

PATENT SPECIFICATION

820,180

NO DRAWINGS.

Inventors:—GERALD BERTRAM LUSH and HERBERT AUBREY STEVENSON.



Date of filing Complete Specification : Aug. 26, 1957.

Application Date : Sept. 18, 1956. No. 28525/56.

Complete Specification Published : Sept. 16, 1959.

Index at Acceptance:—Classes 2(3), C1E7K3, C2A(1:5), C2B3(A1:E:F:G1), C2R(15:16:17); and 81(1), E1C(3B3:4A2:4A3).

International Classification:—A611. C07c.

COMPLETE SPECIFICATION.

New Salts of Alpha-(4-chloro-2-methylphenoxy)-propionic Acid and Herbicidal Compositions containing them.

We, BOOTS PURE DRUG COMPANY LIMITED, a British Company, of Station Street, Nottingham, 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 new chemical compounds and to new compositions of matter which have been found to possess valuable properties. In particular the new compositions produce a morphological response, which may result in death, in cleavers (*Galium species* such as *Galium aparine*) and chickweed (*Stellaria media*). They also possess a good range of activity against other weeds commonly found in cereal crops.

The invention consists in the salts of alpha - (4 - chloro - 2 - methylphenoxy)-propionic acid (referred to in the Specification as C.M.P.P.) with primary, secondary or tertiary alkyl or hydroxyalkyl amines and in compositions for the control of cleavers and chickweed in cereal crops which comprise aqueous solutions of alpha-(4-chloro-2-methylphenoxy)-propionic acid in the form of a salt with a primary, secondary or tertiary alkyl or hydroxyalkyl amine. The finding of such specific activity in aqueous solutions of salts of this acid is both novel and unexpected. Such activity has not previously been described in this or any other derivatives of phenoxypropionic acid, and is very surprising in view of the lack of activity of a similar nature shown by the correspondingly substituted phenoxyacetic acid and phenoxybutyric acid derivatives. For example the amine salts of 4-chloro-2-

methylphenoxy-acetic acid are, for all practical purposes, inactive against cleavers even when applied at excessive rates, e.g. at the equivalent of 4 lb. of the acid per acre.

Another surprising feature of the alpha-(4 - chloro - 2 - methylphenoxy) - propionic acid amine salts of this invention is that when applied at rates up to the equivalent of 3.6 lb. of the acid per acre they are not toxic to wheat, barley and oats, even, in the case of barley and oats and certain wheat varieties, when applied at very early stages of growth. At these early stages even the equivalent of 1 lb. of acid of M.C.P.A. per acre causes severe toxicity.

The compounds of the invention may be prepared conveniently by heating alpha-(4-chloro-2-methylphenoxy)-propionic acid with an equivalent amount of a primary, secondary or tertiary alkyl or hydroxyalkylamine so as to form a homogeneous melt which on cooling gives the required salt in solid form, which may be recrystallised, if desired, from a suitable solvent for example, ethylene dichloride. Alternatively, a solution of equivalent amounts of acid and amine in a suitable solvent may be heated, the required salt crystallising from the solution on cooling. Suitable amines which may be employed to form salts according to the invention include diethylamine, diethanolamine, monoethanolamine, triethanolamine and ethylamine.

The compositions of the invention may be prepared either by dissolving the compounds of the invention in water or by dissolving alpha - (4 - chloro - 2 - methylphenoxy) - propionic acid in a solution of the amine in water. The concentration of the resulting

[Price 3s. 6d.]

solution may be adjusted as required by the addition of further water. It has been found possible to prepare solutions containing as much as 32% w/v calculated as free acid of the above-mentioned acid, which are stable on storage over a wide range of temperature such as is likely to be encountered in agricultural practice. It is possible to obtain solutions of even higher concentration, e.g. up to 60%, but these are not very stable at temperatures below 0° C. and, therefore, it is preferred to supply the 32% w/v solutions. It is customary and convenient to market herbicidal compositions based on hormone weedkillers in a highly concentrated form such as we have described and to instruct the user to dilute the compositions with a suitable quantity of water before application to growing crops. However, new techniques of spraying are being developed which make it possible to spray some of the highly concentrated solutions effectively without diluting them with water. It should be understood, therefore, that the compositions according to the invention comprise both the highly concentrated form in which the compositions are marketed and the diluted forms in which the compositions are more often employed in agriculture.

The concentration of active ingredient in the compositions of the invention which are applied to crops is largely dependent on the type of machine which is used in applying the compositions. The actual concentration of the active ingredient in the solution applied to the crops may vary within wide limits and is not of significant importance. The most popular current practice is to use 10-25 gallons of herbicidal composition per acre and the important consideration is the total quantity of active ingredient applied per unit area of the crop to be treated. Thus, we have found that excellent control of cleavers in cereal crops can be achieved by the application of such an amount of the compositions of the invention that the alpha-(4-chloro-2-methylphenoxy)-propionic acid is applied to the crop at a rate of 2.4 lb. per acre.

Although it is normally possible to control cleavers in corn crops by application of 2.4 lb. per acre of the salts of this invention under favourable conditions it is possible to obtain the desired control with a dosage rate of 2 lb. per acre whilst under unfavourable conditions it is necessary to apply the salt at a rate of up to 3.6 lb. per acre.

In this Specification rate of dosage always refers to the equivalent amount of acid and thus a dosage rate of 2 lb. amine salt per acre means sufficient amine salt to supply 2 lb. of the free acid per acre.

The variables which arise in the application of the compositions of the present invention are :-

(1) I. The concentration of the solution of the salt supplied to the consumer which lies between 10% and 60% w/v but is preferably 32% w/v calculated as the free acid.

(2) V. The rate of application of the solution in gallons per acre which is determined by the apparatus available for spraying and the density of the crop and is usually between 10 and 25 gallons per acre.

(3) R. The rate of application of the salt calculated as the free acid per acre and this should be between 2 lb. and 3.6 lb. per acre.

(4) A. The concentration of the solution which is applied to the ground and this is between 1.0% and 3.6% w/v.

(5) D. The number of volumes of aqueous medium to be added to 1 volume of the solution of concentration I to give the solution of concentration A; within the limits set for the other variables this must be from 1¹/₂ to 74.

Of the above-mentioned variables I is fixed by the manufacture of the herbicidal compositions, R is chosen from between the limits set and depends upon climatic conditions and V is fixed by the apparatus used to apply the herbicidal compositions and also the density of the crops. Knowing I, V and R, then D and A can be determined by the use of the following equations :-

$$A = \frac{10R}{V} \quad \dots \quad (1)$$

$$D = \frac{I}{A} - 1 \quad \dots \quad (2)$$

The calculations may be simplified by combining equations (1) and (2) to give the following equation (3) :-

$$D = \frac{IV}{10R} - 1 \quad \dots \quad (3)$$

As before knowing I, V and R, then D can be determined from equation 3. The limits set on I, V and R are such that the dilution volume D will always give a solution having a concentration A which is between 1.0% and 3.6% w/v.

The compositions of the invention may also comprise a small amount of a wetting agent.

The following non-limitative examples illustrate the invention.

EXAMPLE 1.

In the preparation of the diethanolamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid a mixture of 21.45 grams of alpha-(4-chloro-2-methylphenoxy)-

propionic acid and 10.5 grams of diethanolamine is heated at 100° C. with stirring until a homogeneous melt is obtained. The solid which results from allowing the melt to cool is recrystallised twice from ethylene dichloride. There is thus obtained the diethanolamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid in the form of a colourless crystalline solid which has a melting point of 84—85° C. (Found: N, 4.6%. $C_{14}H_{22}O_3NCl$ requires N, 4.4%).

EXAMPLE 2.

In the preparation of the triethanolamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid a mixture of 21.45 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid and 14.9 grams of triethanolamine is heated at 100° C. with stirring until a homogeneous melt is obtained. This is allowed to cool and the resulting solid is recrystallised twice from ethylene dichloride. There is thus obtained the triethanolamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid in the form of a crystalline solid which has a melting point of 118—119° C. (Found: N, 3.8%. $C_{16}H_{24}O_3NCl$ requires N, 3.85%).

EXAMPLE 3.

In the preparation of the diethylamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid a mixture of 21.45 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid and 7.3 grams of diethylamine is heated at 100° C. with stirring until a homogeneous melt is obtained. This is allowed to cool and the solid thus obtained is recrystallised twice from ethylene dichloride. There is thus obtained the diethylamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid in the form of a crystalline solid which has a melting point of 96—98° C. (Found: N, 5.1%. $C_{16}H_{22}O_3NCl$ requires N, 4.9%).

EXAMPLE 4.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with stirring and warming in a solution of 1.56 grams of diethanolamine in 8 c.c. of water, and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethanolamine which may be diluted with water before application to crops for the control of cleavers.

EXAMPLE 5.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-

propionic acid is dissolved with stirring and warming in a solution of 1.09 grams of diethylamine in 8 c.c. of water, and the volume of the resulting solution is adjusted to 10 c.c. by addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethylamine. The solution is diluted with water before application to crops for the control of cleavers.

EXAMPLE 6.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with a stirring and warming in a solution of 1.56 grams of diethanolamine in 8 c.c. of water. To the solution is added 0.1 c.c. of Ethylan C.P. (a proprietary wetting agent which is a condensate of ethylene oxide and an octylphenol) and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethanolamine. The solution is diluted with water before application to crops for the control of cleavers.

EXAMPLE 7.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with stirring and warming in a solution of 1.09 grams of diethylamine in 8 c.c. of water. To the solution is added 0.1 c.c. of Ethylan C.P. and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethylamine. The solution is diluted with water before application to crops for the control of cleavers.

WHAT WE CLAIM IS:—

1. A new herbicidal compound comprising a salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid with a primary, secondary or tertiary alkyl or hydroxyalkyl amine.
2. A salt as claimed in Claim 1, in which the amine is diethanolamine, triethanolamine or diethylamine.
3. A herbicidal composition comprising a salt as claimed in Claim 1 dissolved in an aqueous medium.
4. A herbicidal composition as claimed in Claim 3 and comprising a wetting agent.
5. A composition for the control of



propionic acid and 10.5 grams of diethanolamine is heated at 100° C. with stirring until a homogeneous melt is obtained. The solid which results from allowing the melt to cool is recrystallised twice from ethylene dichloride. There is thus obtained the diethanolamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid in the form of a colourless crystalline solid which has a melting point of 84–85° C. (Found: N, 4.6% $C_{14}H_{22}O_3NCl$ requires N, 4.4%).

EXAMPLE 2.

In the preparation of the triethanolamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid a mixture of 21.45 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid and 14.9 grams of triethanolamine is heated at 100° C. with stirring until a homogeneous melt is obtained. This is allowed to cool and the resulting solid is recrystallised twice from ethylene dichloride. There is thus obtained the triethanolamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid in the form of a crystalline solid which has a melting point of 118–119° C. (Found: N, 3.8% $C_{14}H_{22}O_3NCl$ requires N, 3.85%).

EXAMPLE 3.

In the preparation of the diethylamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid a mixture of 21.45 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid and 7.3 grams of diethylamine is heated at 100° C. with stirring until a homogeneous melt is obtained. This is allowed to cool and the solid thus obtained is recrystallised twice from ethylene dichloride. There is thus obtained the diethylamine salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid in the form of a crystalline solid which has a melting point of 96–98° C. (Found: N, 5.1% $C_{14}H_{22}O_3NCl$ requires N, 4.9%).

EXAMPLE 4.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with stirring and warming in a solution of 1.56 grams of diethanolamine in 8 c.c. of water, and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethanolamine which may be diluted with water before application to crops for the control of cleavers.

EXAMPLE 5.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-

propionic acid is dissolved with stirring and warming in a solution of 1.09 grams of diethylamine in 8 c.c. of water, and the volume of the resulting solution is adjusted to 10 c.c. by addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethylamine. The solution is diluted with water before application to crops for the control of cleavers.

EXAMPLE 6.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with stirring and warming in a solution of 1.56 grams of diethanolamine in 8 c.c. of water. To the solution is added 0.1 c.c. of Ethylan C.P. (a proprietary wetting agent which is a condensate of ethylene oxide and an octylphenol) and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethanolamine. The solution is diluted with water before application to crops for the control of cleavers.

EXAMPLE 7.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with stirring and warming in a solution of 1.09 grams of diethylamine in 8 c.c. of water. To the solution is added 0.1 c.c. of Ethylan C.P. and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethylamine. The solution is diluted with water before application to crops for the control of cleavers.

WHAT WE CLAIM IS:—

1. A new herbicidal compound comprising a salt of alpha-(4-chloro-2-methylphenoxy)-propionic acid with a primary, secondary or tertiary alkyl or hydroxyalkyl amine.
2. A salt as claimed in Claim 1, in which the amine is diethanolamine, triethanolamine or diethylamine.
3. A herbicidal composition comprising a salt as claimed in Claim 1 dissolved in an aqueous medium.
4. A herbicidal composition as claimed in Claim 3 and comprising a wetting agent.
5. A composition for the control of

cleavers which contains as active ingredient alpha - (4 - chloro - 2 - methylphenoxy)-propionic acid in the form of a salt with a primary, secondary or tertiary alkyl or hydroxyalkyl amine.

6. A composition in a form suitable for use in the control of cleavers after dilution with water which contains as active ingredient alpha - (4 - chloro - 2 - methylphenoxy)-propionic acid in the form of a salt with a primary, secondary or tertiary alkyl or hydroxyalkyl amine, and in a concentration of the order of 32% w/v calculated as free acid.

7. A composition as claimed in Claim 5 or Claim 6 in which the salt is a salt of alpha - (4 - chloro - 2 - methylphenoxy)-propionic acid and diethanolamine.

8. A composition as claimed in Claim 5 and Claim 6 in which the salt is a salt of alpha - (4 - chloro - 2 - methylphenoxy) - propionic acid and triethanolamine.

9. A composition as claimed in Claim 5 or Claim 6 in which the salt is a salt of alpha - (4 - chloro - 2 - methylphenoxy) - propionic acid and diethylamine.

10. A method of preparing a solution suitable for control of cleavers in cereal crops which comprises diluting a solution comprising alpha - (4 - chloro - 2 - methylphenoxy) - propionic acid in the form of a salt with a primary, secondary or tertiary alkyl or hydroxyalkyl amine dissolved in an aqueous medium and being present therein at a concentration of between 10% and 60% w/v (I) 1 volume of the solution at concentration I being diluted with D volumes of aqueous medium to provide a composition which is suitable for application to non-susceptible cereal crops at a rate of between

10—25 gallons per acre (V) thereby providing between 2 lb.—3.6 lb. of the salt calculated as the free acid per acre (R) the actual values of I, V and R lying between the stipulated limits and the value of D also lying between 1 $\frac{1}{2}$ and 74 and being determined by use of the equation:—

$$D = \frac{IV}{10R} - 1.$$

11. A method as claimed in Claim 10 wherein R is 2.4 lb. per acre.

12. A method of preparing a solution suitable for the control of cleavers as claimed in Claim 10 or 11 wherein the solution comprises a wetting agent.

13. A method of preparing a solution suitable for the control of cleavers as claimed in any one of Claims 10 to 12 wherein the amine is diethanolamine.

14. A method of preparing a solution suitable for the control of cleavers as claimed in any one of Claims 10 to 12 wherein the amine is triethanolamine.

15. A method of preparing a solution suitable for the control of cleavers as claimed in any one of Claims 10 to 12 wherein the amine is diethylamine.

16. A composition suitable for the control of cleavers whenever prepared by a method as claimed in any one of Claims 10 to 15.

For the Applicants:
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51/52 Chancery Lane,
London, W.C.2.

PROVISIONAL SPECIFICATION.

New Salts of Alpha-(4-chloro-2-methylphenoxy)-propionic Acid and Herbicidal Compositions containing them.

We, BOOTS PURE DRUG COMPANY LIMITED, a British Company, of Station Street, Nottingham, do hereby declare this invention to be described in the following statement:—

This invention relates to new compositions of matter which have been found to possess valuable properties. In particular the new compositions produce a morphological response, which can result in death, in cleavers (Galium species, such as Galium Aparine) and chickweed (Stellaria media). They also possess a good range of activity against other weeds commonly found in cereal crops.

The invention consists in compositions suitable for the control of cleavers and chickweed in cereal crops, comprising aqueous solutions of alpha-(4-chloro-2-methylphen-

oxy)-propionic acid in the form of a salt with an amine. The finding of such specific activity in aqueous solutions of salts of this acid, is both novel and unexpected. Such activity has not previously been described in this or any other derivatives of phenoxy-propionic acid, and is very surprising in view of the lack of activity of a similar nature shown by the correspondingly substituted phenoxyacetic acid and phenoxybutyric acid derivatives.

The amines which may be used in the compositions of the invention are those amines which can be applied to growing plants without producing phytotoxicity and the primary, secondary and tertiary alkyl and hydroxyalkyl amines are particularly

valuable for this purpose. Thus the amines which may be employed in the compositions of the invention include diethyl amine, diethanolamine, monoethanolamine, triethanolamine and ethylamine. The compositions of the invention are prepared by dissolving the above-mentioned acid in a solution of the amine in water. The concentration of the resulting solution may be adjusted as required, by the addition of further water. It has been found possible to prepare solutions containing as much as 32% w/v calculated as free acid of the above-mentioned acid, which are stable on storage over a wide range of temperature such as is likely to be encountered in agricultural practice. It is possible to obtain solutions of even higher concentration, but these are not very stable at temperatures below 0° C. It is customary and convenient to market compositions of plant growth regulating agents in a highly concentrated form such as we have described and to instruct the user to dilute the compositions with a suitable quantity of water before application to growing crops.

The concentration of active ingredient in the diluted compositions of the invention which are applied to crops is largely dependent on the type of machine which is used in applying the compositions. The actual concentration of the active ingredient in the solution applied to the crops may vary within wide limits and is not of significant importance. The important consideration is the total quantity of active ingredient applied per unit area of the crop to be treated. Thus, we have found that excellent control of cleavers in cereal crops can be achieved by the application of such an amount of the compositions of the invention that the alpha-(4-chloro-2-methylphenoxy)-propionic acid is applied to the crop at a rate of the order of 2 lb. per acre.

It is understood, therefore, that the compositions according to the invention comprise both the highly concentrated form in which the compositions are marketed and the diluted forms in which the compositions are actually employed in agriculture.

The compositions of the invention may also comprise a small amount of a wetting agent.

The following non-limitative examples illustrate the invention.

EXAMPLE 1.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with stirring and warming in a solution of 1.56 grams of diethanolamine in 8 c.c. of water. To the solution is added 0.1 c.c. of Ethylan C.P. (a proprietary wetting agent which is a condensate of ethylene oxide and an octylphenol) and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethanolamine. The solution is diluted with water before application to crops for the control of cleavers.

EXAMPLE 2.

In the preparation of a herbicidal composition according to the invention 3.2 grams of alpha-(4-chloro-2-methylphenoxy)-propionic acid is dissolved with stirring and warming in a solution of 1.09 grams of diethylamine in 8 c.c. of water. To the solution is added 0.1 c.c. of Ethylan C.P. and the volume of the resulting solution is adjusted to 10 c.c. by the addition of water. There is thus obtained a solution containing 32% w/v of alpha-(4-chloro-2-methylphenoxy)-propionic acid (calculated as free acid) in the form of its salt with diethylamine. The solution is diluted with water before application to crops for the control of cleavers.

For the Applicants:
GILL, JENNINGS & EVERY,
Chartered Patent Agents,
51/52 Chancery Lane,
London, W.C.2.

R.A.H.