

PATENT SPECIFICATION

(11) 1220 056

1220056

NO DRAWINGS

- (21) Application No. 8174/67 (22) Filed 21 Feb. 1967
 (23) Complete Specification filed 2 Feb. 1968
 (45) Complete Specification published 20 Jan. 1971
 (51) International Classification C 07 d 13/10 A 01 n 9/20
 (52) Index at acceptance

C2C 183—188—289 1E1K4 200 202 211 213 221 225
 226 22Y 253 25Y 273—280—287 30Y 340 34Y
 3A13B3 577 627 728 72Y 791 79Y KA

A5E 1C4B2 1C4B3 1C4B4

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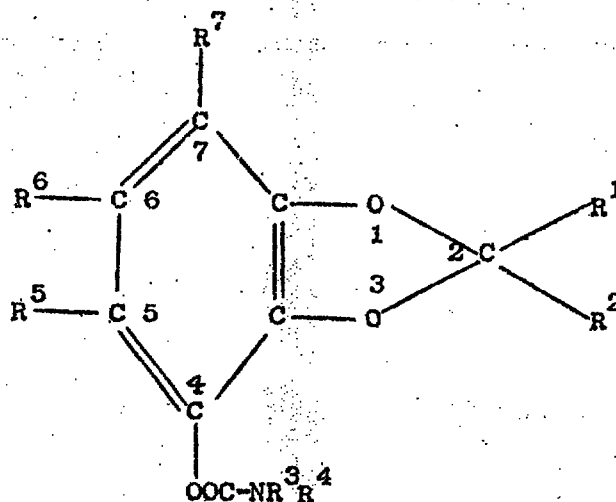


(54) SUBSTITUTED BENZODIOXOLES

(71) We Fisons Pest Control Limited, a British Company, of Harston, Cambridgeshire, 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:—

The present invention relates to certain substituted benzodioxoles which have been found to possess pesticidal activity, to their preparation and to pesticidal compositions containing the same.

Accordingly the present invention is for the substituted benzodioxoles of the formula:—



wherein R¹ and R² are hydrogen or alkyl of 1—6 carbon atoms (e.g. methyl, ethyl or butyl), substituted or unsubstituted, or R¹ and R² together with the linking carbon atom form a cycloalkane or cycloalkene ring of 5 to 7 carbon atoms, and wherein R³ is hydrogen, alkyl of 1—4 carbon atoms (e.g. methyl or ethyl), substituted or unsubstituted, alkanoyl of 2 to 5 carbon atoms (for example acetyl or propionyl) or benzoyl and wherein R⁴ is alkyl of 1—4 carbon atoms (e.g. methyl or ethyl), alkenyl of 2—4 carbon atoms (e.g. allyl) or alkynyl of 2—4 carbon atoms (e.g. propargyl), and R⁵, R⁶ and R⁷ are hydrogen, halogen (chlorine, bromine, iodine or fluorine) or alkyl of 1—4 carbon atoms (e.g. methyl or ethyl), substituted or unsubstituted.

According to a preferred embodiment of the invention R¹ and R² are hydrogen or alkyl of 1 to 6 carbon atoms or together with the linking carbon atom form a cycloalkane ring of 5 to 6 carbon atoms, R³ is hydrogen, alkyl of 1 to 4 carbon atoms, alkanol of 2 to 5 carbon atoms or benzoyl, and R⁵, R⁶ and R⁷ are hydrogen or alkyl of 1 to 4 carbon atoms.

[Price 5s. 0d. (25p)]

The present invention is also for pesticidal compositions comprising as an active ingredient a substituted benzodioxole as identified above, together with a carrier and/or a wetting agent.

5 The present invention is also for the treatment of plants, animals the soil, materials or areas, which comprises applying thereon or thereto a substituted benzodioxole as identified above.

10 The present invention is also for the preparation of the substituted benzodioxoles as identified above which comprises reacting a 4-hydroxyl-1,3-benzodioxole with an isocyanate of the formula R^4NCO or a substituted carbamyl chloride of the formula R^3R^4NCOCl ; in the case of substituted benzodioxoles where R^3 is acyl (i.e. alkanoyl of 2 to 5 carbon atoms or benzoyl), these may be prepared by acylating the corresponding compound where R^3 is hydrogen. The substituted benzodioxoles may also be prepared by reacting a 1,3-benzodioxol-4-chloroformate with an amine or amide of the formula R^3R^4NH . The groups R^3 and R^4 have the significance indicated above.

15 According to a preferred embodiment of the invention the substituted benzodioxole is a compound of the formula above where R^5 , R^6 and R^7 are hydrogen or alkyl of 1 to 4 carbon atoms, and where R^1 and R^2 are methyl groups. Particularly preferred compounds are 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate and 2,2,7-trimethyl-1,3-benzodioxol-4-yl N-methylcarbamate.

20 The substituted benzodioxoles are generally of value as pesticides; they have been found to be of particular value as insecticides, especially against houseflies, caterpillars and aphids. These compounds act as direct insecticides and also have systemic activity. The substituted benzodioxoles are also of value in the control of pests on animals, for example killing ticks on animals, and the invention covers the treatment of animals for this purpose.

25 The substituted benzodioxoles are generally water insoluble and may be formulated in any of the ways commonly adopted for insoluble compounds.

30 For example, the substituted benzodioxoles may be dissolved in a water immiscible solvent, for example a high boiling hydrocarbon, as a carrier, suitably containing dissolved emulsifying agents so that the composition acts as a self-emulsifiable oil on addition to water.

The substituted benzodioxoles may also be admixed with a wetting agent with or without a solid carrier to form a wettable powder which is soluble or dispersable in water, or may be mixed with just a solid carrier to form a solid product.

35 Solid carriers with which the substituted benzodioxoles may be incorporated include clays, sands, talc, mica or solid fertilizers, such products either comprising dust or larger particle size materials.

40 The wetting agents used may comprise anionic compounds such as soaps, fatty sulphate esters such as dodecyl sodium sulphate, octadecyl sodium sulphate and cetyl sodium sulphate, fatty aromatic sulphonates such as alkyl benzene sulphonates or butyl naphthalene sulphonate, more complex fatty sulphonates such as the amide condensation products of oleic acid and N-methyl taurine or the sodium sulphonate of dioctyl succinate.

45 The wetting agents may also comprise non-ionic wetting agents such as condensation products of fatty acids, fatty alcohols or fatty substituted phenols with ethylene oxide, or fatty esters and ethers of sugars or polyhydric alcohols, or the products obtained from the latter by condensation with ethylene oxide, or the products known as block copolymers of ethylene oxide and propylene oxide. The wetting agents may also comprise cationic agents such as cetyl trimethylammonium bromide.

50 The pesticidal composition may also be in the form of an aerosol composition, suitably using a cosolvent and a wetting agent, in addition to the propellant, which is suitably a polyhalogenated alkane such as dichlorodifluoromethane.

55 The pesticidal compositions according to the present invention may contain in addition to the substituted benzodioxoles other active insecticides, bactericides and fungicides. It has been found that particular advantages are obtained with mixtures with other insecticides.

60 In their various applications the compounds of the invention may be used at various rates; thus for example for the treatment of plants for the control of pests on plants the compounds are suitably applied at a rate of about 0.25—16 ounces per acre (17—1120 g. per hectare) and preferably 0.5—4 ounces per acre (35—280 g. per hectare); for the treatment of animals for the control of ticks, the animal is suitably dipped in or sprayed with a solution containing 30—300 parts per million of the active compound.

65 The following Examples are given to illustrate the present invention. The parts and percentages are by weight unless otherwise indicated.

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EXAMPLE 1

2,2-Dimethyl-4-hydroxy-1,3-benzodioxole (14 parts) in benzene (25 parts) was treated with methyl isocyanate (6 parts) and a few drops of triethylamine with cooling. After standing for 30 minutes, the crystals of 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate which formed were filtered off and washed with benzene then with petroleum (boiling point below 40°C.) to yield the pure compound as a white solid, melting point 129—130°C. (16 parts, 85% yield).

Analysis:

Found: C, 59.35; H, 5.90; N, 6.35
 $C_{11}H_{13}NO_2$ requires: C, 59.18; H, 5.87; N, 6.28%

EXAMPLES 2—9

The process of Example 1 was repeated replacing the 2,2-dimethyl-4-hydroxy-1,3-benzodioxole by the appropriate substituted hydroxy-1,3-benzodioxole to form the following compounds:

2-ethyl-2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate, melting point 86—87°C.

2,2-tetramethylene-1,3-benzodioxol-4-yl N-methylcarbamate, melting point 123—124°C.

2,2-pentamethylene-1,3-benzodioxol-4-yl N-methylcarbamate, melting point 90—91°C.

2-tert-butyl-2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate, melting point 89—90°C.

2,2,7-trimethyl-1,3-benzodioxol-4-yl N-methylcarbamate, melting point 146—147°C.

2,2,6-trimethyl-1,3-benzodioxol-4-yl N-methylcarbamate, melting point 136—138°C.

2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate, melting point 135—137°C.
 1,3-benzodioxol-4-yl N-methylcarbamate, melting point 146—148°C.

EXAMPLE 10

A stirred solution of 50 parts of phosgene in 200 parts of benzene was treated over one hour with a solution of 4-hydroxy-2,2-dimethyl-1,3-benzodioxole (33 parts) and dimethylaniline (24 parts) in benzene (150 parts) and stirred for a further 2 hours. The solution was then filtered, washed with water, dried and the 2,2-dimethyl-1,3-benzodioxole-4-yl chloroformate (41 parts, boiling point 83—84°C./0.5 mm.) distilled off.

To a cold stirred solution of sodium carbonate (9.5 parts) and propargylamine hydrochloride (8.2 parts) in water (50 parts) and ether (40 parts) was added a solution of the chloroformate (16 parts) in ether (40 parts). After stirring for one hour, the ethereal solution was washed, dried and evaporated to give 14.9 parts of 2,2-dimethyl-1,3-benzodioxol-4-yl N-propargylcarbamate, melting point 107—109°C.

In a similar way by reacting the chloroformate with allylamine and dimethylamine respectively, the following compounds were prepared:—

2,2-dimethyl-1,3-benzodioxol-4-yl N-allylcarbamate, melting point 93—95°C.

2,2-dimethyl-1,3-benzodioxol-4-yl N,N-dimethylcarbamate, boiling point 119—122°C at 0.5 mm. Hg. pressure.

EXAMPLE 11

EXAMPLE A

A solution of pyrogallol (50 parts) in ethyl methyl ketone (200 parts) was stirred and heated to 50°C, then phosphorus pentoxide (200 parts) was added portionwise at such a rate that the temperature remained about 80°C. After stirring for a further 30 minutes at about 50°C. the liquid layer was poured into cold water (1000 parts) and the crude product isolated by extracting with benzene and evaporating the extracts. The residual liquid was distilled. The product was 4-hydroxy-2-ethyl-2-methyl-1,3-benzodioxole (39.5 parts), boiling point 84—85°C./0.4 mm., melting point 48—50°C.

EXAMPLE B

A solution of pyrogallol (63 parts) in 2,2-dimethoxypropane (100 parts) and benzene (100 parts) containing toluenesulphonic acid (0.01 parts) was slowly distilled

through a fractionating column during 4 hours, removing liquid (150 parts), b.p. 57—64°C. A few drops of triethylamine were then added and the mixture thoroughly washed with water, dried and evaporated. Distillation gave 4-hydroxy-2,2-dimethyl-1,3-benzodioxole (36 parts), boiling point 110°C./0.7 mm., which was purified by recrystallisation from carbon tetrachloride. Melting point 88—90°C.

EXAMPLE 12

In a similar way to Example 11A the following compounds were prepared:—

4-hydroxy-2,2-diethyl-1,3-benzodioxole, melting point 56—58°C.

4-hydroxy-2,2-pentamethylene-1,3-benzodioxole, boiling point 130—134°C. at 0.4 mm. Hg pressure.

4-hydroxy-2,2-tetramethylene-1,3-benzodioxole, melting point 59—62°C.

4-hydroxy-2-tertiarybutyl-2-methyl-1,3-benzodioxole, melting point 79—81°C.

EXAMPLE 13

2,2-Dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate (prepared as in Example 1) (8 parts) was refluxed for 15 minutes in acetic anhydride (40 parts) with a few drops of concentrated sulphuric acid. Sodium acetate (1 part) was added and most of the acetic anhydride was distilled off under vacuum. The remaining oil was poured into water (200 parts) and after standing for 1 hour was extracted into ether three times. The ether solution was washed with aqueous sodium bicarbonate solution and with water, then dried over sodium sulphate. The ether was distilled off under reduced pressure to yield 2,2-dimethyl-2,3-benzodioxol-4-yl N-acetyl-N-methylcarbamate, which recrystallized from petroleum as a yellow crystalline solid, melting point 76—77°C. (5.5 parts, 58% yield).

Analysis:

Found: C, 59.10; H, 5.90; N, 5.05

$C_{13}H_{13}NO_3$ requires: C, 58.86; H, 5.70; N, 5.28%

EXAMPLES 14—15

The process of Example 13 was repeated replacing the carbamate starting material successively by 2,2-dimethyl-1,3-benzodioxol-4-yl N-propargyl carbamate and 2-ethyl-2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate giving 2,2-dimethyl-1,3-benzodioxol-4-yl N-acetyl-N-propargyl carbamate, boiling point 138—140°C./0.5 mm. Hg. pressure and 2-ethyl-2-methyl-1,3-benzodioxol-4-yl N-acetyl-N-methylcarbamate, boiling point 124—126°C./0.4 mm. Hg. pressure.

EXAMPLES 16—19

9 centimetre diameter filter papers treated with aqueous acetone solutions of each of the compounds 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate, 2,2-dimethyl-1,3-benzodioxol-4-yl N-acetyl-N-methylcarbamate and 1,3-benzodioxol-4-yl N-methylcarbamate at rates equivalent to 100 milligrams per square foot (100 mgm./0.09 m²) of the active ingredient were placed in 9 centimetre diameter Petri dishes. Batches of adult female houseflies (*Musca domestica*) lightly anaesthetised with carbon dioxide were then introduced into the dishes and a glass lid placed over each. After 24 hours the flies were examined and were all found to be dead.

EXAMPLES 20—27

7 Centimetre diameter circular discs of cabbage leaves were painted with 1 millilitre aqueous acetone solutions of each of the following compounds:

2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate,

2,2-dimethyl-1,3-benzodioxol-4-yl N-acetyl-N-methylcarbamate,

2,2,7-trimethyl-1,3-benzodioxol-4-yl N-methylcarbamate

2,2-dimethyl-1,3-benzodioxol-4-yl N-allylcarbamate,

2,2-dimethyl-1,3-benzodioxol-4-yl N-propargylcarbamate,

2,2-dimethyl-1,3-benzodioxol-4-yl N-acetyl-N-propargylcarbamate,

2-ethyl-2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate and

2,2-tetramethylene-1,3-benzodioxol-4-yl N-methylcarbamate, in each case at concentrations equivalent to leaf applications of 10, 5, 1, 0.5 and 0.25 pounds per acre (11.2, 5.6, 1.12, 0.56 and 0.28 Kg./hectare) of active ingredient. When the deposit on the leaf discs had dried, each leaf disc was placed in a 9 centimetre diameter Petri dish, infested with ten second instar larvae of the cabbage white butterfly (*Pieris brassicae*) and covered with a glass lid. Three replications were made with

each compound at each concentration level. After 48 hours the larvae were examined and were all found to be dead.

EXAMPLES 28—29

Aqueous suspensions containing 100 parts per million of 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate and 2,2-dimethyl-1,3-benzodioxol-4-yl N-acetyl-N-methylcarbamate were sprayed at a rate equivalent to 50 gallons per acre 585 litres per hectare on young field beans (*Vicia faba*) infested with adult apterous veitch aphids (*Megoura viciae*). After treatment the plants were enclosed in glass cages with gauze tops for ventilation. Each treatment produced complete kill of the aphids in 24 hours as compared with no kill on control plants.

EXAMPLE 30

A wettable powder formulation was made by micronising the following:—

2,2-dimethyl-1,3-benzoxazol-4-yl N-methylcarbamate	25%
Hoe S1/263 (sodium salt of sulphonated condensation product of a long chain alcohol with ethylene oxide)	3%
China Clay	72%

This was suitable for dispersion in water and spraying on plants.

EXAMPLE 31

A 5% granular formulation was made up as follows: Limestone grit and 2% Carbowax (Carbowax is a Registered Trade Mark) were tumbled for 30 minutes. 5% Finely ground 2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate was then added and tumbled for 15 minutes. 1.25% Of Calflo E (a proprietary calcium silicate; Calflo is a Registered Trade Mark) was then added and tumbled for a further 75 minutes to prevent sticking of the granules. The granules were finally sieved through a 12-mesh sieve.

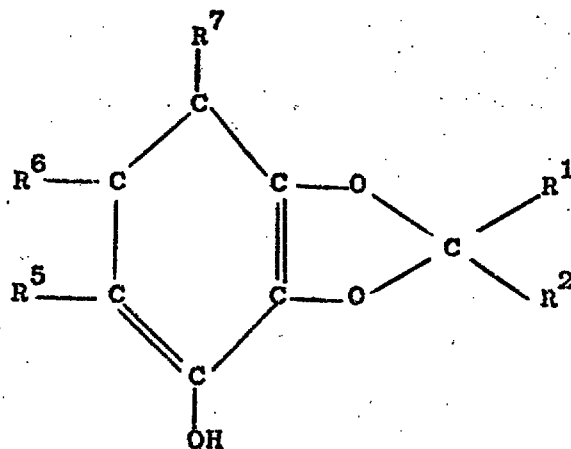
EXAMPLE 32

Cylindrical pads of cotton wool, approximate diameter 1 cm., length 2 cms. were treated with $\frac{1}{2}$ ml. of acetone solutions of the following carbamates:—

2,2-dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate,
2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate,
2,2,7-trimethyl-1,3-benzodioxol-4-yl N-methylcarbamate,
2,2,6-trimethyl-1,3-benzodioxol-4-yl N-methylcarbamate,
2-ethyl-2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate,
2,2-diethyl-1,3-benzodioxol-4-yl N-methylcarbamate,
2-tert-butyl-2-methyl-1,3-benzodioxol-4-yl N-methylcarbamate.

After leaving for 12 hours to dry, the pads were treated with 1 ml. of sheep blood serum and infested with 20 first instar larvae of the sheep blowfly (*Lucilia sericata*). After 24 hours, the blowflies were examined and found to be all dead; insects similarly infested on untreated pads were unaffected.

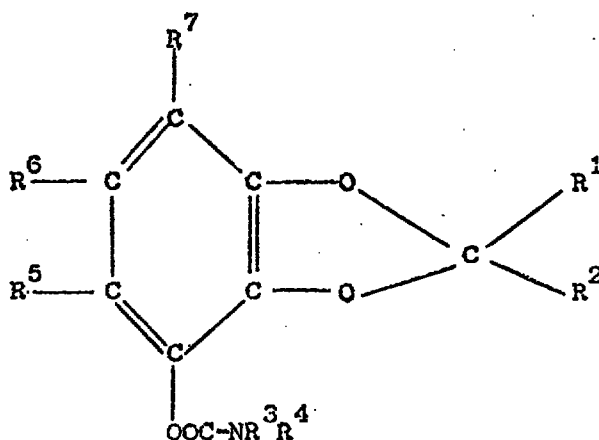
The intermediate hydroxy benzodioxoles of the formula:—



wherein R^1 , R^2 , R^5 , R^6 and R^7 are as defined above, excluding the cases where R^1 and R^2 are hydrogen or methyl when R^5 , R^6 and R^7 are all hydrogen, are new compounds. These compounds are suitably prepared from 1,2,3-trihydroxybenzene (pyrogallol) by reaction with the appropriate ketone in the presence of phosphorus pentachloride using the ketone as solvent.

WHAT WE CLAIM IS:—

1. A pesticidal composition comprising as an active ingredient a substituted benzodioxole of the formula:—



wherein R^1 and R^2 are hydrogen or alkyl of 1 to 6 carbon atoms, substituted or unsubstituted, or R^1 and R^2 together with the linking carbon atom form a cycloalkane or cycloalkene ring of 5 to 7 carbon atoms, where R^3 is hydrogen, alkyl of 1 to 4 carbon atoms, substituted or unsubstituted, alkanoyl of 2 to 5 carbon atoms or benzoyl and R^4 is alkyl of 1 to 4 carbon atoms, alkenyl of 2 to 4 carbon atoms or alkynyl of 2 to 4 carbon atoms, and where R^5 , R^6 and R^7 are hydrogen, halogen or alkyl of 1 to 4 carbon atoms, substituted or unsubstituted, together with a carrier and/or a wetting agent.

2. A pesticidal composition as claimed in claim 1 which contains a wetting agent.

3. A pesticidal composition as claimed in claim 1 or claim 2 which also contains another active material which is an insecticide, bactericide or fungicide.

4. A pesticidal composition as claimed in any of the preceding claims wherein the carrier is a solid.

5. A pesticidal composition as claimed in any of claims 1 to 4 wherein the carrier is a water-immiscible solvent for the substituted benzodioxole.

6. A pesticidal composition as claimed in any of the preceding claims wherein R^5 , R^6 and R^7 are hydrogen or alkyl of 1 to 4 carbon atoms, and wherein R^1 and R^2 are methyl.

7. A pesticidal composition as claimed in claim 1 substantially as hereinbefore described.

8. A pesticidal composition as claimed in claim 1 substantially as hereinbefore described and illustrated in any of the preceding Examples 16—32.

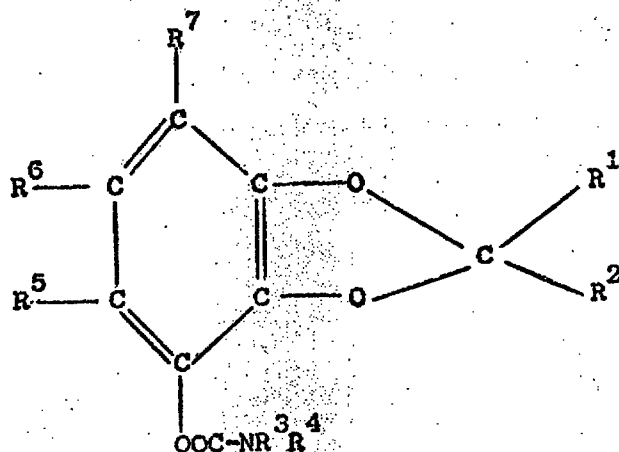
9. The substituted benzodioxoles of the formula:—



wherein R^1 , R^2 , R^5 , R^6 and R^7 are as defined above, excluding the cases where R^1 and R^2 are hydrogen or methyl when R^5 , R^6 and R^7 are all hydrogen, are new compounds. These compounds are suitably prepared from 1,2,3-trihydroxybenzene (pyrogallol) by reaction with the appropriate ketone in the presence of phosphorus pentachloride using the ketone as solvent.

WHAT WE CLAIM IS:—

1. A pesticidal composition comprising as an active ingredient a substituted benzodioxole of the formula:—



wherein R^1 and R^2 are hydrogen or alkyl of 1 to 6 carbon atoms, substituted or unsubstituted, or R^1 and R^2 together with the linking carbon atom form a cycloalkane or cycloalkene ring of 5 to 7 carbon atoms, where R^3 is hydrogen, alkyl of 1 to 4 carbon atoms, substituted or unsubstituted, alkanoyl of 2 to 5 carbon atoms or benzoyl and R^4 is alkyl of 1 to 4 carbon atoms, alkenyl of 2 to 4 carbon atoms or alkynyl of 2 to 4 carbon atoms, and where R^5 , R^6 and R^7 are hydrogen, halogen or alkyl of 1 to 4 carbon atoms, substituted or unsubstituted, together with a carrier and/or a wetting agent.

2. A pesticidal composition as claimed in claim 1 which contains a wetting agent.

3. A pesticidal composition as claimed in claim 1 or claim 2 which also contains another active material which is an insecticide, bactericide or fungicide.

4. A pesticidal composition as claimed in any of the preceding claims wherein the carrier is a solid.

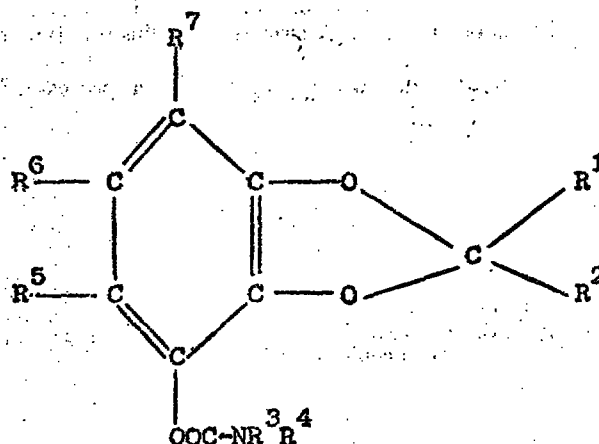
5. A pesticidal composition as claimed in any of claims 1 to 4 wherein the carrier is a water-immiscible solvent for the substituted benzodioxole.

6. A pesticidal composition as claimed in any of the preceding claims wherein R^5 , R^6 and R^7 are hydrogen or alkyl of 1 to 4 carbon atoms, and wherein R^1 and R^2 are methyl.

7. A pesticidal composition as claimed in claim 1 substantially as hereinbefore described.

8. A pesticidal composition as claimed in claim 1 substantially as hereinbefore described and illustrated in any of the preceding Examples 16—32.

9. The substituted benzodioxoles of the formula:—



wherein R^1 and R^2 are hydrogen or alkyl of 1 to 6 carbon atoms, substituted or unsubstituted, or R^1 and R^2 together with the linking carbon atom form a cycloalkane or cycloalkene ring of 5 to 7 carbon atoms, where R^3 is hydrogen, alkyl of 1 to 4 carbon atoms, substituted or unsubstituted, alkanoyl of 2 to 5 carbon atoms, or benzoyl, and R^4 is alkyl of 1 to 4 carbon atoms, alkenyl of 2 to 4 carbon atoms or alkynyl of 2 to 4 carbon atoms, and where R^5 , R^6 and R^7 are hydrogen, halogen or alkyl of 1 to 4 carbon atoms, substituted or unsubstituted.

10. Substituted benzodioxoles as claimed in claim 9 wherein R^1 and R^2 are hydrogen or alkyl of 1 to 6 carbon atoms or together with the linking carbon atom form a cycloalkane ring of 5 or 6 carbon atoms, where R^3 is hydrogen, alkyl of 1 to 4 carbon atoms, alkanoyl of 2 to 5 carbon atoms or benzoyl and where R^5 , R^6 and R^7 are hydrogen or alkyl of 1 to 4 carbon atoms.

11. Substituted benzodioxoles as claimed in claim 10 wherein R^1 and R^2 are methyl.

12. Substituted benzodioxoles as claimed in claim 9 substantially as hereinbefore described and illustrated in any of the Examples.

13. Substituted benzodioxoles as claimed in claim 9 which are specifically named herein.

14. 2,2-Dimethyl-1,3-benzodioxol-4-yl N-methylcarbamate.

15. 2,2,7-Trimethyl-1,3-benzodioxol-4-yl N-methylcarbamate.

16. A process for the treatment of plants, animals, the soil, materials and areas, which comprises applying thereon or thereto a substituted benzodioxole as claimed in any of claims 9—15.

17. A process for the preparation of substituted benzodioxoles as claimed in claim 9 which comprises reacting the corresponding 4-hydroxy-1,3-benzodioxole with an isocyanate of the formula R^3NCO or a substituted carbamyl chloride of the formula R^3R^4NCOCl .

18. A process for the preparation of substituted benzodioxoles as claimed in claim 9 which comprises reacting the corresponding 1,3-benzodioxolyl-4-chloroformate with an amine or amide of the formula R^3R^4NH .

19. A process for the preparation of substituted benzodioxoles as claimed in claim 9 in which R^3 is alkanoyl of 2 to 5 carbon atoms or benzoyl, which comprises acylating the corresponding compound where R^3 is hydrogen.

20. Processes for the preparation of substituted benzodioxoles as claimed in claim 9 substantially as hereinbefore described.



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21. Processes for the preparation of substituted benzodioxoles as claimed in claim 9 substantially as hereinbefore described and illustrated in any of Examples 1—10 and 13—15.

22. Substituted benzodioxoles when prepared by a process as claimed in any of claims 17—21.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1971.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

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