

PATENT SPECIFICATION

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(54) AN α -[4-(5-FLUOROMETHYL-2-PYRIDYLOXY)PHENOXY]ALKANECARBOXYLIC ACID DERIVATIVE AND ITS USE AS A HERBICIDE

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

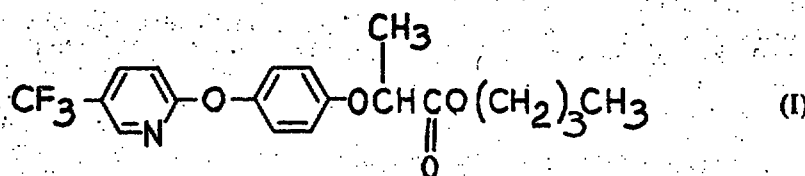
This invention relates to an α -[4-(5-fluoromethyl-2-pyridyloxy)phenoxy]alkane carboxylic acid derivative useful as a herbicide for agriculture and horticulture.

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

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

The present invention resides in n-butyl α -[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate.

The compound of the invention obeys the following formula (I):



and its boiling point is 160—163°C/1 mm Hg.

The invention further provides a herbicidal composition comprising a herbicidally effective amount of the compound of the above formula (I) and an agriculturally acceptable adjuvant.

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

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

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

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

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

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

Specific examples of preparing the herbicidal compound of this invention are shown below. Unless otherwise indicated herein, all parts, percents, ratios and the like are by weight.

Preparation Example 1

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

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

5.1 g of 2 - (4 - hydroxyphenoxy) - 5 - trifluoromethylpyridine obtained as

described in (a) or (b) above, and 4.2 g of n-butyl α -bromopropionate were dissolved in 50 ml of methyl ethyl ketone, and the solution was allowed to react for 2 hours in the presence of 3.3 g of anhydrous potassium carbonate while refluxing at 80°C. After completion of the reaction, water was added to the reaction product to dissolve any remaining solid, and the mixture was concentrated under reduced pressure to distill out the methyl ethyl ketone. The residue was then extracted with toluene and the extract was washed with water and dried over anhydrous sodium sulfate. The toluene was then removed by evaporation to obtain an oily product. The resulting oily product was distilled to obtain the desired product having a boiling point of 160—163°C/1 mmHg.

Preparation Example 2

9.1 g of 2 - chloro - 5 - trifluoromethylpyridine and 23.3 g of n-butyl α - (4 - hydroxyphenoxy)propionate were dissolved in 50 ml of dimethyl sulfoxide, and the solution was allowed to react at 150°C for 2 hours in the presence of 13.8 g of anhydrous potassium carbonate while stirring. The reaction product was allowed to cool, poured into ice-water and the resulting oily substance was extracted with toluene. The toluene layer was washed several times with water, dried over anhydrous sodium sulfate and the toluene was removed by distillation to obtain an oily substance (i).

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

The oily substances (i) and (ii) obtained above were combined and adsorbed onto a silica gel column followed by elution with toluene. The toluene was distilled off from the resulting eluate to obtain the desired product.

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

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

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

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

The herbicidal compound of this invention is most suitably applied to upland farms, especially upland farms where broad-leaved crops are cultivated, and can also be applied to orchards, forests and various non-agricultural lands. The compound of this invention can be applied as a soil treatment or a foliar treatment in upland farm conditions or under flooded conditions. A suitable rate of application varies according to various factors such as the climate condition, the soil condition, the form of the chemical, the time of application, the method of application, or the types of cultivated crops to which it is applied and the main weeds to be controlled. When the compound of this invention is used in the form of a solid preparation

(e.g., dust or granules), the amount of the active ingredient is 0.1 to 1,000 g per are (100 m²), preferably 0.5 to 500 g, and more preferably 1 to 250 g, per are.

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

5 TEST EXAMPLE 1 5

Each 1/3,000 are (1/30 m²) flat was charged with soil to provide an upland condition. Predetermined amounts of seeds of edible barnyard grass, radish and soybeans were sown, and covered with soil containing seeds of graminaceous weeds such as large crab-grass (*Digitaria adscendens* HENR.), barnyard grass (*Echinochloa crus-galli* BEAUV.), green foxtail (*Setaria viridis* BEAUV.), etc., to a thickness of about 1 cm. Two days after sowing, an aqueous dispersion of the herbicidal compound of the invention was sprayed thereon, and the growth of the weeds was visually evaluated 30 days after the spraying. On a scale of growth inhibition having 10 grades in which a value of 10 indicated that the growth was completely inhibited and a value of 1 indicated no inhibition, values of 10 were obtained for the growth of barnyard grass and graminaceous weeds and values of 1 for that of radish and soybeans both when the concentration of the compound of the invention was 50 g/are and when it was decreased to 25 g/are.

20 TEST EXAMPLE 2 20

Each 1/3,000 are (1/30 cm²) pot was charged with soil to provide an upland condition, and predetermined amounts of seeds of edible barnyard grass and soybeans were sown, and covered with soil to a thickness of about 1 cm. When the edible barnyard grass reached a 2.5-leaf stage, aqueous dispersions of the herbicidal compound of the invention were applied to the foliage in amounts of 200 and 400 ppm respectively. Twenty days after the treatment with the compound, the growth of the barnyard grass and soybeans was visually evaluated, and the degree of growth inhibition was evaluated on the same scale as in Test Example 1. In both cases it was found that the growth of barnyard grass was completely inhibited (a scale value of 10), whereas the soybeans exhibited no inhibition (a scale value of 1).

30 WHAT WE CLAIM IS:— 30

- 1. N - butyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate.
- 2. A herbicidal composition comprising a herbicidally effective amount of n - butyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate, as an active ingredient, and an agriculturally acceptable adjuvant.
- 3. A method of controlling weeds comprising applying a herbicidally effective amount of the herbicidal composition as claimed in Claim 2.

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(e.g., dust or granules), the amount of the active ingredient is 0.1 to 1,000 g per are (100 m²), preferably 0.5 to 500 g, and more preferably 1 to 250 g, per are.

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

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TEST EXAMPLE 1

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TEST EXAMPLE 2

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2. A herbicidal composition comprising a herbicidally effective amount of n - butyl α - [4 - (5 - trifluoromethyl - 2 - pyridyloxy)phenoxy]propionate, as an active ingredient, and an agriculturally acceptable adjuvant.

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3. A method of controlling weeds comprising applying a herbicidally effective amount of the herbicidal composition as claimed in Claim 2.

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