuum. The resulting syrup was added to a stirred solution of 30 ml (0.028 mole) of concentrated aqueous NH_4OH in 40 ml of acetonitrile. The mixture was stirred at a temperature of 25°C for 15 minutes and filtered, thus recovering crystals of solid product which had formed. The recovered crystals had a melting temperature of 140-42°C. On elemental analysis, the crystals were found to contain 49.50% carbon; 3.44% hydrogen; 10.01% chlorine; and 7.76% nitrogen. Theoretical composition for 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionamide is 49.94% carbon; 3.35% hydrogen; 9.83% chlorine; and 7.76% nitrogen.

Other propionamides of the invention prepared using procedures similar to the foregoing are as follows.



X	Y	A	Melting Temperature °C	Elemental Analysis, % By Weight* C	H	N	Cl
Cl	CF_3	$-NH_2$	151 -152	48.56 (49.94)	3.37 (3.35)	7.57 (7.77)	9.57 (9.83)
CF_3	Cl	$-NHCH_3$	146 -147	51.14 (51.78)	3.73 (3.76)	7.37 (7.47)	9.63 (9.46)
CF_3	CF_3	$-N\ n-C_4H_9)_2$	$(n_D^{25°} = 1.4844)$	56.30 (56.91)	5.48 (5.57)	5.06 (5.33)	--
CF_3	--	$-N(CH_3)_2$	$(n_D^{25°} = 1.5247)$	57.99 (57.6)	5.04 (4.84)	7.74 (7.9)	--
CF_3	--	$-NH_2$	69 - 70	55.3 (55.22)	4.09 (4.02)	8.62 (8.58)	--
CF_3	CF_3	$-NH_2$	150.5-152	48.78 (48.75)	3.17 (3.05)	6.96 (7.1)	--
CF_3	Cl	$-NHCH_3$	146 -147	51.19 (51.28)	3.73 (3.76)	7.37 (7.47)	9.63 (9.46)
CF_3	Cl	$-NH(OCH_3)$	135 -136	--	--	--	--
CF_3	Cl	$-NHCH_2CH_2OH$	$(n_D^{25°} = 1.5434)$	50.71 (50.44)	3.81 (3.98)	6.41 (6.92)	8.96 (8.76)

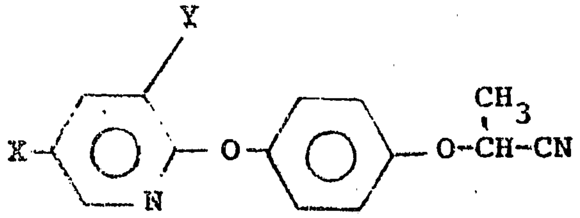
*Theoretical composition shown in parenthesis

Example 4

2-[4-(5-Chloro-3-trifluoromethyl-2-pyridyloxy)-phenoxy]propionamide (4.5 g; 0.01248 mole) was refluxed with 20 ml of phosphorous oxychloride for 1.75 hours. The $POCl_3$ was distilled off, and the remaining reaction mixture was poured over ice and extracted with heptane. On cooling, a crystalline product was obtained having a melting range of 61.5-62.5°C. The anticipated product was 2-[4-(5-chloro-3--trifluoromethyl-2-pyridyloxy)phenoxy]propionitrile. The following elemental analysis was obtained:

	C	H	N	Cl
Calculated	52.57%	2.94%	8.18%	10.35%
Found	52.48%	3.01%	8.17%	10.14%

Other active nitrile compounds similarly prepared include the following.



X	Y	Melting Temperature °C	Elemental Analysis, % By Weight* C	H	N	Cl
CF_3	Cl	49-52	52.71 (52.57)	3.07 (2.94)	10.47 (10.35)	7.47 (8.17)
CF_3	H	38-40	58.16 (58.44)	3.79 (3.57)	8.81 (9.08)	--
CF_3	CF_3	54-55	49.94 (51.07)	2.76 (2.68)	7.25 (7.44)	

*Theoretical composition shown in parenthesis

Example 5

In each of a series of metal salt preparations 60 milligrams of one of the propanoic acids of the invention was stirred into several milliliters of water and an aqueous solution of base added thereto in the amount needed for neutralization plus a slight excess estimated to be 10% excess upon obtaining a color change to yellow-green in universal indicator. The propanoic acids, the molar amounts employed, the bases employed and the estimated amounts of such bases are tabulated as follows, the propanoic acid being identified by ring substitution on the pyridyl ring:

Ring Substituents 5	3	Propanoic Acid, moles	Base	mg of Base (estimated)
CF_3	-	0.183	NaOH	7.34
CF_3	Cl	0.165	KOH	9.25
CF_3	CF_3	0.152	$*NH_4OH$	5.32

*The NH_4OH was employed in the form of concentrated ammonium hydroxide.

The aqueous solutions so obtained are conveniently used in herbicidal applications with or without further dilution. The salts may be recovered by evaporation of the water from the solutions and purified by careful recrystallization, if desired.

Magnesium and calcium salts are prepared in substantially the manner described above.

Example 6

In each of a series of amine salt preparations, mg of one of the propanoic acids of the invention was stirred into several ml of water and a solution of alkyl amine or alkanolamine added thereto in the amount needed for neutralization plus an estimated 10 percent excess of base being to be reached upon titrating to the yellow-green color of universal indicator. The propanoic acids, identified by ring substituents, the molar amount of propanoic acid, the base employed and the estimated amounts of each base, are as follows:

Ring Substituents 5	 3	Propanoic Acid, moles	 Base	mg of Base (estimated)
CF_3	-	0.183	$NH_2C_2H_5OH$	11.19
CF_3	Cl	0.165	$(C_2H_5)_3N$	16.68
Cl	CF_3	0.165	$C_2H_5NH_2$	7.43

The aqueous solutions so obtained are conveniently used in herbicidal applications with or without further dilution. The salts may be recovered by evaporation of water from the solutions and purified by recrystallization, if desired.

Other amine salts, such as the triethanolamine, diethanolamine, tripropylamine, or the butylamine salt, are prepared in substantially the manner described above.

Example 7

Sodium borohydride (6.35 g; 0.1716 mole) was dissolved in 25 ml of water and added over a ten minute period to a solution of methyl 2-[4-(3,5-bis(trifluoromethyl)-2--pyridyloxy)phenoxy]propionate (11.7 g; 0.02859 mole) dissolved in 155 ml of warm methanol. During the addition, the temperature was kept between 25 and 30°C. The mixture was stirred at room temperature for 40 minutes and was then allowed to warm to 42°C over a 25 minute period. The methanol [illegible] removed by distillation, and cold water was added [illegible] which was then extracted [illegible]. The solvents were distilled off, leaving an orange colored oil with an index of refraction of 1.5028 at 25°C. The anticipated product was 2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)phenoxy]propanol. The product had the following elemental analysis:

	C	H	N
Calculated	50.40%	3.44%	3.67%
Found	51.01	3.64	3.86

2-[4-(3-Chloro-5-trifluoromethyl-2-pyridyloxy)-phenoxy]propanol, n_D^{25} 1.5377, was prepared by similar procedure. Elemental analysis:

	C	H	N	Cl
Calculated	51.81	3.77	4.03	10.2
Found	51.75	3.91	4.04	10.32

Example 8

2-[4-(3,5-Bis(trifluoromethyl)-2-pyridyloxy)phenoxy]-propanol (5.45 g; 0.0171 mole) was dissolved in 75 ml of toluene and placed in a round bottom flask, and 1.8 g of triethylamine was added thereto. Then octoyl chloride (3.05 g; 0.01875 mole) as a solution in 18 ml of toluene was added to the propanol over a 3-minute period at a temperature of 25-30°C. The mixture was stirred for about an hour at ambient room temperature and then refluxed for about one hour. At the end of the reaction period, the separated hydrochloride salt was filtered off, and the toluene was stripped off. The residue was poured into ice water and extracted with heptane. The heptane extracts were dried, and the heptane was removed by distillation, leaving an oil with a refractive index of 1.4740 at 25°C. The anticipated product was 2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)phenoxy]propyl octanoate. The product had the following elemental analysis:

	C	H	N
Calculated	56.80	5.36	2.76
Found	58.0	5.88	2.79

2-[4-(3-Chloro-5-trifluoromethyl-2-pyridyloxy)-phenoxy]propyl acetate, n_D^{25} 1.5230, was prepared by similar procedure. Elemental analysis:

	C	H	N	Cl
Calculated	52.38	3.88	3.59	9.10
Found	52.26	3.99	3.69	9.38

Example 9

Sodium hydride (0.8 g; 0.0334 mole) is dissolved in 30 ml of dry dimethyl formamide, and then a solution of 2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)phenoxy]propanol (5.5 g; 0.0176 mole) in 50 ml of dry dimethylformamide is added to the sodium hydride solution over a four-minute period and then stirred for an hour at 40-50°C. A solution of 1-bromobutane (2.4 g; 0.0175 mole) in 25 ml of dry dimethy formamide is then added over a six-minute period. The reaction mixture is then slowly heated to 90°C over a 30-minute period and held at 90°C for one hour and ten minutes. The reaction mixture is then stirred and heated at 105-115°C for 2 hours. The dimethylformamide is then strippe off under partial vacuum and the crude product poured into cold water and extracted with heptane. The heptane is remove by distillation, leaving an oil, 2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)phenoxy]propyl n-butyl ether.

Example 10

The following series of preparations illustrate an alternate method of synthesizing the propanoate esters and from such compounds the propanoic acids of the invention. A solution of the sodium salt of 4-methoxyphenol was prepared by dissolving the methoxyphenol (7.45 g; 0.06 mole) in 45 ml of dimethylsulfoxide and adding a solution of sodium hydroxide (2.4 g; 0.06 mole) in 7 ml of water. A solution of 2-chloro-5-(trifluoromethyl)pyridine (9.0 g; 0.05 mole) i 40 ml of dimethylsulfoxide was then added to the above sodiu phenate solution over an 11 minute period. During the addition, the temperature rose to about 80°C, and then the reaction mixture was heated to 124°C over 26 minutes and the temperature maintained for 15 minutes. At the end of this time, the reaction mixture was cooled to 75°C and poured over ice. The solid product was collected on a filter, washed, and taken up in a toluene-hexane mixture. This solution on cooling yielded 9.7 grams of solid product having a melting temperature of 49.5-50.5°C and having a composition of 58.02% carbon; 3.86% hydrogen; and 5.22% nitrogen. The theoretical composition is 57.99% carbon; 3.74% hydrogen; and 5.20% nitrogen, confirming the product to be 5-(trifluoromethyl)-2-(4-methoxyphenoxy)pyridine.

The 5-(trifluoromethyl)-2-(4-methoxyphenoxy)pyridine (10.95 g; 0.0407 mole) was refluxed with 50 ml of 48 percent by weight aqueous hydrobromic acid solution for one hour. At the end of this time, the reaction mixture was cooled, poured over ice and the separated solids collected on a filter. The product was purified by taking it up in dilute caustic solution, extracting the solution with chloroform to remove unreacted starting material and then acidifying the solution to precipitate free phenol. The dried crystalline phenol product had a melting temperature of 89-91°C and was found to contain 56.21% carbon; 3.27% hydrogen; and 5.44% nitrogen. The theoretical composition of 4-(5-trifluoromethyl-2-pyridyloxy)phenol is 56.48% carbon; 3.16% hydrogen; and 5.49% nitrogen.

The 4-(5-trifluoromethyl-2-pyridyloxy)phenol (4.95 g; 0.0194 mole) was dissolved in dimethylsulfoxide (41 ml); then sodium hydroxide (0.78 g; 0.014 mole) was added as a dry powder and the mixture stirred for about 10 minutes and warmed to about 80°C. Ethyl 2-bromopropionate (4.2 g; 0.023 mole) was then added and the mixture stirred for about 35 minutes at 96°C. The solution was then cooled, poured over ice and the oil, which separated, taken up in petroleum ether containing 20 percent by volume methylene chloride. The separated solvent phase was stripped of solvent leaving an oily product weighing 6.3 g. An infrared scan of a sample of the oil confirmed the ester structure of the anticipated ethyl 2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate.

Ethyl 2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]-propionate (6.3 g; 0.0177 mole) was dissolved in 28 ml of ethanol, and a solution of sodium hydroxide (1.06 g; 0.0266 mole) in 28 ml of water was added. The reaction mixture was heated to 75°C for 5 minutes and then poured into 150 ml of cold water and acidified with 4 g of concentrated hydrochloric acid. The crude acid product, which precipitated, was washed with hot petroleum ether and dried. The resulting product had a melting temperature of 97-100°C and was found on analysis to contain 54.91% carbon; 3.77% hydrogen; and 4.28% nitrogen. The theoretical composition for 2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionic acid is 55.05% carbon; 3.70% hydrogen; and 4.28% nitrogen, indicating the expected product was obtained.

Example 11

4-Mercaptophenol (7.6 gm., 0.06 mole) was dissolved in 70 ml of dimethyl sulfoxide, and a solution of sodium hydroxide (2.4 gm., 0.6 mole) in 3.0 ml of water was added. The mixture was warmed to 50° and stirred under nitrogen for 10 minutes to form the sodium thiophenate salt. A solution of 2-chloro-5-(trifluoromethyl)pyridine (10.9 gm., 0.06 mole) in 60 ml of dimethylsulfoxide was then added all at once. The mixture was heated to 100° and held there for 1.5 hours. At the end of this time it was poured into 500 ml of cold water. An emulsion formed; therefore, 60 ml of a saturated solution of ammonium chloride was added. The product precipitated as a sticky solid. The aqueous layer was decanted, the solid washed with more water then taken up in hot heptane, dried with solid sodium sulfate and decolorized with charcoal. In the filtrate, a white solid product precipitated and was separated and found to have a melting temperature of 89-93°C.

The so-prepared 4-[5-(trifluoromethyl)-2-pyridylthio]phenol (10 gms., 0.037 mole) was dissolved in 80 ml of dimethylsulfoxide, and dry, powdered sodium hydroxide (6.7 gm., 0.37 mole) was added. The mixture was warmed to about 40° and stirred until the base was all in solution indicating that the desired sodium phenate had formed. Ethyl bromopropionate (6.7 gm., 0.37 mole) was then added all at once. The reaction was run at 100-105° for 2.0 hours, then cooled and poured into 450 ml of cold water. The ester was extracted into methylene chloride, the extract dried and solvent removed leaving the product as an oil weighing 13.5 gm.

This was used without further purification for the next step which was hydrolysis of the ester to the metal salt in aqueous alkaline medium.

The ethyl 2-[4-(5-trifluoromethyl-2-pyridylthio)-phenoxy]propionate (13.5 gm., 0.37 mole) was dissolved in 50 ml of 95% ethanol and a solution of sodium hydroxide (3.0 gm., 0.075 mole) in 25 ml of water was added. The mixture was refluxed at 80° for about 6 minutes, then cooled, poured into 400 ml of cold water, and extracted with 250 ml of methylene chloride to remove any base-insoluble impurities. The aqueous solution containing the sodium salt of the acid was acidified to pH 1 with concentrated hydrochloric acid. The product which precipitated as a gummy solid was washed with water (after decanting) and taken up in hot methylcyclohexane. On cooling, the product precipitated as white crystals having a melting temperature of 118-120°C and a composition of, by weight, 52.38% carbon; 3.66% hydrogen; 4.00% nitrogen and 9.07% sulfur. The theoretical composition of 2-[4-(5-trifluoromethyl-2-pyridylthio)phenoxy]propanoic acid is 52.5% carbon; 3.5% hydrogen; 4.08% nitrogen and 9.34% sulfur.

Example 12

4-Mercaptophenol (6.4 gm., 0.051 mole) was dissolved in 70 ml of dimethylsulfoxide and a solution of sodium hydroxide (2.04 gm., 0.051 mole) in 3.0 ml of water was added. The mixture was warmed to about 50° and stirred under nitrogen for 10 minutes to form the sodium thiophenate salt. A solution of 2,3-dichloro-5-(trifluoromethyl)pyridine (11.0 gm., 0.051 mole) in 60 ml of dimethylsulfoxide was next added at once. The mixture was then heated at 95-100° for 2.5 hours, then poured into 500 ml of cold water and allowed to stand for 45 minutes. The solid was then collected on a filter, washed and taken up in about one liter of boiling hexane. The product precipitated on cooling as a white solid melting at 94-96°C.

The so-prepared 4-[3-chloro-5-trifluoromethyl-2-pyridylthio]phenol (11.0 gm., 0.036 mole) was dissolved in 80 ml of dimethylsulfoxide and dry powdered sodium hydroxide (1.44 gm., 0.036 mole) was added. The mixture was warmed and stirred until the base was all in solution, showing that the desired sodium phenate had formed. Ethyl bromopropionate (6.5 gm., 0.036 mole) was then added all at once. The reaction was run at 100° for 2.0 hours, then cooled and poured into 500 ml of water. Most of the product precipitated as a white semi-solid. The aqueous layer, which was decanted off was extracted with 300 ml of methylene chloride. The extract was separated, solvent removed, and the residue added to the main product. This was washed thoroughly with water [illegible] residual dimethylsulfoxide and used without further purifi[illegible] the hydrolys

The so-prepared ethyl 2-[4-(3-chloro-5-trifluoromethyl-2-pyridylthio)phenoxy]propionate (14.6 gm., 0.[illegible] mole) was dissolved in 60 ml of 95% ethanol, and a solution of sodium hydroxide (2.9 gm., 0.072 mole) in 25 ml of water was added. The mixture was heated at reflux for about 4 minutes, then cooled and poured into 400 ml of water. The solution was acidified to pH 1 with concentrated hydrochloric acid which precipitated the product as a sticky solid. This was taken up in a boiling mixture of hexane and methyl cyclohexane. After drying, filtering, and cooling, the white crystalline product separated and was collected on a filter and exhibited a melting temperature of 132-134°C and was found to contain, by weight, 47.64% carbon; 3.14% hydrogen; 3.51% nitrogen; 9.25% chlorine and 8.44% sulfur. The theoretical composition of 2-[4-(3-chloro-5-trifluoromethyl-2-pyridylthio)phenoxy]propanoic acid is 47.69% carbon; 2.93% hydrogen; 3.70% nitrogen; 9.38% chlorine and 8.48% sulfur.

Example 13

A mixture of 90 ml of thionyl chloride and 9.0 g of 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]-propanoic acid was heated at reflux temperature for 34 minutes. The excess thionyl chloride was removed on a still, and the resulting acid chloride was dissolved in 30 ml of benzene. This was added to a reaction flask containing 2.1 g methoxyamine hydrochloride in 20 ml of benzene plus a solution of 3.8 g of potassium carbonate in 3.5 ml of water. The reaction mixture was then refluxed for 2 hours. The salt was filtered off and the volatiles removed. The crude solids were taken up in heptane and crystallized. From this, 6.75 g of the solid was obtained which had a melting point of 135-6 C and an elemental analysis of, by weight: C = 48.98%; H = [illegible] N = 7.16%; and Cl = 8.90%. The theoretical composition of 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]-N-methoxypropanamide is C = 49.18%; H = 3.61%; N = 7.17 [illegible] Cl = 9.07%.

Example 14

A mixture of 60 ml of thionyl chloride and 6.0 g of 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]-propanoic acid was refluxed for 30 minutes. The excess thionyl chloride was removed on a still using aspirator vacuum. The resulting acid chloride was dissolved in 25 ml toluene. This solution was then added to a reaction flask containing 2.1 g 2-butoxyethanol, 1.85 g triethyl amine, and 27 ml toluene and the mixture refluxed for about 2 hours. The salt was filtered off and the volatiles removed. The crude product was taken up in n-hexane, purified with activated carbon, and the hexane removed. 7.05 G of amber oil was obtained which had a refractive index of 1.5061 at 25°C and an elemental analysis of: C = 54.27%; H = 4.97%; N = 3.21%; and Cl = 7.77%. Calculated values for 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propanoic acid, 2-butoxyethyl ester are: C = 54.61%; H = 5.02%; N = 3.03%; and Cl = 7.68%.

Example 15

A mixture of 80 ml of thionyl chloride and 8.0 g of 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]-propanoic acid was refluxed for 38 minutes. The excess thionyl chloride was then removed on a still using aspirator vacuum. The resulting acid chloride was dissolved in 30 ml toluene. This solution was then added to a reaction flask containing 2.1 g of butyl mercaptan, 2.5 g of triethyl amine, and 25 ml of toluene. The mixture was slowly heated to 98°C over one hour and then refluxed for about 45-50 minutes. The salt was filtered out and the volatiles removed. The crude product was taken up in n-hexane, purified with activated carbon, and the hexane removed. The resulting 9.[illegible] g [illegible] amber oil had a refractive index of [illegible] at 25°C and [illegible] retical [illegible]

2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]thiopropanoic acid S-butyl ester is: C = 52.59%; H = 4.41%; N = 3.23%; Cl = 8.17%; and S = 7.39%.

The compounds of the present invention have been found to have advantage over prior art compounds in the control of perennial grassy weeds in that the present compounds control a broader spectrum of such weeds than the counterpart compounds while exhibiting a higher level of activity or control at like dosage rates. In addition, the present compounds are sufficiently tolerant towards most broad leafed crops to contemplate control of grassy weeds therein at substantially commercially practicable levels, particularly so with the preferred compounds.

For such uses, unmodified active ingredients of the present invention can be employed. However, the present invention embraces the use of the compounds in composition form with an inert material known in the art as an adjuvant or carrier in solid or liquid form. Thus, for example, an active ingredient can be dispersed on a finely-divided solid and employed therein as a dust. Also, the active ingredients, as liquid concentrates or solid compositions comprising one or more of the active ingredients can be dispersed in water, typically with aid of a wetting agent, and the resulting aqueous dispersion employed as a spray. In other procedures, the active ingredients can be employed as a constituent of organic liquid compositions, oil-in-water and water-in-oil emulsions or water dispersions, with or without the addition of wetting, dispersing, or emulsifying agents. Suitable adjuvants of the foregoing type are well known to those skilled in the art.

The concentration of the active ingredients in solid or liquid compositions generally is from about 0.0003 to about 95 percent by weight or more. Concentrations from about 0.05 to about 50 percent by weight are often employed. In compositions to be employed as concentrates, the active ingredient can be present in a concentration from about 5 to about 98 weight percent. The active ingredient compositions can also contain other compatible additaments, for example, phytotoxicants, plant growth regulants, pesticides and the like and can be formulated with solid particulate fertilizer carriers such as ammonium nitrate, urea and the like.

The present compounds which are substituted propanol or propyl ethers are more effective in preemergent operations than in postemergent applications.

The exact rate to be applied is dependent not only on a specific active ingredient being applied, but also on a particular action desired (e.g., general or selective control the plant species to be modified and the stage of growth thereof as well as the part of the plant to be contacted with the toxic active ingredient. Thus, all of the active ingredients of the present invention and compositions containing the same may not be equally effective at similar concentrations or against the same plant species. In non--selective preemergence and foliar treatments, the active ingredients of the invention are usually applied at an approximate rate of from about 0.5 to about 5 pounds/acre (0.56-5.6 kg./hectare), but lower or higher rates may be appropriate in some cases such as 0.01 to about 20 pounds/ac (0.011-22.4 kg./hectare). In preemergent operations for selective uses a dosage of about 0.05 to about 20 pounds/acr (0.056-22.4 kg./hectare) is generally applicable, a rate of 0.2 to 4 pounds/acre (0.224-4.48 kg./hectare) being preferre and about 0.75 to about 1 pound/acre (0.84-1.12 kg./hectare) being most preferred.

In selective postemergent operations a dosage of about 0.01 to about 20 pounds/acre (0.011-22.4 kg./hectare) is generally applicable, although not all compounds are equally effective and some weeds are more difficult to control. Thus, a dosage rate in the range of about 0.05 to about 0.75 pounds/acre (0.056-0.84 kg./hectare) is preferred in postemergent control of annual grassy weeds, while about 0.5 to about 5 pounds/acre (0.56-5.6 kg./hectare) is a preferred dosage range for the postemergent control of perennial grassy weeds.

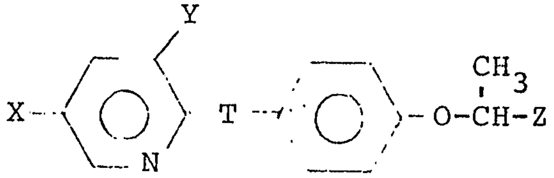
The following examples illustrate effects of the compounds of this invention. Plant species used in these tests were the following.

Common Name	Scientific Name
Barnyard grass	Echinochloa crusgalli
Bermuda grass	Cynodon dactylon
Bluegrass	Poa spp.
Cheatgrass	Bromus tectorum
Corn	Zea mays
Cotton	Gossypium spp.
Crabgrass	Digitaria spp.
Foxtail	Setaria spp.
Johnson grass	Sorghum halepense
Morning glory	Lpomoea purpuria
Pigweed	Amaranthus spp.
Rice	Zizania aquitica
Sorghum	Sorghum vulgare
Soybean	Glycine soja
Velvet leaf	Abutilon theophrasti
Wheat	Triticum
Wild oats	Avena fatua

Example 16

In representative operations, each compound to be utilized in a series of tests is dissolved in acetone to one-half of the final volume (twice the final concentration) to be used and the acetone solution in each case is admixed with an equal volume of water containing 0.1 percent by weight of surface active material. The compositions, generally in the nature of an emulsion, were employed to treat separate respective seed beds of sandy loam soil of good nutrient content wherein each seed bed contained separate groups of viable seeds, each group being of one plant specie. The various beds were positioned side by side and exposed to substantially identical conditions of temperature and light. Each bed was maintained so as to prevent any interaction with test compounds in different seed beds. Each seed bed was treated with one of the compositions as a soil drench applied uniformly throughout the surface of the bed. The compositions were applied to the seed beds so that different seed beds of a given plant specie were treated with one of each of the test compounds. Another seed bed was treated only with water to serve as a control. After treatment, the seed beds were maintained for two weeks under greenhouse conditions conducive for good plant growth and watered as necessary. The specific plant specie, test compound and dosage and the percent preemergent control obtained are set forth in the table below. Control refers to the reduction in growth compared to the observed results of the same specie.

PREEMERGENCE CONTROL OF PLANT SPECIES



Compound Tested				Dosage In Lbs Per Acre (kg./hectare)		Plant Species							
X	Y	Z	T			Corn	Rice	Wheat	Wild Oats	Fox-tail	Barn-yard Grass	Crab-grass	Johnson Grass
Cl	CF_3	-CN	0	1	(1.12)	95	70	0	40	100	95	100	100
CF_3	--	$-\overset{O}{\overset{\|}{C}}-OCH_3$	0	0.5 0.125	(0.56) (0.14)	100 100	100 80	100 100	100 100	100 95	100 98	100 100	100 100
Cl	CF_3	$-\overset{O}{\overset{\|}{C}}NH_2 1$	0	1	(1.12)	100	90	100	100	100	100	100	100
CF_3	Cl	$-\overset{O}{\overset{\|}{C}}NHCH_3$	0	0.5	(0.56)	100	98	100	70	100	100	100	100
CF_3	--	$-\overset{O}{\overset{\|}{C}}-NH_2$	0	0.5 0.125	(0.56) (0.14)	100 95	100 60	100 90	100 60	100 98	100 100	100 100	100 95
CF_3	CF_3	-CN	0	10	(11.2)	--	--	--	40	95	100	100	--
CF_3	--	[illegible]	S	0.125	(0.14)	100	100	30	95	95	100	100	97
[illegible]	CF_3	[illegible]	0	1	(1.12)	100	98	40	90	100	100	100	90

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PREEMERGENCE CONTROL OF PLANT SPECIES (Cont.)

[illegible]				Dosage In Lbs Per Acre		Plant Species							
	Y	Z	T	(kg./hectare)		Corn	Rice	Wheat	Wild Oats	Fox-tail	Barn-yard Grass	Crab-grass	Johnson Grass
[illegible]	CF_3	[illegible] $(CH_2)_6CH_3$	0	1	(1.12)	70	0	60	90	80	60	100	90
CF_3	--	$-\overset{O}{\overset{\parallel}{C}}N(CH_3)_2$	0	1	(1.12)	70	95	98	90	100	60	100	90
CF_3	--	$-CN$	0	10	(11.2)	--	--	--	100	100	100	100	--
CF_3	Cl	$-CN$	0	10	(11.2)	--	--	--	100	100	100	100	--
[illegible]	[illegible]	$-\overset{O}{\overset{\parallel}{C}}OCH_3$	0	10	(11.2)	--	--	--	100	100	100	100	--
[illegible]		[illegible]	0	10	(11.2)	--	--	--	90	98	9[illegible]	95	--
[illegible]	[illegible]	$-CH_2OH$	0	10	(11.2)	--	--	--	100	100	100	100	--
CF_3	Cl	$-CH_2O\overset{O}{\overset{\parallel}{C}}CH_3$	0	10	(11.2)	--	--	--	100	100	100	100	--
CF_3	Cl	$-\overset{O}{\overset{\parallel}{C}}OC_4H_9$	0	10	(11.2)	--	--	--	100	100	100	100	--
[illegible]	CF_3	$-\overset{O}{\overset{\parallel}{C}}O(CH_2)_7CH_3$	0	10	(11.2)	--	--	--	100	100	100	100	-
[illegible]	Cl	$-\overset{O}{\overset{\parallel}{C}}NH_2$	0	10	(11.2)	--	--	--	100	100	100	100	--
[illegible]	[illegible]	[illegible]	0	10	(11.2)	-	--	--	100	100	100	100	

PREEMERGENCE CONTROL OF PLANT SPECIES (Cont.)

Compound Tested				Dosage In Lbs Per Acre (kg./hectare)	Plant Species							
X	Y	Z	T		Corn	Rice	Wheat	Wild Oats	Fox-tail	Barn-yard Grass	Crab-grass	Johnson Grass
Cl	CF_3	$-\overset{O}{\overset{\|}{C}}-OH$	0	10 (11.2)	--	--	--	100	100	100	100	--
CF_3	CF_3	$-\overset{O}{\overset{\|}{C}}-OH$	0	10 (11.2)	--	--	--	100	100	100	100	--
CF_3	Cl	$-\overset{O}{\overset{\|}{C}}-OH$	0	10 (11.2)	--	--	--	100	100	100	100	--
CF_3	--	$-\overset{O}{\overset{\|}{C}}-OH$	0	10 (11.2)	--	--	--	100	100	100	100	--

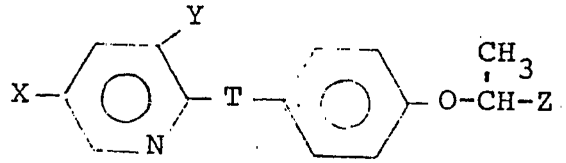
Example 17

To illustrate the phytotoxic properties of the various active ingredients of the present invention in post-emergent application, a group of controlled greenhouse experiments is described below.

Various species of plants were planted in beds of good agricultural soil in a greenhouse. After the plants had emerged and grown to a height of about 2-6 inches (5-15 cm.) a portion of the plants were sprayed with an aqueous mixture, made by mixing a selected active ingredient and emulsifier or dispersant with about 1:1 water-acetone, employing sufficient amounts of the treating composition to provide application rates of 4000 parts per million (ppm) or about 10 pounds per acre (11.2 kg./hectare) and in some cases at lower rates. Other portions of the plants were left untreated to serve as controls.

After 2 weeks, the effect of the respective test ingredients used on respective groups of plants was evaluated by a comparison with the control groups of the plants. The results are tabulated in the following table.

POSTEMERGENCE CONTROL OF PLANT SPECIES



Compound Tested				Dosage in PPM	Plant Species							
X	Y	Z	T		Corn	Rice	Wheat	Wild Oats	Fox-tail	Barn-yard Grass	Crab-grass	Johnson Grass
Cl	CF_3	$-\overset{\overset{O}{\|}}{C}OC_4H_9$	0	500	100	0	40	100	100	100	100	100
				125	80	--	0	80	98	100	98	98
CF_3	Cl	$-\overset{\overset{O}{\|}}{C}NHCH_3$	0	125	95	98	40	70	100	80	100	100
				31.5	70	90	20	70	98	40	100	100
CF_3	Cl	$-\overset{\overset{O}{\|}}{C}NH_2$	0	62.5	100	80	60	80	100	100	100	100
				15.6	100	80	60	98	98	100	99	100
CF_3	Cl	$-\overset{\overset{O}{\|}}{C}OH$	0	62.5	100	90	95	100	100	100	100	100
				15.6	100	30	60	--	95	100	98	100
CF_3	--	$-\overset{\overset{O}{\|}}{C}NH_2$	0	62.5	95	--	60	100	100	90	100	100
				15.6	95	--	40	20	60	90	90	98
CF_3	--	$-\overset{\overset{O}{\|}}{C}-OH$	0	62.5	100	70	50	80	90	70	98	100
				15.6	80	40	30	10	90	20	90	95

POSTEMERGENCE CONTROL OF PLANT SPECIES (Cont.)

Compound Tested				Dosage in PPM	Plant Species							
X	Y	Z	T		Corn	Rice	Wheat	Wild Oats	Fox-tail	Barn-yard Grass	Crab-grass	Johnson Grass
CF_3	CF_3	$-CN$	0	4000	--	--	--	100	90	100	100	--
Cl	CF_3	$-CN$	0	4000	--	--	--	--	80	60	100	--
Cl	CF_3	$-\overset{\overset{O}{\|}}{C}NH_2$	0	4000	--	--	--	100	100	100	100	--
CF_3	--	$-\overset{\overset{O}{\|}}{C}OCH_3$	0	4000	--	--	--	--	100	100	100	--
CF_3	--	$-CN$	0	4000	--	--	--	--	100	100	100	--
CF_3	Cl	$-CN$	0	4000	--	--	--	--	100	100	100	--
CF_3	CF_3	$-\overset{\overset{O}{\|}}{C}OCH_3$	0	4000	--	--	--	100	100	100	100	--
CF_3	CF_3	$-CH_2OH$	0	4000	--	--	--	95	95	70	98	--
CF_3	Cl	$-CH_2OH$	0	4000	--	--	--	100	100	100	100	--
CF_3	Cl	$-CH_2O\overset{\overset{O}{\|}}{C}CH_3$	0	4000	--	--	--	100	100	100	100	--
CF_3	Cl	$-\overset{\overset{O}{\|}}{C}O(CH_2)_3CH_3$	0	4000	--	--	--	100	100	100	100	--
CF_3	CF_3	$-\overset{\overset{O}{\|}}{C}-O-C_8H_{17}$	0	4000	--	--	--	99	100	100	100	--

POSTEMERGENCE CONTROL OF PLANT SPECIES (Cont.)

Compound Tested				Dosage in PPM	Plant Species							
X	Y	Z	T		Corn	Rice	Wheat	Wild Oats	Fox-tail	Barn-yard Grass	Crab-grass	Johnson Grass
CF_3	Cl	$-\overset{\overset{O}{\|}}{C}-OCH_3$	0	4000	--	--	--	100	98	100	100	--
Cl	CF_3	$-\overset{\overset{O}{\|}}{C}OH$	0	4000	--	--	--	100	100	100	100	--
CF_3	CF_3	$-\overset{\overset{O}{\|}}{C}OH$	0	4000	--	--	--	100	100	100	100	--
CF_3	Cl	$-\overset{\overset{O}{\|}}{C}-OH$	S	28	100	20	*--	60	100	100	100	100
				14	30	0	--	0	100	80	98	100
				7	0	--	--	--	80	30	90	100

*Wheat was not run at these lower dosage rates as control at 111 ppm was only 20% and at 55.5 ppm control was zero.

Example 18

In a series of tests clearly demonstrating the herbicidal properties of the compounds of the present invention applied in postemergent application, various metal and amine salts of propanoic acids prepared in aqueous solution as described hereinabove and brought initially to a dilution of 4000 ppm were applied to growing plants under greenhouse conditions.

Various species of plants were planted in pots containing good agricultural soil in a greenhouse. After the plants had emerged and grown to a height of about 2-6 inches (5-15 cm.), some of the plants were sprayed, respectively, with a respective one of the said aqueous solutions, then diluted and sprayed on other respective selected plants at lower rates, each species of plant not being run at all rates. Other plants were left untreated to serve as controls. Still other plants, plants of Bermuda grass, blue grass, Johnson grass and cheat grass, were allowed to grow to 6-8 inches (15-20 cm.) then four times cut back to 2 inches (5 cm.) and allowed to regrow, all over about a 6-7 week period providing established plants.

After about two weeks, the effect of the respective test ingredients used on various respective plants was evaluated by comparison with the control group of plants. The results showed that the potassium and triethylamine salts of 2-[4-(5-trifluoromethyl-3-chloro-2-pyridyloxy)phenoxy]-propanoic acid applied (a) at a rate of 4000 ppm gave complete control of Bermuda grass, sorghum and barnyard grass while showing little or no control of cotton; (b) at a rate of 2000 ppm gave substantial to complete control of bluegrass and rice while showing no effect on soybeans; (c) at a rate of 1000 ppm gave complete control of Johnson grass, crabgrass and yellow foxtail; and (d) at a rate of 500 ppm exhibited complete control of cheat grass, corn, wheat and wild oats.

In addition, the ethanolamine and sodium salts of 2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propanoic acid applied (a) at a rate of 4000 ppm gave complete control of Bermuda grass, sorghum and barnyard grass while showing no adverse effects on cotton; (b) at a rate of 2000 ppm gave 70% control of bluegrass and complete control of rice while having no adverse effects on soybeans; (c) at a rate of 1000 ppm showed complete control of Johnson grass and crabgrass and fair to excellent control of yellow foxtail, and (d) at a rate of 500 ppm gave complete control of [illegible], corn, wheat and wild oats.

Further, the ethylamine salt of 2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propanoic acid and the ammonium salt of 2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy)-phenoxy]propanoic acid gave nearly as good control of the same plants at the rates recited above as described for the salts rated in the preceding paragraphs.

The same salts applied in preemergent operations using the solutions described above and applied at [illegible] the range of about 10 to about 1.25 pounds per acre [illegible] 1.4 kg./hectare) in a manner similar to that described in Example 16 showed substantially complete to complete control of crabgrass, yellow foxtail, barnyard grass, wild oats, wheat and no control of cotton velvet leaf or annual morning-glory at the higher rates and the same or substantially the same excellent control at the lower rates.

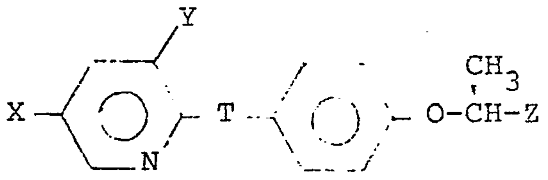
Example 19

In preemergent operations carried out in a similar to that described in Example 15, [illegible] acre (11.2 kg./hectare) of active ingredient -2-[4-(3,5-bis(trifluoromethyl)-2-pyridyloxy) [illegible] propanamide gave 50 percent control of crabgrass control of wild oats, foxtail, barnyard grass, cotton, pigweed, annual morning glory or velvet leaf, while N,N-dimethyl-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]-propanamide showed complete control of wild oats, foxtail barnyard grass and crabgrass.

In postemergent operations carried out in the same manner as that described in Example 17, applying active ingredient at the rate of 4000 ppm, the above described N,N-di-n-butyl propanamide showed 80 percent control of cotton and 60 percent control of velvet leaf but no control of wild oats, foxtail, barnyard grass, crabgrass or annual morning glory, while the above identified N,N-dimethyl propanamide exhibited complete control of wild oats, foxtail, barnyard grass and crabgrass.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A trifluoromethylpyridyl(oxy/thio)phenoxy propionic compound corresponding to the formula



wherein T is oxygen or sulfur;

X is Cl, Br, or CF_3;

Y is H, Cl, Br, or CF_3, provided at least one of X and Y is CF_3;

Z is $-\overset{O}{\overset{\|}{C}}-OR$, $-\overset{O}{\overset{\|}{C}}NR_1R_2$, $-\overset{O}{\overset{\|}{C}}-O^{\ominus}M^{\oplus}$, $-CN$, $-CH_2OR_3$, $-CH_2O\overset{O}{\overset{\|}{C}}R_4$, or $-\overset{O}{\overset{\|}{C}}SR_5$;

M is ${}^{\oplus}NHR_1R_1R_1$, Na, K, Mg, or Ca;

R is H, C_{1-8} alkyl, benzyl, chlorobenzyl, or C_{3-6} alkoxyalkyl;

R_1 is H, C_{1-4} alkyl, or C_{2-3} hydroxyalkyl;

R_2 is R_1 or $-OCH_3$;

R_3 is H or C_{1-4} alkyl;

R_4 is C_{1-7} alkyl; and

R_5 is C_{1-4} alkyl.

2. 2-[4-(3,5-Bis(trifluoromethyl)-2-pyridyl propionic acid.

3. 2-[4-(5-Trifluoromethyl-2-pyridyloxy)phe propionic acid.

4. 2-[4-(3-Chloro-5-trifluoromethyl-2-py phenoxy]propionic acid.

5. 2-[4-(5-Chloro-3-trifluoromethyl-2-py phenoxy]propionic acid.

6. 2-[4-(3,5-Bis(trifluoromethyl)-2-pyridyloxy)-phenoxy]propanol.

7. 2-[4-(3-Chloro-5-trifluoromethyl-2-pyridyloxy)-phenoxy]propanol.

8. 2[4-(3-Chloro-5-trifluoromethyl-2-pyridylthio)-phenoxy]propionic acid.

9. A herbicidal composition comprising a compound claimed in any one of Claims 1 to 8 in admixture with a carrier therefor.

10. A method for controlling undesired plant growth which comprises applying to plants a compound claimed in any one of Claims 1 to 8 or a composition claimed in Claim 9.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 78 10 029

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
	FR - A - 2 278 675 (ISHIHARA SANGYO KAISHA LTD.) * Pages 1-4 * --	1,9
	FR - A - 2 329 632 (ISHIHARA SANGYO KAISHA LTD.) * Pages 1,2 * --	1,9
	FR - A - 2 288 089 (ISHIHARA SANGYO KAISHA LTD.) * Pages 1,2 * --	1,9
	JP - A - 76 142 537 (ISHIHARA SANGYO) * Abstract derwent * --	1,9
P	FR - A - 2 359 129 (CIBA-GEIGY) * Pages 1-3 * ----	1,9

CLASSIFICATION OF THE APPLICATION (Int.Cl.²)

C 07 D 213/64
C 07 D 213/70
A 01 N 9/22//
C 07 D 213/61

TECHNICAL FIELDS SEARCHED (Int.Cl.²)

C 07 D 213/64
C 07 D 213/63
C 07 D 213/62
C 07 D 213/70
A 01 N 9/22

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	21-08-1978	VERHULST

EPO Form 1503.1 06.78