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INSECTICIDE COMPRISING MONO-ALKYLATED DIPHENYLENE SULFIDES AND METHOD OF USING SAME

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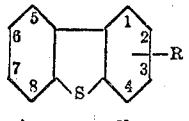
12 Claims. (Cl. 167—33)

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This invention relates to insecticides. It is particularly directed to a new class of insecticidal compounds for combatting larvae of chewing insects, such as codling moth larvae or the larvae of the Mexican bean beetle.

We have found that mono-alkylated diphenylene sulfides containing from 1 to 8 carbon atoms in the alkyl side chain possess insecticidal properties and are particularly suitable for combatting the larvae of chewing insects. The preferred compounds of our invention are the monoalkylated diphenylene sulfides containing from 3 to 6 carbon atoms in the alkyl side chain, especially the monoalkylated diphenylene sulfides in which the alkyl group is a straight chain radical containing from 3 to 6 carbon atoms. The insecticides of our invention are non-toxic to warm blooded animals and hence may be sprayed on fruit, vegetables and other edible substances without danger to humans. We have found that the toxicity of the monoalkylated diphenylene sulfides of this invention to insects is considerably higher than the toxicity displayed by unsubstituted diphenylene sulfide or by dialkylated diphenylene sulfides.

The compounds which may be employed in accordance with this invention may be any monoalkylated diphenylene sulfide containing from 1 to 8 carbon atoms in the alkyl side chain; such compounds have the following general structural formula:



in which R denotes an alkyl group containing from 1 to 8 carbon atoms. As above noted, the preferred compounds of this invention are those containing from 3 to 6 carbon atoms in the alkyl side chain, especially those compounds in which the alkyl side chain is a straight chain containing from 3 to 6 carbon atoms. Monoalkylated diphenylene sulfides substituted in the nucleus by a halogen atom, e. g. chlorine or bromine, may also be employed in accordance with this invention.

The straight chain monoalkylated diphenylene sulfides of this invention may be readily prepared by reacting diphenylene sulfide with a fatty acid acyl halide containing the same number of carbon atoms as it is desired to have in the side chain of the monoalkylated diphenylene sulfide product and then reducing the monoacylated diphenylene sulfide to the corresponding monoalkyl derivative, e. g. by treatment with zinc amalgam in the presence of mineral acid. The branched chain monoalkylated diphenylene sulfides of this invention may be prepared by condensing an appropriate alkyl halide with diphenylene sulfide in the presence of a condensing agent such as aluminum chloride. While the position of the alkyl group on the diphenylene sulfide nucleus is not regarded as important from the standpoint of insecticidal activity, it is believed that in preparing the monoalkylated diphenylene sulfides by the methods above described, products are produced in which the alkyl group is located mainly at the 2 (or 6) position of the diphenylene sulfide nucleus.

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The insecticides of this invention may be applied to the host, e. g. fruit or foliage or other food of the insect, if chewing insects are to be combatted. They are compatible with and therefore may be used in combination with other stomach or contact insecticides, fungicides, and supplementary materials such as hydrated lime, diluents, sticking, spreading and wetting agents, etc. commonly used in combination with insecticides. The compounds of our invention are usually applied in combination with a carrier therefor, e. g. in the form of an aqueous spray prepared by dispersing the insecticidal compound in an aqueous medium, which may also contain a finely ground clay dispersed therein, or in the form of a dust prepared by dispersing the insecticide in an inert powder, such as a powdered clay.

Several compounds coming within the scope of this invention have been tested to determine their toxicity against the Mexican bean beetle larvae. In carrying out these tests the compounds to be tested were emulsified in an aqueous medium with the aid of Aerosol OT (the active ingredient of which is di-(sec. octyl) sodium sulfosuccinate) to form an emulsion containing the test compound in a concentration of 1:400. Approximately 50 cc. of the emulsion thus prepared were sprayed on each bean plant and the spray permitted to dry. When the spray was dry, 5 to 10 3rd instar bean beetle larvae were placed on each plant and confined thereon by screen cages. At the end of 120 hours the dead and moribund larvae were counted and the percentage control calculated according to the formula:

$$\text{Per cent control} = \frac{X - Y}{X} \times 100$$

wherein X equals percent living on check plant and Y equals percent living on treated plant.

For purposes of comparison tests under the same conditions were also conducted with diphenylene sulfide and a dialkylated diphenylene sulfide. The results of these tests are indicated in the following table:

Compound Tested	Per cent Control
Diphenylene Sulfide	75
Ethyldiphenylene Sulfide	90
n-Propyldiphenylene sulfide	100
n-Butyldiphenylene sulfide	100
Mixed Amyldiphenylene sulfide [1]	95
sec. Amyldiphenylene sulfide	94.1
n-Hexyldiphenylene sulfide	100
n-Heptyldiphenylene sulfide	90
Di-isopropyl diphenylene sulfide	50

[1] Prepared from a mixture of straight and branched chain amyl halides.

The above tests clearly establish the superiority of our monoalkylated diphenylene sulfides over unalkylated or dialkylated diphenylene sulfides.

Tests were also carried out to determine the effectiveness of compounds coming within the scope of this invention when used in dusts for control of Mexican bean beetle larvae. In these tests the test compounds were mixed with an inert clay known as "Pyrax ABB" and the mixture then ground in a ball mill, the proportions being such that dusts containing 10% by weight of the compounds were formed. The dusts were applied to young bean plants and each plant was then infested with five 3rd instar larvae, the larvae being confined on the plant. At the end of 120 hours the dead and moribund larvae were counted and the percentage control calculated by the formula given above. The results obtained were as follows:

Compound Tested	Per cent Control
Diphenylene Sulfide	90
Ethyldiphenylene sulfide	100
n-Propyldiphenylene sulfide	100
n-Butyldiphenylene sulfide	100
n-Hexyldiphenylene sulfide	100

The above tests, in addition to establishing the superiority of the insecticides of this invention over diphenylene sulfide, also demonstrated that when using the preferred compounds of our invention, i. e. those in which the alkyl group contains from 3 to 6 carbon atoms in a straight chain, feeding on the host plant by the insects is far less, so that damage to the plant is much lower than when diphenylene sulfide is used, indicating these preferred compounds have a repellent action as well as a toxic action.

Tests were also conducted with several of the compounds coming within the scope of this invention to determine their effectiveness for control of codling moth larvae. In carrying out these tests bentonite and water were mixed in the proportions of one part of bentonite to 200 parts of water, and sufficient of the test compound was then added to the bentonite-water mixture to form a suspension in which the concentration of the test compound was 1:400; the bentonite acts as a sticking agent. Apples were prepared for spraying by plugging the stem and calyx ends with wax and dipping each apple at the calyx end into hot wax to cover the lower fifth of the apple surface. The solution to be tested was then sprayed on the revolving apples with two atomizers; each apple was sprayed until the spray solution started to run off, the apple then permitted to dry, and the dried apple resprayed, this procedure being repeated three times to insure complete coverage of the surface of the apple. Five mature apples were used in each test, each of them being infested with 5 newly hatched codling moth larvae. Percent control was calculated as above described. The results of these tests were as follows:

Compound Tested	Per cent Control
Ethyldiphenylene sulfide	93
n-Propyldiphenylene sulfide	100
n-Butyldiphenylene sulfide	75
tert. Butyldiphenylene sulfide	100
sec. Amyldiphenylene sulfide	100
Mixed Amyldiphenylene sulfide	81.2
n-Hexyldiphenylene sulfide	100

In a test identical with the one above described, a 3:800 dispersion of tert. amyl diphenylene sulfide in water containing no bentonite gave 90.9% control against codling moth larvae as compared with only 63.6% control with diphenylene sulfide under the same conditions.

The following examples illustrate preparation of compounds of this invention. Amounts are given in parts by weight.

Example 1

75 parts of diphenylene sulfide and 45 parts of n-butyryl chloride were dissolved in 439 parts of carbon disulfide. The mixture was cooled to 0° C. and 125 parts of aluminum chloride were added thereto. The mixture was then agitated at from 0° to 5° C. for 6 hours and permitted to stand at 0° C. overnight. Dilute hydrochloric acid was then added to the reaction mixture and the acidified mass was extracted with ether. The ether layer was washed with dilute sodium carbonate, then water and finally dried. n-Butyryldiphenylene sulfide boiling at 205° to 210° C. at 3 mm. pressure was recovered by fractionation.

35 parts of the n-butyryldiphenylene sulfide were dissolved in 87 parts of xylene and the solution was added to a mixture of 24 parts of concentrated hydrochloric acid with zinc amalgam prepared by mixing 100 parts of mossy zinc, 5 to 10 parts of mercuric chloride, 6 parts of concentrated hydrochloric acid, and 100 to 150 parts of water, agitating the mixture for 5 minutes and decanting the aqueous solution. The mixture was then agitated while passing hydrogen chloride therethrough at temperatures between 140° and 150° C. for seven hours. At the end of this time the mixture was permitted to stand for two days, the zinc removed by filtration, and the xylene layer separated, washed with sodium carbonate solution and distilled, whereby n-butyldiphenylene sulfide having a boiling range of between 190° and 192° C. at 3 mm. pressure was recovered.

Example 2

27.6 parts of diphenylene sulfide were dissolved in 63 parts of carbon disulfide, 5 parts of anhydrous aluminum chloride were added thereto and the mixture brought to refluxing temperature. 13.9 parts of tertiary butyl chloride were then added to the refluxing mixture over a period of one and one-half hours; at the end of this time the mixture was refluxed for an additional six hours. The resultant mixture was poured over ice, and the carbon disulfide layer separated,

washed with water and distilled to remove the carbon disulfide. The product was then refractionated whereby tertiary butyldiphenylene sulfide was recovered having a boiling range between 185° and 192° C. at 5 mm. pressure.

Since certain changes may be made in the above products without departing from the scope of the invention, it is intended that all matter in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. An insecticide adapted for combating larvae of chewing insects comprising a monoalkylated diphenylene monosulfide, the alkyl group of which contains from 3 to 6 carbon atoms, admixed with a carrier therefor.

2. An insecticide adapted for combating larvae of chewing insects comprising a monoalkylated diphenylene monosulfide, the alkyl group of which is a straight chain radical containing from 3 to 6 carbon atoms, admixed with a carrier therefor.

3. A monoalkylated diphenylene monosulfide, the alkyl group of which contains from 3 to 6 carbon atoms.

4. A monoalkylated diphenylene monosulfide, the alkyl group of which is a straight chain radical containing from 3 to 6 carbon atoms.

5. A method of combating larvae of chewing insects which comprises applying to the insect host a composition containing as its essential active insecticidal ingredient a monoalkylated diphenylene monosulfide, the alkyl group of which contains from 3 to 6 carbon atoms.

6. A method of combating larvae of chewing insects which comprises applying to the insect host a composition containing as its essential active insecticidal ingredient a monoalkylated diphenylene monosulfide, the alkyl group of which is a straight chain radical containing from 3 to 6 carbon atoms, admixed with a carrier.

7. n-Butyl diphenylene monosulfide.

8. Tert. amyl diphenylene monosulfide.

9. n-Hexyl diphenylene monosulfide.

10. A method of combating larvae of chewing insects which comprises applying to the insect host a composition containing as its essential active insecticidal ingredient n-butyl diphenylene monosulfide.

11. A method of combating larvae of chewing insects which comprises applying to the insect host a composition containing as its essential active insecticidal ingredient tert. amyl diphenylene monosulfide.

12. A method of combating larvae of chewing insects which comprises applying to the insect host a composition containing as its essential active insecticidal ingredient n-hexyl diphenylene monosulfide.

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