

PATENT SPECIFICATION

NO DRAWINGS

Inventor: QUENTIN FRANCIS SOPER

1,149,139



Date of Application and filing Complete Specification: 6 Oct., 1967.

No. 45898/67.

Complete Specification Published: 16 April, 1969.

© Crown Copyright 1969.

Index at acceptance:—C2 C(2D43D, 2D43H, 2D43S2, 2D43S4); A5 E(1C4A3, 1C4A4, 1C4B3, 1C4B4, 1C17)

Int. Cl.:—C 07 c 143/78

COMPLETE SPECIFICATION

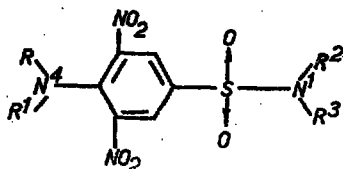
New Herbicidal Compounds and Compositions

We, ELI LILLY AND COMPANY, a Corporation of the State of Indiana, United States of America, of 740 South Alabama Street, City of Indianapolis, State of Indiana, United States of America, 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 concerns novel substituted sulfanilamide compounds having broad though selective herbicidal activity and herbicidal compositions containing these compounds.

It is the object of this invention to provide compounds and compositions which are toxic to both grasses and broadleaf weeds in their germinating stage but which are non-toxic to crop plants, and the use of which can eliminate weed grasses and certain broadleaf weeds selectively from crop plants such as corn, cotton, and soybeans and their close relatives in the plant kingdom.

The novel compounds provided by this invention are of the formula:



wherein

R, when taken separately, is hydrogen, C₁—C₄ alkenyl, or C₃—C₆ alkyl;

R¹, when taken separately, is C₃—C₄ alkenyl, or C₃—C₆ alkyl;

R and R¹, when R is not hydrogen, contain a total of from 4 to 8 carbons;

R and R¹, when taken together with the nitrogen atom to which they are attached, form a pyrrolidino, piperidino, or morpholino ring;

R² and R³, when taken together with the nitrogen atom to which they are attached, form a pyrrolidino or aziridino ring;

R² and R³, when taken separately, are the same or different and are hydrogen, C₁—C₈ alkyl, allyl, phenyl, or C₃—C₆ cycloalkyl;

When R² is hydrogen, R³ contains less than 7 carbons; and

R² and R³, when neither is hydrogen, contain a total of not more than 4 carbon atoms.

In the above groups, C₁—C₈ alkyl can be illustratively methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl, isobutyl, *n*-amyl, isoamyl, *sec*-amyl, or the like.

C₃—C₆ alkyl can be illustratively *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *n*-amyl, isoamyl, *n*-hexyl, isohexyl, or the like.

C₃—C₆ cycloalkyl can be illustratively cyclopropyl, cyclobutyl, or cyclopentyl.

C₃—C₄ alkenyl can be illustratively allyl, methallyl, or crotyl.

As examples of compounds which have the desired herbicidal activity and which can be successfully employed as weed-killing agents in accordance with this invention, there may be mentioned 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide; N¹ - methyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide; N²,N¹ - dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide; N¹ - allyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide; 3,5 - dinitro - N²,N⁴,N⁴ - tri(*n* - propyl)sulfanilamide; N¹ - ethyl - 3,5 - dinitro - N⁴,N⁴ - (di - *n* - propyl)sulfanilamide, N¹ - cyclopropyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide; N¹ - ethyl - N¹ - methyl - 3,5 - di - nitro - N⁴,N⁴ - di(*n* - propyl)-

[Price 4s. 6d.]

5 sulfanilamide; N^4 - (1 - ethylpropyl) - N^4 - methyl - 3,5 - dinitrosulfanilamide, N^4 - (1 - ethylpropyl) - N^1, N^1 - dimethyl - 3,5 - dinitrosulfanilamide, N^4 - (1 - ethylpropyl) - 3,5 - dinitrosulfanilamide, N^1, N^1 - diethyl - 3,5 - dinitro - N^4, N^4 - di(n - propyl)sulfanilamide; 4 - (aziridinosulfonyl) 2,6 - dinitro - N, N - di(n - propyl)aniline, and the like.

10 The present invention further provides a herbicidal composition comprising a new compound as defined above and a suitable carrier therefor.

15 The new compounds preferably are formulated for use as pre-emergent selective herbicides either as dusts, spray concentrates, spreadable granules, or wettable powders. Although the compounds are soluble in aqueous 20 10 percent sodium or potassium hydroxide, they are quite insoluble in water. For the preparation of emulsion-type sprays or wettable powders, the compounds desirably are formulated with a wetting agent or surfactant, polyoxyethylenesorbitan monolaurate, polyoxyethylenesorbitan mono-oleate, polyoxyglycol ethersulfonate, alkylaminododecylbenzene sulfonate or the like. In the preparation of spreadable granules, the inert diluent used may be calcite or attapulgitic clay.

30 In accordance with this invention, a soil area or locus infested with weed grass seeds and broadleaf weed seeds, is treated with a compound as defined above or with a dust, granular formation, or spray containing such 35 a compound as the herbicidally active ingredient. Typical soil areas which can be treated include crop-growing areas in which crops other than grasses will be grown; e.g., flower beds, strawberry patches, and similar areas 40 of cultivation. Compositions containing the herbicidally active compounds are sprayed, dusted, or spread by other methods well known by the art onto the crop areas at the rate of around 0.1 to 8.0 pounds per acre or 45 somewhat more if necessary, for example 0.5 pound of active ingredient per acre. For most field applications, we prefer to spray or dust the herbicidal compositions of this invention at the rate of about 0.5 to 4 pounds of active 50 ingredient per acre. If, however, the herbicidal compositions are spread in a granular form over the area to be treated, we prefer to employ a greater amount of active material per acre, suitably in the range of about 1 to 55 about 8 pounds of an active sulfonamide.

The novel compositions of the present invention possess the surprising and wholly unexpected ability to control certain undesirable plants unaffected by previously known weed control agents. These include Jimsonweed (*Datura stramonium*); common ragweed (*Ambrosia artemisiifolia*); Venice mallow (*Hibiscus triondum*); and Velvet leaf (*Abutilon theophrasti*).

65 In addition seedlings and germinating seeds

of many other varieties of weeds are killed by the above treatment process, including such undesirable grasses as the crabgrasses (*Digitaria sanguinalis*, and *Digitaria ischaemum*); green and yellow foxtails (*Setaria viridis* and *Setaria leuiscens*); and broadleaf weeds such as pigweed (*Amaranthus retroflexus*).

When sprays or dusts containing a substituted sulfonamide as represented by the above formula are applied at the rate of about 0.5 75 pound of herbicidal compound per acre to flats planted to crops, for example, soybeans, and infested with foxtail seeds, crabgrass seeds, and Velvet leaf seeds, germination of these weed species is completely inhibited without harm to the crop. In fact, application rates from as low as 0.125 pound per acre to as high as 8 pounds per acre have been shown to effectuate control of these undesirable weeds. 85

In addition to eliminating crabgrass, foxtail, and pigweed, the present novel compounds control ragweed, Velvet leaf, Jimsonweed, and Venice mallow in crop lands.

The herbicidal compositions of this invention can be employed in other useful ways. For example, spray or dust compositions as provided by this invention can be used to eradicate crabgrass, Velvet leaf, Jimsonweed, and the other undesirable weeds from perennial flower beds or to destroy germinating seeds of an undesired grass in turf. Other methods of employing the selective herbicidal compositions of this invention will be readily apparent to those skilled in the art. 95 100

The novel compounds coming within the scope of this invention are prepared by reaction of an appropriately substituted benzenesulfonyl halide with ammonium hydroxide, or a primary amine or a secondary amine, to yield the corresponding benzenesulfonamide, unsubstituted, monosubstituted, or disubstituted on the sulfonamide nitrogen atom, respectively. 105

For example, a mixture of 3,5 - dinitro - 4 - [di(n - propyl)amino]benzenesulfonyl chloride and an excess of concentrated ammonium hydroxide, the excess acting as solvent, is heated to reflux temperature for several hours. The reaction product mixture is cooled, poured onto crushed ice, and filtered. The filtrate is concentrated to dryness *in vacuo* and recrystallized from a mixture of acetone and petroleum ether to yield 3,5 - dinitro - N^4, N^4 - di(n - propyl)sulfanilamide as a solid, having a melting point of about 137—138° C. 110 115 120

Other of the novel compounds can be prepared by allowing a 4-halobenzenesulfonamide to react at reflux temperature with an appropriate secondary amine in the presence of triethylamine, to take up the halo acid formed in the reaction to yield the N^4, N^4 - dialkylaminobenzenesulfonamide. This method of preparation of the novel compounds is illus- 125 130



ital

trated as follows: A mixture of 4 - chloro - 3,5 - dinitro - N,N - dimethylbenzene - sulfonamide, di(*n*-propyl)amine and triethylamine is refluxed for several hours and worked up as described, supra, to yield N¹,N¹ - dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl) - sulfanilamide as a solid having a melting point of about 137° C.

EXAMPLE 1

3,5 - Dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide

A mixture of 5 gm. of 3,5 - dinitro - 4 - [di(*n* - propyl) - amino]benzenesulfonyl chloride and 3.5 gm. of concentrated ammonium hydroxide solution was heated to refluxing for about three hours. The reaction product mixture was cooled and poured into 200 ml. of ether. The mixture was filtered, concentrated *in vacuo* to dryness and the residue recrystallized from a mixture of acetone and petroleum ether to yield 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide as a solid having a melting point of about 137—138° C.

Following the general procedure of Example 1 and using appropriate amines the following compounds were prepared:

N¹ - Methyl - 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide, 3,5 - dinitro - 4 - [di(*n* - propyl)amino]benzenesulfonyl chloride and methylamine. Melting point: 145—146° C.

N⁴ - (1 - Ethylpropyl) - N¹ - methyl - 3,5 - dinitrosulfanilamide, from 3,5 - dinitro - 4 - [1 - (ethylpropyl)amino]benzenesulfonyl chloride and methylamine. Melting point: 57—60° C.

N⁴ - (1 - Ethylpropyl) - N¹,N¹ - dimethyl - 3,5 - dinitrosulfanilamide, from 3,5 - dinitro - 4 - [1 - (ethylpropyl)amino]benzenesulfonyl chloride and dimethylamine. Melting point: 119—120° C.

3,5 - Dinitro - 4 - (N - piperidino)benzenesulfonamide, from 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonylchloride and concentrated ammonium hydroxide. Melting point: 224—226° C.

N¹ - Methyl - 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonamide, from 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonyl chloride and methylamine. Melting point: 145—146° C.

N¹,N¹ - Dimethyl - 3,5 - dinitro - 4 - (N - piperidino) - benzenesulfonamide from 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonyl chloride and dimethylamine. Melting point: 138—139° C.

EXAMPLE 2

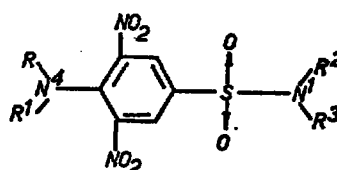
N¹,N¹ - Dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide

A mixture of 3 g. of 4 - chloro - 3,5 -

dinitro - N,N - dimethylbenzenesulfonamide, 1.5 g. of di(*n* - propyl)amine, and 1.5 g. of triethylamine was refluxed for about three hours. The reaction product mixture was worked up as described in Example 1 to yield N¹,N¹ - dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl) - sulfanilamide as a solid having a melting point of about 137° C. Yield: 1.5 g.

WHAT WE CLAIM IS:—

1. Compounds of the formula:



wherein

R, when taken separately, is hydrogen, C₁—C₄ alkenyl, or C₃—C₆ alkyl;

R¹, when taken separately, is C₃—C₄ alkenyl or C₃—C₆ alkyl;

R and R¹, when R is not hydrogen, contain a total of from 4 to 8 carbons;

R and R¹, when taken together with the nitrogen atom to which they are attached, form a pyrrolidino, piperidino, or morpholino ring;

R² and R³, when taken together with the nitrogen atom to which they are attached, form a pyrrolidino or aziridino ring;

R² and R³, when taken separately, are the same or different, and are hydrogen, C₁—C₆ alkyl, allyl, phenyl, or C₃—C₆ cycloalkyl;

When R² is hydrogen, R³ contains less than 7 carbons; and

R² and R³, when neither is hydrogen, contain a total of not more than 4 carbon atoms.

2. 3,5 - Dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide.

3. N¹ - methyl - 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide.

4. N¹,N¹ - dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide.

5. N¹ - allyl - 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide.

6. 3,5 - Dinitro - N¹,N⁴,N⁴ - tri(*n* - propyl)sulfanilamide.

7. The new compounds having herbicidal activity substantially as herein described with particular reference to any one of the specific examples.

8. A herbicidal composition which comprises a compound as defined in any of claims 1 to 7, and a suitable carrier therefor.

9. A herbicidal composition substantially as

5 treated as follows: A mixture of 4 - chloro - 3,5 - dinitro - N,N - dimethylbenzene - sulfonamide, di(*n*-propyl)amine and triethylamine is refluxed for several hours and worked up as described, supra, to yield N¹,N¹ - dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl) - sulfanilamide as a solid having a melting point of about 137° C.

EXAMPLE 1

10 3,5 - Dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide

A mixture of 5 gm. of 3,5 - dinitro - 4 - [di(*n* - propyl) - amino]benzenesulfonyl chloride and 3.5 gm. of concentrated ammonium hydroxide solution was heated to refluxing for about three hours. The reaction product mixture was cooled and poured into 200 ml. of ether. The mixture was filtered, concentrated *in vacuo* to dryness and the residue recrystallized from a mixture of acetone and petroleum ether to yield 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide as a solid having a melting point of about 137—138° C.

Following the general procedure of Example 1 and using appropriate amines the following compounds were prepared:

N¹ - Methyl - 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide, 3,5 - dinitro - 4 - [di(*n* - propyl)amino]benzenesulfonyl chloride and methylamine. Melting point: 145—146° C.

N⁴ - (1 - Ethylpropyl) - N¹ - methyl - 3,5 - dinitrosulfanilamide, from 3,5 - dinitro - 4 - [1 - (ethylpropyl)amino]benzenesulfonyl chloride and methylamine. Melting point: 57—60° C.

N⁴ - (1 - Ethylpropyl) - N¹,N¹ - dimethyl - 3,5 - dinitrosulfanilamide, from 3,5 - dinitro - 4 - [1 - (ethylpropyl)amino]benzenesulfonyl chloride and dimethylamine. Melting point: 119—120° C.

3,5 - Dinitro - 4 - (N - piperidino)benzenesulfonamide, from 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonylchloride and concentrated ammonium hydroxide. Melting point: 224—226° C.

N¹ - Methyl - 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonamide, from 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonyl chloride and methylamine. Melting point: 145—146° C.

N¹,N¹ - Dimethyl - 3,5 - dinitro - 4 - (N - piperidino) - benzenesulfonamide from 3,5 - dinitro - 4 - (N - piperidino)benzenesulfonyl chloride and dimethylamine. Melting point: 138—139° C.

EXAMPLE 2

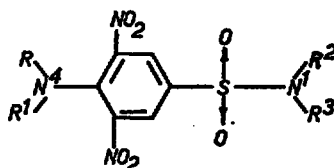
N¹,N¹ - Dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl)sulfanilamide

A mixture of 3 g. of 4 - chloro - 3,5 -

dinitro - N,N - dimethylbenzenesulfonamide, 1.5 g. of di(*n* - propyl)amine, and 1.5 g. of triethylamine was refluxed for about three hours. The reaction product mixture was worked up as described in Example 1 to yield N¹,N¹ - dimethyl - 3,5 - dinitro - N⁴,N⁴ - di(*n* - propyl) - sulfanilamide as a solid having a melting point of about 137° C. Yield: 1.5 g.

WHAT WE CLAIM IS:—

1. Compounds of the formula:



wherein

R, when taken separately, is hydrogen, C₁—C₄ alkenyl, or C₃—C₆ alkyl;

R¹, when taken separately, is C₃—C₄ alkenyl or C₃—C₆ alkyl;

R and R¹, when R is not hydrogen, contain a total of from 4 to 8 carbons;

R and R¹, when taken together with the nitrogen atom to which they are attached, form a pyrrolidino, piperidino, or morpholino ring;

R² and R³, when taken together with the nitrogen atom to which they are attached, form a pyrrolidino or aziridino ring;

R² and R³, when taken separately, are the same or different, and are hydrogen, C₁—C₆ alkyl, allyl, phenyl, or C₃—C₆ cycloalkyl;

When R² is hydrogen, R³ contains less than 7 carbons; and

R² and R³, when neither is hydrogen, contain a total of not more than 4 carbon atoms.

2. 3,5 - Dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide.

3. N¹ - methyl - 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide.

4. N¹, N¹ - dimethyl - 3,5 - dinitro - N⁴, N⁴ - di(*n* - propyl)sulfanilamide.

5. N¹ - allyl - 3,5 - dinitro - N⁴,N⁴ - di(*n*-propyl)sulfanilamide.

6. 3,5 - Dinitro - N¹,N⁴,N⁴ - tri(*n* - propyl)sulfanilamide.

7. The new compounds having herbicidal activity substantially as herein described with particular reference to any one of the specific examples.

8. A herbicidal composition which comprises a compound as defined in any of claims 1 to 7, and a suitable carrier therefor.

9. A herbicidal composition substantially as



herein described with particular reference to
any one of the specific examples.

BOULT, WADE & TENNANT, ~~S~~
111 & 112, Hatton Garden, London, E.C.1.
Chartered Patent Agents,
Agents for the Applicant(s).

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1969.
Published by the Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

