

PATENT SPECIFICATION

(11) 1343 163

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(52) Index at acceptance

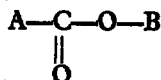
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 1C15D3 1C15E 1C2K 1C5E 1C5J 1C6A2B
 1C6A4 1C6C 1C6D

(54) CYCLOPROPANE CARBOXYLATES, PROCESSES FOR PRODUCING THEM AND COMPOSITIONS CONTAINING THEM

(71) We, SUMITOMO CHEMICAL COMPANY LIMITED, a corporation organized under the laws of Japan, of 15, Kitahama-5-chome, Higashi-ku, Osaka, Japan, 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:—

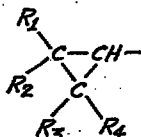
The present invention relates to cyclopropanecarboxylates and insecticidal compositions containing them.

More particularly, according to the present invention there is provided a cyclopropanecarboxylate of the formula (I)

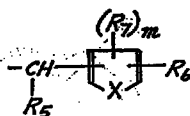


(I)

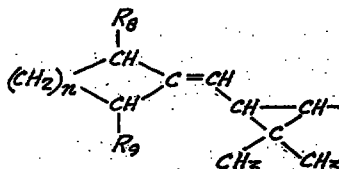
wherein A is a group of the formula



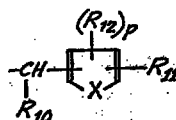
wherein R_1 is a hydrogen atom or a methyl or ethyl group, R_2 is a methyl, ethyl, 2-methyl-1-propenyl or 2-methoxycarbonyl-1-propenyl group when R_1 is a hydrogen atom, or R_2 is a methyl or ethyl group when R_1 is a methyl or ethyl group, and R_3 and R_4 are each independently a hydrogen atom or a methyl or ethyl group, provided that R_1 , R_3 and R_4 are not each simultaneously a hydrogen atom, and B is a group of the formula



wherein R_8 is a C_{2-5} alkynyl or a C_{2-5} alkenyl group, R_9 is a C_{2-5} alkynyl, a C_{2-5} alkenyl or a C_{1-5} alkoxy C_{1-5} alkyl group, R_7 is a C_{1-5} alkyl or a C_{1-5} alkoxy group or a halogen atom, m is 0, 1 or 2, and X is an oxygen or sulfur atom, or A is a group of the formula



wherein R_8 and R_9 are each independently a hydrogen atom or a C_{1-5} alkyl group and n is 1, 2 or 3, and B is a group of the formula



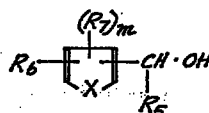
wherein R_{10} is a C_{1-5} alkyl, C_{2-5} alkynyl, C_{2-5} alkenyl or a phenyl group, which phenyl group is unsubstituted, or substituted by a halogen atom, or a C_{1-5} alkyl or a C_{1-5} alkoxy group, R_{11} is a C_{1-5} alkyl, a C_{2-5} alkenyl, a C_{2-5} alkynyl, a C_{1-5} alkoxy- C_{1-5} alkyl, benzyl, furylmethyl or thenyl group, R_{12} is a C_{1-5} alkyl or C_{1-5} alkoxy group or a halogen atom, p is 0, 1 or 2, and X is as defined above. There is also provided an insecticidal composition containing as an active ingredient the said cyclopropanecarboxylate, and an inert carrier substance.

Pyrethrum extract (containing pyrethrin) and analogues thereof, (e.g. synthetic allethrin) have previously been used in environmental sanitation, agriculture and horticulture, because of their prominent insecticidal activities, particularly their rapid knock down effect, without any toxic effect on mammals and because insects can build up hardly any resistance to such insecticidal agents.

On the other hand, they have been found to be unsatisfactory for a wide range of uses because of their relatively high production cost and insufficient persistence properties (i.e. their ability to be effective over a long period of time).

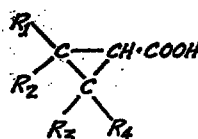
Insecticidal compositions within the present invention have prominent insecticidal activity and can be produced at a lower cost, when compared with those of conventional insecticidal compositions.

The present invention also provides a process for preparing a cyclopropanecarboxylate of the formula (I), which includes reacting an alcohol of the formula (II),



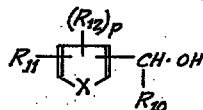
(II)

wherein R_5 , R_6 , R_7 , X and m are as defined above, with a cyclopropanecarboxylic acid of the formula (IV),



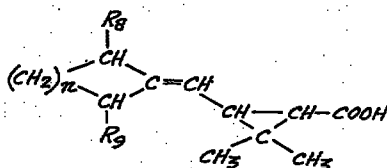
(IV)

wherein R_{11} , R_{12} , R_3 and R_4 are as defined above, or a reactive derivative thereof, or reacting an alcohol of the formula (III),



(III)

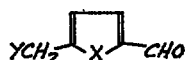
wherein R_{10} , R_{11} , R_{12} , X and p are as defined above, or a reactive derivative thereof, with a cyclopropanecarboxylic acid of the formula (V),



(V)

wherein R_8 , R_9 and n are as defined above, or a reactive derivative thereof, optionally, in the presence of a suitable solvent, a reaction promoting agent and an esterification catalyst.

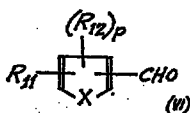
Alcohols represented by the formula (II) are novel compounds and may easily be prepared by reacting an aldehyde represented by the formula,



wherein X is as defined above and Y is a chlorine or bromine atom, with an ethynyl-magnesium halide.

In processes within the present invention, the reactive derivative of the alcohol of the formula (III) which can be used includes an alcohol in which the hydroxy group in the molecule is replaced by a halogen atom or a tosyloxy group, the reactive derivative of the cyclopropanecarboxylic acid of the formula (IV) includes an acid halide and an anhydride thereof and the reactive derivative of the cyclopropanecarboxylic acid of the formula (V) includes an acid halide, an anhydride, a C_{1-5} alkyl ester and an alkali metal salt thereof. All of these reactive derivatives may be prepared easily using a conventional procedure, for example, the reactive derivative of the cyclopropanecarboxylic acid (IV) may be prepared by using a thionyl halide, a phosphorus chloride or acetic anhydride.

The cyclopropanecarboxylic acid of the formula (V) which is used in a process within the present invention may be prepared by the process described in C.R. Acad. Sc. Paris, 1969, P.2199 by Leon Velluz et al. The alcohol of the formula (III) may be prepared by reacting a corresponding aldehyde of the formula (VI),



(VI)

wherein R_{11} , R_{12} , X and P are as defined above, with a Grignard compound of the formula (VII),



(VII)

wherein R_{10} is as defined above, and Y is a halogen atom such as bromine or iodine.

Processes within the present invention will be explained in more detail below.

When the cyclopropanecarboxylic acid per se is used, the reaction with the alcohol is controlled under anhydrous conditions using a dehydrating agent such as dicyclohexylcarbodiimide in the presence of a suitable inert solvent at room temperature or at an elevated temperature, when the desired compound can be obtained in a high yield.

When a halide of the cyclopropanecarboxylic acid is used, the reaction with the alcohol is carried out to completion at room temperature in the presence of an organic tertiary base such as pyridine or triethylamine as a dehydro-halogenation agent. The halide used may optionally be any halide, but is usually an acid chloride. In this reaction, it is preferable to use an inert solvent such as benzene, toluene or petroleum benzene, when the reaction proceeds more smoothly.

Further when an acid anhydride is used as the reactive derivative of the cyclopropanecarboxylic acid, the reaction with the alcohol may be conducted without a reaction promoting agent at room temperature. In this reaction, it is preferable to conduct the reaction at an elevated temperature in order to accelerate the reaction, and it is also preferable to use an inert solvent such as toluene or xylene in order to allow the reaction to proceed more smoothly, but they are not always necessary.

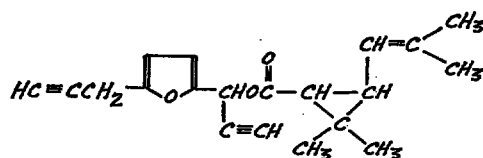
The cyclopropanecarboxylates represented by the formula (I), of course, include their geometrical isomers which exist due to the stereoisomeric nature of the cyclopropanecarboxylic acids of the formulae (IV) and (V), and their optical isomers which exist due to the asymmetric carbon atom of the alcohols of the formulae (II) and (III), and of the cyclopropanecarboxylic acids of the formulae (IV) and (V).

Using processes within the present invention, the following compounds can easily be prepared, but the present invention is not limited to these.

Compound No.

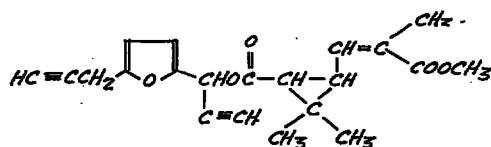
Formula

(1)



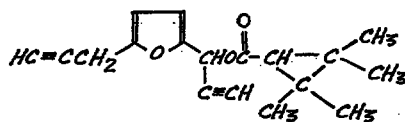
5-Propargyl- α -ethynylfurfurylchrysanthemate

(2)



5-Propargyl- α -ethynylfurfurylpyrethrate

(3)



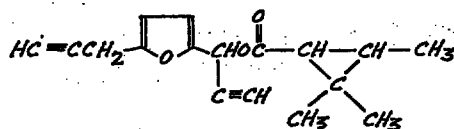
5-Propargyl- α -ethynylfurfuryl 2',2',3',3'-tetramethylcyclopropanecarboxylate

Compound No.

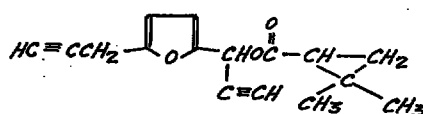
Formula

(4)

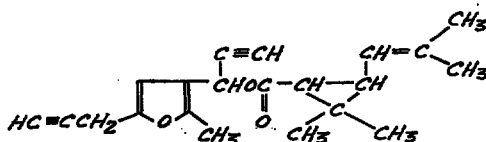
(12)

5-Propargyl- α -ethynylfurfuryl 2',2',3'-trimethylcyclopropanecarboxylate

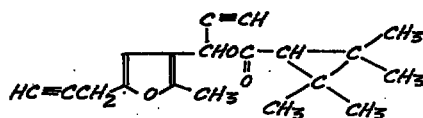
(5)

5-Propargyl- α -ethynylfurfuryl-2',2'-dimethylcyclopropanecarboxylate

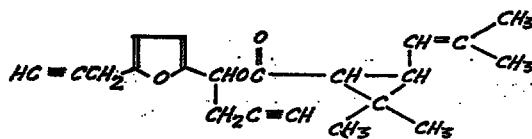
(6)

2-Methyl-5-propargyl-3-(α -ethynyl)furylmethylchrysanthemate

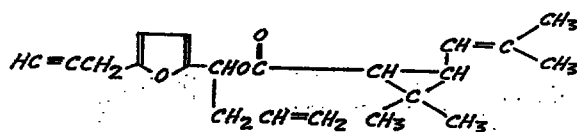
(7)

2 - Methyl - 5 - propargyl - 3 - (α - ethynyl)furylmethyl 2',2',3',3' - tetramethyl-cyclopropanecarboxylate

(8)

5-Propargyl- α -propargylfurfurylchrysanthemate

(9)

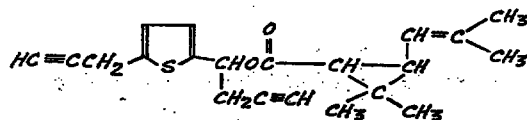
5-Propargyl- α -allylfurfurylchrysanthemate

Compound No.

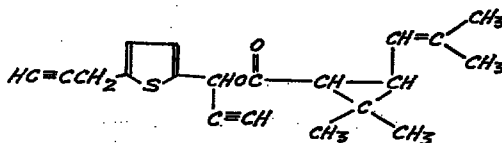
Formula

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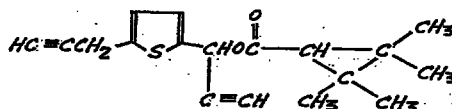
(10)

5-Propargyl-2-(α -propargyl)thenylchrysanthemate

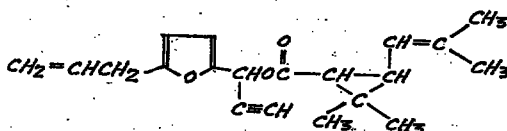
(11)

5-Propargyl-2-(α -ethynyl)thenylchrysanthemate

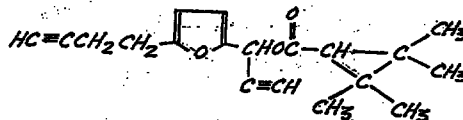
(12)

5-Propargyl-2-(α -ethynyl)thenyl 2',2',3',3'-tetramethylcyclopropanecarboxylate

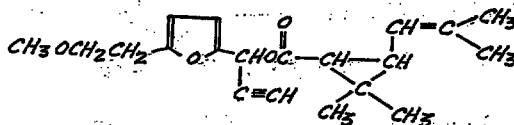
(13)

5-Allyl- α -ethynylfurfurylchrysanthemate

(14)

5-(3'-Butynyl)- α -ethynylfurfuryl 2',2',3',3'-tetramethylcyclopropanecarboxylate

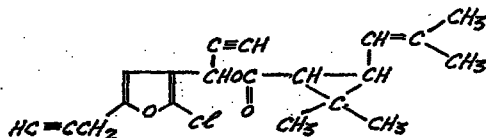
(15)

5-Methoxyethyl- α -ethynylfurfurylchrysanthemate

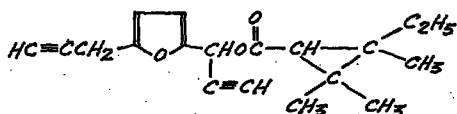
Compound No.

Formula

(16)

2-Chloro-5-propargyl-3-(α -ethynyl)furylmethylchrysanthemate

(17)

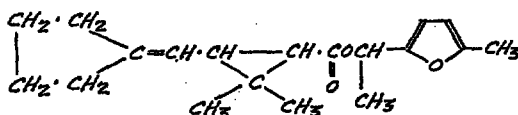


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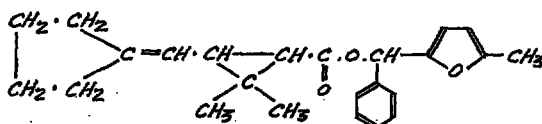
5-Propargyl- α -ethynylfurfuryl 2',2',3'-trimethyl-3'-ethylcyclopropanecarboxylate

5

(18)

5-Methyl- α -methylfurfuryl 2'-cyclopentylidenemethyl-3',3'-dimethylcyclopropane-1'-carboxylate

(19)

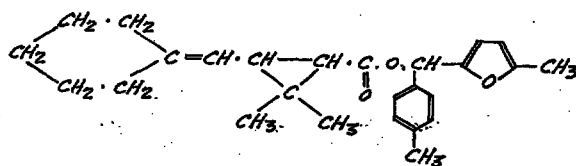


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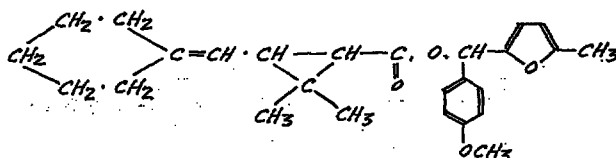
5-Methyl- α -phenylfurfuryl 2'-cyclopentylidenemethyl-3',3'-dimethylcyclopropane-1'-carboxylate

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(20)

5-Methyl- α -(p-tolyl)furfuryl 2'-cyclohexylidenemethyl-3',3'-dimethylcyclopropane-1'-carboxylate

(21)



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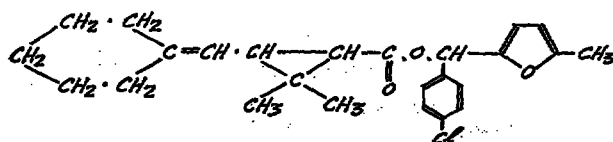
5-Methyl- α -(p-anisyl)furfuryl 2'-cyclohexylidenemethyl-3',3'-dimethylcyclopropane-1'-carboxylate

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Compound No.

Formula

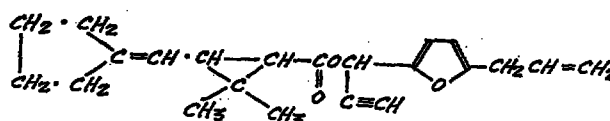
(22)



5 - Methyl - α - (p - chlorophenyl)furfuryl 2' - cyclohexylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

(23)

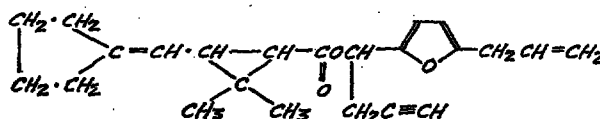
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5

5 - Allyl - α - ethynylfurfuryl 2' - cyclopentylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

(24)

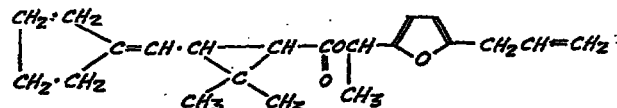


10

5 - Allyl - α - propargylfurfuryl 2' - cyclopentylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

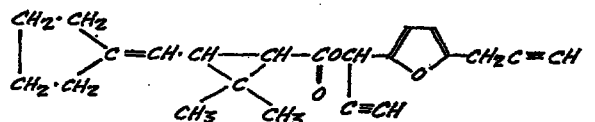
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(25)



5 - Allyl - α - methylfurfuryl 2' - cyclopentylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

(26)

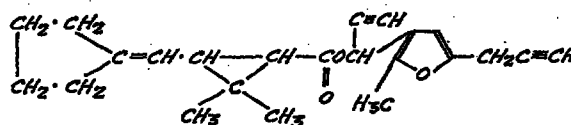


15

5 - Propargyl - α - ethynylfurfuryl 2' - cyclopentylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

15

(27)

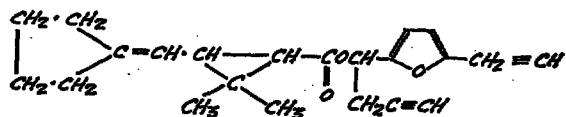


2 - Methyl - 5 - propargyl - 3 - (α - ethynyl)furylmethyl 2' - cyclopentylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

Compound No.

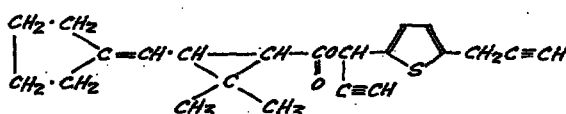
Formula

(28)



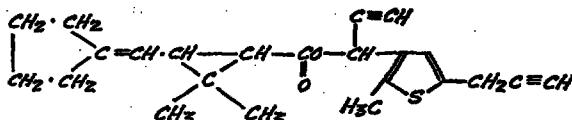
5 - Propargyl - α - propargylfurfuryl 2' - cyclopentylidenemethyl - 3',3' - dimethyl-
cyclopropane - 1' - carboxylate

(29)



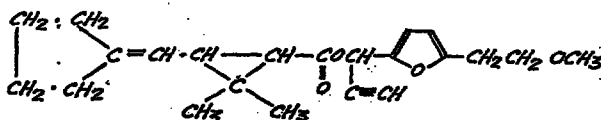
5 - Propargyl - 2 - (α - ethynyl)thenyl 2' - cyclopentylidenemethyl - 3',3' - dimethyl-
cyclopropane - 1' - carboxylate

(30)



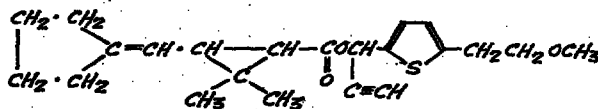
2 - Methyl - 5 - propargyl - 3 - (α - ethynyl)thenyl 2' - cyclopentylidenemethyl - 3',3' -
dimethylcyclopropane - 1' - carboxylate

(31)



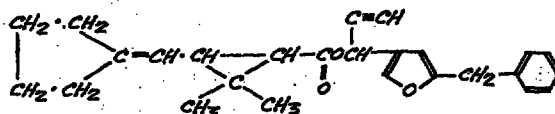
5 - (2' - Methoxyethyl) - α - ethynylfurfuryl 2'' - cyclopentylidenemethyl - 3'',3'' -
dimethylcyclopropane - 1'' - carboxylate

(32)



5 - (2' - Methoxyethyl) - 2 - (α - ethynyl)thenyl 2'' - cyclopentylidenemethyl - 3'',3'' -
dimethylcyclopropane - 1'' - carboxylate

(33)

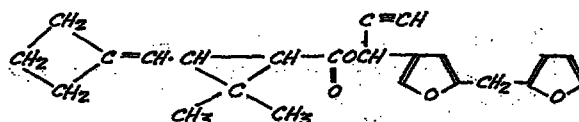


5 - Benzyl - 3 - (α - ethynyl)furylmethyl 2' - cyclopentylidenemethyl - 3',3' - di-
methylcyclopropane - 1' - carboxylate

Compound No.

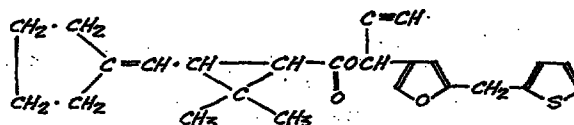
Formula

(34)



5 - Furfuryl - 3 - (α - ethynyl)furylmethyl 2' - cyclobutylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

(35)



5 - (2' - Thenyl) - 3 - (α - ethynyl)furylmethyl 2' - cyclopentylidenemethyl - 3',3' - dimethylcyclopropane - 1' - carboxylate

Processes within the present invention will be illustrated in more detail with reference to the following standard reactions.

A. Reaction between the alcohol and the carboxylic acid halide

A solution of 0.05 mol of the alcohol in 3 times its own volume of dry benzene is mixed with 0.075 to 0.15 mol of pyridine. 0.05 to 0.053 mol of the carboxylic acid chloride is dissolved in 3 times its own volume of dry benzene, and the resulting solution is added dropwise to the solution previously prepared above, when an exothermic reaction proceeds. The reaction mixture is allowed to stand overnight with stirring, and is thereafter mixed with cool water to dissolve the pyridine hydrochloride thus deposited, and the aqueous layer is separated. The organic layer is washed with 5% aqueous hydrochloric acid solution, an aqueous solution saturated with sodium bicarbonate, and an aqueous solution saturated with sodium chloride in this order, and is dried over anhydrous sodium sulfate. Benzene is thereafter distilled out, and the residue is optionally, purified by means of, for example, silica gel chromatography or recrystallization, when the desired compound is obtained.

B. Dehydration reaction between the alcohol and the carboxylic acid

A mixture of 0.05 mol of each of the alcohol and the carboxylic acid in 3 times its own volume of benzene, and 0.08 mol of dicyclohexylcarbodiimide is allowed to stand over night in a sealed vessel. The mixture is then heated under reflux for 2 hours to complete the reaction, and is thereafter cooled. The dicyclohexylurea thus deposited is separated by filtration, and the filtrate is treated using a procedure similar to that of the standard process A, when the desired compound is obtained.

C. Reaction between the alcohol and the carboxylic acid anhydride

A solution of 0.05 mol of the alcohol in 3 times its own volume of toluene is mixed with 0.05 mol of the carboxylic anhydride (prepared by the reaction between the carboxylic acid and acetic anhydride), and the mixture is heated at 100°C for 3 hours, and is thereafter cooled and neutralized with a 5 to 10% aqueous sodium hydroxide solution to recover the carboxylic acid by-product. The organic layer is treated using a procedure similar to that of the standard process A, when the desired compound is obtained.

D. Ester interchange between the alcohol and the lower alkyl ester of the carboxylic acid

A mixture of 0.05 mol of the alcohol and 0.05 mol of the ethyl cyclopropanecarboxylate in 5 times its own volume of toluene, and 0.005 mol of sodium ethoxide is heated under reflux, and the ethanol produced during the reaction is removed by formation of an azeotropic mixture with toluene using a rectifying column. The reaction mixture is thereafter mixed with cool water, and the organic layer separated is treated using a procedure similar to that of the standard process A, when the desired compound is obtained.

E. Reaction between the halide derived from the alcohol and the carboxylic acid

Into a solution of 0.05 mol of the halide derived from the alcohol and 0.06 mol of the carboxylic acid in 3 times its own volume of acetone, kept at 15 to 20°C, a solution of 0.08 mol of triethylamine in 3 times its own volume of acetone is added dropwise, while being stirred. After the dropwise addition, the mixture is refluxed for 2 hours to complete the reaction, and is cooled. Triethylamine hydrochloride deposited is separated by filtration and acetone is removed from the filtrate. The residual liquid is mixed with 3 times its own volume of benzene, and the mixture is treated using a procedure similar to that of the standard process A, when the desired ester is obtained.

F. Reaction between the tosylate of the alcohol and the carboxylic acid salt.

Into a solution of 0.05 mol of the tosylate in 3 times its own volume of acetone, 0.06 mol of the sodium carboxylate (prepared by reacting the carboxylic acid with an equimolar amount of sodium hydroxide in water, and removing the water by distillation) is added gradually at room temperature, while being stirred. After the addition, the mixture is refluxed for 30 minutes to complete the reaction. The solid deposited is separated by filtration, after cooling, and acetone is removed from the filtrate. The residue is dissolved in 3 times its own volume of benzene, and the solution is treated using a procedure similar to that of the standard process A, when the desired compound is obtained.

In carrying out the standard processes mentioned above, the amounts of the starting materials, may optionally be decreased in a fixed ratio. As an Example, the results obtained when the compound (I) was synthesized using the standard process (A) from the carboxylic halide and the alcohol as shown.

Example of the synthesis.

A solution of 2.0 g (0.013 mol) of 5-propargyl- α -ethynylfurfuryl alcohol and 2.9 g (0.037 mol) of pyridine in 30 ml of dry benzene was cooled and kept at 10°C or below with ice, and a solution of 2.3 g (0.013 mol) of chrysanthemoyl chloride in 5 ml of dry benzene was added dropwise thereto. The ice-water bath was removed after the addition, and the mixture was stirred at room temperature overnight to complete the reaction. The reaction mixture was poured into cool water to dissolve pyridine hydrochloride deposited, and the organic layer was thereafter isolated. The organic layer was washed with 5% aqueous hydrochloric acid solution, a saturated aqueous solution of sodium bicarbonate and a saturated aqueous solution of sodium chloride, and was dried over anhydrous sodium sulfate. Benzene was distilled off under a reduced pressure, when 3.8 g of a yellowish orange oil of 5-propargyl- α -ethynylfurfuryl chrysanthemate (n_D^{25} 1.5049) was obtained.

Elemental Analysis

	C (%)	H (%)
Found	77.48	7.20
Calculated	77.39	7.15
(as $C_{20}H_{22}O_3$)		

The results obtained using the standard processes are shown in the following Table.

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester			
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n _D ²⁵)	Elemental analysis C H S
1	α -[5-propargyl-furyl-2] prop-2-ynyl alcohol	chrysanthemic acid chloride	A	(1)	87	1.5049	Found 77.48 7.20 Calc'd 77.39 7.15 (as C ₂₀ H ₂₂ O ₃)
2	α -[5-propargyl-furyl-2] prop-2-ynyl alcohol	pyrethric acid chloride	A	(2)	85	1.5174	Found 71.28 6.29 Calc'd 71.17 6.26 (as C ₂₁ H ₂₂ O ₆)
3	α -[5-propargyl-furyl-2] prop-2-ynyl alcohol	2,2,3,3-tetra-methylcyclopropanecarboxylic acid chloride	A	(3)	88	(m.p.: 77.5°—78.5°C)	Found 76.23 7.19 Calc'd 76.03 7.09 (as C ₁₈ H ₂₀ O ₃)
4	α -[5-propargyl-furyl-2] prop-2-ynyl alcohol	2,2,3-trimethyl-cyclopropane-carboxylic acid chloride	A	(4)	85	1.4921	Found 75.32 6.80 Calc'd 75.53 6.71 (as C ₁₇ H ₁₈ O ₃)

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester			
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n_D^{25})	Elemental analysis C H S
5	α -[5-propargyl-furyl-2] prop-2-ynyl alcohol	2,2-dimethylcyclopropanecarboxylic acid chloride	A	(5)	88	1.4962	Found 74.71 6.21 Calc'd 74.98 6.29 (as $C_{19}H_{18}O_3$)
6	α -[2-methyl-5-propargylfuryl-3] propargyl alcohol	chrysanthemic acid chloride	A	(6)	81	1.5037	Found 77.39 7.41 Calc'd 77.45 7.46 (as $C_{21}H_{24}O_3$)
7	α -[2-methyl-5-propargylfuryl-3] propargyl alcohol	2,2,3,3-tetramethylcyclopropanecarboxylic acid chloride	A	(7)	80	1.4936	Found 76.39 7.38 Calc'd 76.48 7.43 (as $C_{19}H_{22}O_3$)
8	α -[5-propargyl-furyl-2] but-3-ynyl alcohol	chrysanthemic acid chloride	A	(8)	83	1.4700	Found 77.91 7.55 Calc'd 77.75 7.46 (as $C_{21}H_{24}O_3$)
9	α -[5-propargyl-furyl-2] but-3-enyl alcohol	chrysanthemic acid chloride	A	(9)	88	1.4747	Found 77.40 8.18 Calc'd 77.27 8.03 (as $C_{21}H_{26}O_3$)

20

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester					
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n _D ²⁵)	Elemental analysis		
							C	H	S
10	α-[5-propargyl-thienyl-2] but-3-ynyl alcohol	chrysanthemic acid chloride	A	(10)	83	1.4970	Found 74.19 Calc'd 74.08 (as C ₃₁ H ₃₄ O ₂ S)	7.20 7.10	9.38 9.42
11	α-[5-propargyl-thienyl-2] prop-2-ynyl alcohol	chrysanthemic acid chloride	A	(11)	82	1.5272	Found 73.38 Calc'd 73.58 (as C ₂₉ H ₃₂ O ₂ S)	6.65 6.79	9.78 9.82
12	α-[5-propargyl-thienyl-2] prop-2-ynyl alcohol	2,2,3,3-tetra-methylcyclopropanecarboxylic acid chloride	A	(12)	85	1.5226	Found 71.65 Calc'd 71.96 (as C ₁₈ H ₂₀ O ₂ S)	6.78 6.71	10.70 10.67
13	α-[5-allylfuryl-2] prop-2-ynyl alcohol	chrysanthemic acid chloride	A	(13)	82	1.4986	Found 76.79 Calc'd 76.89 (as C ₃₀ H ₃₄ O ₃)	7.74 7.74	— —
14	α-[5-but-3-ynyl-furyl-2] prop-2-ynyl alcohol	2,2,3,3-tetra-methylcyclopropanecarboxylic acid chloride	A	(14)	84	1.4774	Found 76.55 Calc'd 76.48 (as C ₁₉ H ₂₂ O ₃)	7.53 7.43	— —

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester			
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n _D ²⁵)	Elemental analysis C H S
15	α -[5-methoxy-ethylfuryl-2]prop-2-ynyl alcohol	chrysanthemetic acid chloride	A	(15)	83	1.4960	Found 72.69 7.91 — Calc'd 72.70 7.93 — (as C ₂₀ H ₂₆ O ₄)
16	α -[2-chloro-5-propargylfuryl-3]prop-2-ynyl alcohol	chrysanthemetic acid chloride	A	(16)	78	1.5120	Found 69.70 6.08 10.11 Calc'd 69.66 6.14 10.28 (as C ₂₀ H ₂₁ O ₈ Cl)
17	α -[5-propargyl-furyl-2]prop-2-ynyl alcohol	2,2,3-trimethyl-3-ethylcyclopropanecarboxylic acid chloride	A	(17)	82	1.4772	Found 76.19 7.55 — Calc'd 76.48 7.43 — (as C ₁₉ H ₂₂ O ₃)
18	α -[5-methylfuryl-2]ethanol	2-cyclopentyl-idenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(18)	94	1.5061	Found 75.53 8.69 — Calc'd 75.46 8.67 — (as C ₁₉ H ₂₈ O ₃)
19	α -[5-methylfuryl-2]benzyl chloride	2-cyclopentyl-idenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid	E	(19)	86	1.5555	Found 78.98 7.81 — Calc'd 79.09 7.74 — (as C ₂₄ H ₂₈ O ₃)

22

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester			
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n _D ²⁵)	Elemental analysis
							C
20	α -[5-methylfuryl-2] p-methylbenzyl alcohol	2-cyclohexylidene-methyl-3,3-dimethylcyclopropane-1-carboxylic acid	B	(20)	88	1.5565	Found 79.44 8.15 Calc'd 79.55 8.22 (as C ₂₈ H ₃₂ O ₃)
21	α -[5-methylfuryl-2] p-methoxybenzyl alcohol	2-cyclohexylidene-methyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(21)	91	1.5572	Found 76.58 7.81 Calc'd 76.44 7.90 (as C ₂₈ H ₃₂ O ₄)
22	α -[5-methylfuryl-2] p-chlorobenzyl alcohol	2-cyclohexylidene-methyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(22)	95	1.5578	Found 72.83 7.15 8.67 Calc'd 72.71 7.08 8.59 (as C ₂₈ H ₃₂ O ₃ Cl) (Cl)
23	α -[5-allylfuryl-2] prop-2-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid ethyl ester	D	(23)	83	1.5153	Found 77.95 7.81 Calc'd 78.08 7.74 (as C ₂₈ H ₃₆ O ₃)

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester			
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n _D ²⁰)	Elemental analysis C H S
24	α -[5-allylfuryl-2]but-3-ynyl alcohol	2-cyclopentylidene-methyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(24)	92	1.5244	Found 78.24 8.19 Calc'd 78.37 8.01 (as C ₂₉ H ₃₈ O ₂)
25	α -[5-allylfuryl-2]ethanol	2-cyclopentylidene-methyl-3,3-dimethylcyclopropane-1-carboxylic acid anhydride	C	(25)	85	1.5116	Found 76.86 8.71 Calc'd 76.79 8.59 (as C ₂₁ H ₂₈ O ₂)
26	α -[5-propargyl-furyl-2] prop-2-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(26)	94	1.5216	Found 78.69 7.28 Calc'd 78.54 7.19 (as C ₂₂ H ₂₄ O ₂)
27	α -[2-methyl-5-propargylfuryl-2-] prop-2-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(27)	96	1.5204	Found 78.98 7.31 Calc'd 78.83 7.48 (as C ₂₃ H ₂₆ O ₂)

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester					
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n_D^{25})	Elemental analysis		
							C	H	S
28	α -[5-propargyl-furyl-2] but-3-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(28)	90	1.4867	Found 79.02 7.49 — Calc'd 78.83 7.48 — (as $C_{23}H_{28}O_8$)		
29	α -[5-propargyl-thienyl-2] prop-2-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(29)	93	1.5439	Found 75.03 6.72 9.21 Calc'd 74.96 6.86 9.10 (as $C_{23}H_{24}O_8S$)		
30	α -[2-methyl-5-propargylfuryl-3] prop-2-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(30)	89	1.5260	Found 75.49 7.23 8.58 Calc'd 75.37 7.15 8.75 (as $C_{23}H_{26}O_8S$)		
31	α -[5-methoxyethylfuryl-2] prop-2-ynyl tosylate	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid sodium salt	F	(31)	81	1.4946	Found 74.28 7.86 — Calc'd 74.13 7.92 — (as $C_{23}H_{28}O_4$)		

Compound No.	Starting material		Process	Obtained cyclopropanecarboxylic acid ester					
	Alcohol or derivative thereof	Cyclopropane-carboxylic acid derivative		Compound No.	Yield (%) of theoretical yield	Refractive index (n _D ²⁵)	Elemental analysis		
							C	H	S
32	α-[5-methoxy-ethylthienyl-2] prop-2-ynyl tosylate	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(32)	92	1.5169	Found 70.90 7.79 8.77 Calc'd 70.93 7.58 8.61 (as C ₂₂ H ₂₈ O ₃ S)	(S)	
33	α-[5-benzylfuryl-3] prop-2-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(33)	90	1.5420	Found 80.19 7.15 — Calc'd 80.38 7.26 — (as C ₂₆ H ₂₈ O ₃)	—	
34	α-[5-furfuryl-furyl-3] prop-2-ynyl alcohol	2-cyclobutylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(34)	83	1.5296	Found 75.91 6.58 — Calc'd 75.80 6.64 — (as C ₂₃ H ₂₄ O ₄)	—	
35	α-[5-thenylfuryl-3] prop-2-ynyl alcohol	2-cyclopentylidenemethyl-3,3-dimethylcyclopropane-1-carboxylic acid chloride	A	(35)	87	1.5408	Found 72.81 6.53 8.61 Calc'd 73.06 6.64 8.13 (as C ₂₄ H ₂₆ O ₃ S)	(S)	

The compound numbers referred to in the Examples given hereinafter correspond to the numbers given in the above Table.

28

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Compounds of the formula (I) are novel compounds which can be useful in practice and have better insecticidal properties than those given in Japanese Patent publication No. 11,318/1970, published in the official gazette and the specification of Belgian Patent No. 738,112. The following Reference Examples are given in order to demonstrate their improved properties.

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All percentages and parts given in these Examples are by weight.

Reference Example-1.

10

Two batches of mosquito coils each containing 0.3% and 0.6% respectively of the compounds (1), (3), (4) and (5), 5-allyl- α -methylfurfuryl chrysanthemate (described in Japanese patent publication No. 11,318/1970), 5-benzyl-3-(α -ethynyl)furylmethyl chrysanthemate and allethrin were prepared.

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A group of about twenty adult northern house mosquitoes was introduced in a (70 cm³) glass chamber, and a mosquito coil ignited at both ends was placed centrally at the bottom of the glass chamber. The number of mosquitoes knocked down as a function of lapse of time was then observed over 24 minutes. The test was repeated several times on each mosquito coil, and the 50% knock down time (KT₅₀) was then calculated. Mosquitoes knocked down after 24 minutes were transferred into an observation cage, were fed and were allowed to stand until the next day, and the numbers of dead and alive were observed to calculate the mortality.

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The results of these tests are shown in the following table.

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Insecticidal effects of the mosquito coils on adult northern house mosquitoes:—

(28)

Compound	0.3% Mosquito coil		0.6% Mosquito coil	
	KT ₅₀ (min. sec.)	Mortality (%)	KT ₅₀ (min. sec.)	Mortality (%)
Compound (1)	10'00"	87	7'24"	93
Compound (3)	5'18"	100	3'24"	100
Compound (4)	8'30"	88	5'24"	95
Compound (5)	8'24"	90	5'30"	97
5-Allyl- α -methylfurfuryl chrysanthemate	23'36"	10	21'00"	18
5-Benzyl-3-(α -ethynyl)- furylmethyl chrysanthemate	23'00"	16	19'06"	30
Allethrin	13'30"	43	10'54"	73

Reference Example 2.

Compounds (1), (3) and (4), 5-allyl- α -methylfurfuryl chrystanthemate defined above, 5-benzyl-3-(α -ethynyl)-furylmethyl chrysanthemate defined above and natural pyrethrin were respectively mixed in desired test concentrations with deodorized kerosene.

A group of twenty houseflies was introduced into a (70 cm³) glass chamber, and 0.7 ml of an oil spray of each of the above compositions was sprayed uniformly into the glass chamber under a pressure of 1.5 Kg/cm² by means of a glass atomizer. The number of flies knocked down was observed as a function of lapse of time, and the flies knocked down after 10 minutes were gathered and fed, and then allowed to stand until the next day. The numbers of dead and alive were observed to calculate KT_{50} (time required for killing 50% of the insects) and mortality, which are shown below.

Insecticidal effects of the oil spray on adult houseflies

Compound	Concentration (%)	KT_{50} (sec.)	Mortality (%)
Compound (1)	0.1	125	72
„ (3)	0.1	110	65
„ (4)	0.1	120	36
5-Allyl- α -methylfurfuryl chrysanthemate	0.5	>600	—
5-Benzyl-3-(α -ethynyl)-furfurylmethyl chrysanthemate	0.5	>600	—
Pyrethrin	0.1	138	35

Reference Example 3.

Compounds (1), (3) and (4), 5-allyl- α -methylfurfuryl chrystanthemate mentioned above, 5-benzyl-3-(α -ethynyl)furylmethyl chysanthemate mentioned above and allethrin were respectively mixed with deodorized kersosene to form 0.2% oil sprays.

5 Ml of each of the oil sprays was sprayed for about 7 seconds by means of Campbell's turn table apparatus [Soap and Sanitary chemicals, Vol. 14, No. 6, 119 (1938)], and the shutter was opened 30 seconds after the start of the spray. A group of about 100 adult houseflies previously introduced into a lower part of the apparatus was exposed to descending mist for 10 minutes, and the number of knocked down flies was observed. All of the flies were transferred into an observation cage, were fed and were then allowed to stand until the next day. The number of dead and alive were observed to calculate the mortality. The results are shown below.

Insecticidal effects of the oil spray on adult houseflies: —

Compound	Concentration (%)	Knock down ratio after 10 min. (%)	Mortality (%)
Compound (1)	0.2	100	100
" (3)	0.2	100	100
" (4)	0.2	100	91
5-Allyl- α -methylfurfuryl chrysanthemate	0.2	0	65
5-Benzyl-3-(α -ethynyl)-furylmethyl chrysanthemate	0.2	0	89
Allethrin	0.2	100	74

In the preparation of an insecticidal composition containing a compound within the present invention as an effective ingredient, it is sometimes preferable to dissolve the compound in an organic solvent such as xylol, methylnaphthalene, acetone or trichloroethane, and by adopting the conventional method applied to the pyrethrum extract or allethrin of using a diluent, these compounds may be formulated into any of the conventional forms such as oil sprays, emulsifiable concentrates, wettable powders, dusts aerosols, mosquito coils, fumigants effective on applying electric heating other types of fumigant such as fumigants effective on causing steam vaporization or fumigants compounded with plastic materials or other suitable materials so that the active ingredients are released as vapour even at room temperature, or compounded with granules and, dusts or solids combined with attractants or baits. In addition, compounds within the present invention may be enhanced in their insecticidal effects by the combination with a synergist for pyrethroids, such as 3,4-methylenedioxy-6-propylbenzylbutyldiethyleneglycol ether (hereinafter referred to as piperonylbutoxide), 1,2-methylenedioxy-4-2-(octylsulfinyl)propylbenzene (hereinafter referred to as sulfoxide), 4-(3,4-methylenedioxyphenyl)-5-methyl-1,3-dioxane (hereinafter referred to as sufroxi-ane), N-(2-ethylhexyl)-bicyclo[2,2,1]hept-5-ene-2,3-dicarboxyimide (hereinafter referred to as MGK-264), N-(4-pentynyl)-phthalimide or O-n-propyl-O-propargyl-phenyl phosphonate (hereinafter referred to as NIA-16388) or particularly in the preparation of mosquito coils, it may also be possible to enhance the effect by the addition of a known additive such as terephthalic acid, isophthalic acid or 2,6-di-tertiary-butyl-p-cresol.

On the other hand, a multipurpose insecticidal composition may also be prepared by the combination of compounds within the present invention with other biological materials, for example, a cyclopropanecarboxylic acid ester type insecticide, such as pyrethrum extract, allethrin, N-(chrysanthemoxymethyl)-3,4,5,6-tetrahydrophthalimide (hereinafter referred to as phthalthrin), or 5-benzyl-3-furylmethyl chrysanthemate [hereinafter referred to as Chrysron (a registered trade mark of Sumitomo Chemical Co., Ltd)], an organic chlorine containing insecticide such as DDT or BHC an organic phosphorus containing insecticide such as O,O-dimethyl-O-(3-methyl-4-nitrophenyl) phosphorothioate [hereinafter referred to as Sumithion (a registered trade mark of Sumitomo Chemical Co., Ltd)], or O,O-dimethyl-O-(2,2-dichlorovinyl)phosphate (hereinafter referred to as DDVP), a carbamate type insecticide such as 1-naphthyl N-methylcarbamate, 3,4-dimethylphenyl N-methylcarbamate or 3,5-dimethylphenyl N-methylcarbamate and other insecticides, fungicides, acaricides and herbicides, and with fertilizers and other agricultural chemicals.

The process for the preparation of insecticides will be illustrated with reference to the following Examples, in which the names of the compounds are represented by the compound numbers mentioned above, and parts and % are by weight, and mesh sizes, where given, are those of the U.S. Sieve, i.e. the mesh value is the number of apertures per inch.

Example 36.

0.2 Part of one of each of the compounds (1) to (35) was dissolved respectively in deodorized kerosene to make it up to 100 parts, when a 0.2% oil spray of each compound was obtained.

Example 37.

Mixtures each of 0.2 part of one of the compounds (1), (3), (7), (23), (26), (27) and (33), with 1 part of piperonylbutoxide were respectively dissolved in deodorized kerosene to make each of them up to 100 parts, when an oil spray of each composition was obtained.

Example 38.

Mixtures each of 0.2 part of one of compounds (18), (22), (29) and (30), with 0.2 part DDVP were respectively dissolve in deodorized kerosene to make each of them up to 100 parts, when an oil spray of each composition was obtained.

Example 39.

20 Parts of one of each of the compounds (1), (4), (5), (6), (8), (12), (16) and (17), 10 parts of the emulsifier Sorpol SM-200 (Trade mark of Toho Chemical Co.) and 70 parts of xylene were respectively mixed and dissolved with stirring, when a series of emulsifiable concentrates each containing 20% of one of these compounds was obtained.

Example 40.

20 Parts of one of each of the compounds (29), (30), (32) and (33), 20 parts of sufroxane, 10 parts of the emulsifier Sorpol SM-200 (as mentioned above), and 50 parts of xylene were respectively mixed and dissolved with stirring, when a series of emulsifiable concentrates was obtained.

Example 41.

Solutions each of 1 g of one of the compounds (1), (3), (12), (14) and (15) in 20 ml of methanol were each uniformly mixed, with stirring, with 99 g of a carrier for a mosquito coil (a mixture of Tabu powder, marc and wood powder in a mixing ratio of 3:5:1), and the methanol was evaporated. The mixtures were then each kneaded with 150 ml of water, and the products were made up in a conventional manner and dried, when a series of mosquito coils was obtained.

Example 42.

Using a procedure similar to that described in Example 41, 0.6 g of one of each of the compounds (23), (25), (26), (27), (28) and (31) were treated using 99.4 g of the same carrier as that mentioned in Example 41, when a series of mosquito coils was obtained.

Example 43.

Solution each of 0.3 g of one of the compounds (18), (23), (26), (29) and (33), with 0.3 g of allethrin in 20 ml of methanol were treated using a procedure similar to that described in Example 41, when a series of mosquito coils was obtained.

Example 44.

Solutions each of 1 part of one of the compounds (1), (6), (13) and (15), with 2 parts of sufroxane in 20 parts of acetone were respectively mixed with 97 parts of 300 mesh diatomaceous earth in a mixing and grinding machine. Evaporation of the acetone gave rise to dusts.

Example 45.

The procedure described in Example 44 was repeated except that 1 part of one of each of the compounds (26), (33) and (34), and 96 parts of 300 mesh diatomaceous earth were used, when a series of dusts was obtained.

Example 46.

Solutions each of 0.3 part of one of the compounds (1), (6), (7), (11) and (15), with 0.1 part of phthalthrin and 0.5 part of Sumithion (Trade mark of Sumitomo Chemical Co., Ltd) in 7.5 parts of xylene and 6.6 parts of deodorized kerosene were introduced into an aerosol vessel, which was equipped with a valve portion, and 85 parts of a propellant (a liquified petroleum gas) was forced under pressure into the vessel through the valve portion, when a series of aerosols was obtained.

Example 47.

The procedure described in Example 46 was repeated, except that 0.2 part of one of each of the compounds (19), (26) and (31), 0.2 part of phthalthrin, 0.5 part of

Sumithion, 7.5 parts of xylene and 6.6 parts of deodorized kerosene were used, when a series of aerosols was obtained.

Example 48.

Using a procedure similar to that described in Example 46, 0.2 part of one of each of the compounds (33), (34) and (35), 1 part of pyrethrum, 2 parts of xylene and 6.6 parts of deodorized kerosene were treated to obtain a series of aerosols.

Example 49.

Mixtures each of 0.2 part of one of the compounds (1), (2), (3) and (11), 0.2 part of phthalthrin, 3.2 parts of piperonylbutoxide, 10.4 parts of deodorized kerosene and 1 part of an emulsifier, Atoms 300 (Trade mark of Atlas Chemical Co.) were emulsified in 50 parts of pure water, and the emulsions were introduced into aerosol vessels together with 35 parts of a mixture of deodorized butane and deodorized propane in a mixing ratio of 3:1, whereby a series of water-based aerosols was obtained.

Example 50.

Using a procedure similar to that described in Example 49, mixtures each of 0.2 part of one of the compounds (25), (27) and (28), with 0.2 part of Chrysron (Trade mark of Sumitomo Chemical Co., Ltd.), 2 parts of piperonylbutoxide, 11.6 parts of deodorized kerosene and 1 part of an emulsifier Atmos 300, were treated to obtain a series of water-based aerosols.

Example 51.

Mixtures each of 20 parts of one of the compounds (1) and (14), with 5 parts of 1-naphthyl-N-methylcarbamate and 5 parts of Sorpol SM-200 were kneaded with 70 parts of 300 mesh talc in a mixing and grinding machine, when a series of wettable powders was obtained.

Example 52.

Using a procedure similar to that described in Example 51, mixtures of 20 parts of one of each of the compounds (26) and (33), with 5 parts of 3,4-dimethylphenyl-N-methylcarbamate and 5 parts of Sorpol SM-200 were treated with 70 parts of 300 mesh talc to obtain a series of wettable powders.

Example 53.

Mixtures each of 5 parts of one of the compounds (1), (33) and (35), with 5 parts of the dispersing agent Toyolignin CT (Trade mark of Toyobo Co.) and 90 parts of GSM clay (Trade mark of Zeaklite Co.), were kneaded in a mixing and grinding machine. Water was then added to the mixtures in a 10% amount based on the weight of the mixture, and the products were kneaded further with stirring, granulated by means of a granulator and air-dried, whereby a series of granules was obtained.

Example 54.

Solutions each of 0.2 g of one of the compounds (1), (26) and (27) with 0.2 g of allethrin in a suitable amount of chloroform were impregnated in asbestos having an area of 2.5×1.5 cm² and 0.3 mm thickness, when a series of insecticidal fibrous fumigants effective when heated on a hot plate was obtained. Materials having an effect equivalent to asbestos, for example, pulp plate may also be used as the fibrous carrier.

Example 55.

A solution of 0.2 part of the compound (3) and 0.2 part of Chrysron in 7 parts of xylene and 7.6 parts of deodorized kerosene was treated using a procedure similar to that described in Example 46, when an aerosol was obtained.

Example 56.

Solutions each of 0.3 g of one of the compounds (1), (3), (6), (7) and (15) with 0.2 g of allethrin in 20 ml of methanol were treated using a procedure similar to that described in Example 41, when a series of mosquito coils was obtained.

Example 57.

Solutions each of 0.2 g of one of the compounds (1), (3), (4) and (5) in a suitable amount of chloroform were treated using a procedure similar to that described in Example 54, when a series of fibrous masses each impregnated with an insecticidal fumigant effective when heated on a hot plate was obtained.

Example 58.

A mixture of 0.3 part of the compound (1), 0.1 part of 3-phenoxybenzyl chrysanthemate, 0.8 part of thanite (isobornyl thiocynoacetate: synergist) 6.5 parts of xylene and 7.3 parts of deodorized kerosene was treated using a procedure similar to that described in Example 46, when an aerosol was obtained.

Example 59.

A solution of 0.3 part of the compound (1), 1.5 parts of S-421 (octachlorodipropyl ether: synergist), 6.2 parts of xylene and 7 parts of deodorized kerosene was treated using a procedure similar to that described Example 46, when an aerosol was obtained.

Example 60.

A mixture of 15 parts of the compound (1), 5 parts of Chrysron and 10 parts of the emulsifier Sorpol SM-200 was dissolved in 70 parts of xylene with stirring, when an emulsifiable concentrate was obtained.

Example 61.

A solution of 0.3 g of the compound (1) and 0.2 g of 5-propargylfurfuryl chrysanthemate in 20 ml of methanol was treated using a procedure similar to that described in Example 41, when a mosquito coil was obtained.

Example 62.

A solution of 0.1 g of the compound (1) and 0.1 g of 5-propargyl-2-methyl-3-furylmethylchrysanthemate in a suitable amount of chloroform was treated using a procedure similar to that described in Example 54, when a fibrous bed impregnated with an insecticidal fumigant effective when heated on a hot plate was obtained.

Example 63.

A mixture of 15 parts of the compound (3), 5 parts of DDVP and 10 parts of the emulsifier Sorpol SM-200 was dissolved in 70 parts of xylene with stirring, when an emulsifiable concentrate was obtained.

Insecticidal effects of the compounds will be further illustrated with reference to the following Test Examples.

Test Example 1.

0.5 Ml of each of the oil sprays obtained in Example 36, and a 0.2% oil spray obtained by treating commercially available allethrin (technical grade) using a procedure similar to that described in Example 36 was sprayed by means of the Campbell's turn table apparatus [Soap and Sanitary Chemicals, Vol. 14, No. 6, 119 (1938)], over about 7 seconds. The shutter was opened 30 seconds after starting to spray, and adult houseflies (a group of about 100 flies) previously introduced into a lower part of the apparatus were exposed to a descending mist for 10 minutes, were transferred to an observation cage, fed, and allowed to stand until the next day. A mortality of 74% was observed for allethrin.

When using an oil spray within the present invention, however, 80% or more of flies were killed.

Test Example 2.

About 50 adult northern house mosquitoes were introduced into a (70 cm³) glass chamber, and 0.7 ml of each of the oil sprays obtained in Examples 37 and 38 was sprayed under a pressure of 20 lb. by means of a glass atomizer, when 80% or more of mosquitoes were knocked down within 10 minutes.

Test Example 3.

Insecticidal effects on adult houseflies of aerosols obtained in Examples 46, 47, 48, 49, 50 and 55 were examined by the aerosol testing method using Peet Grady's chamber (6ft³) [Soap and Chemical Specialities, Blue Book (1965)]. The results were as shown in the following table.

Insecticidal effects of the aerosol:—

Composition		Amounts sprayed (g/1000 ft ³)	Knock down ratio %			Mortality (%)
			5 min	10 min	15 min	
Aerosol of Example 46	Compound (1)	3.1	38	76	92	84
	" (6)	2.9	34	72	90	82
	" (7)	3.0	37	78	92	80
	" (11)	3.0	30	71	88	86
	" (15)	3.1	27	69	86	79
Aerosol of Example 49	Compound (1)	2.9	42	80	96	78
	" (2)	2.9	45	85	98	75
	" (3)	3.0	47	87	98	77
	" (11)	3.0	37	80	95	80
Aerosol of Example 55		3.1	35	78	94	78
Aerosol of Example 47	Compound (19)	3.0	27	72	90	80
	" (26)	3.2	35	78	94	84
	" (31)	3.1	32	75	82	81
Aerosol of Example 48	Compound (33)	3.2	24	76	96	85
	" (34)	2.9	21	72	93	84
	" (35)	3.0	19	70	92	82
Aerosol of Example 50	Compound (25)	3.0	26	78	95	82
	" (27)	3.0	28	79	96	85
	" (28)	3.2	22	75	90	80

Test Example 4.

Emulsifiable concentrates obtained in Example 39 and 40 were diluted 20,000 times with water, and 2 litres of the resultant solution were introduced into a polystyrene case having an area of 23×30 cm² and 6 cm depth. About 100 larvae of the northern house mosquito were introduced therein, and on the next day it was found that 80% or more of larvae were killed by each of the emulsifiable concentrates.

Test Example 5.

Rice plants were grown for 45 days after sowing in 1/50,000 Wagner's pots, and those emulsifiable concentrates containing the compounds (1) and (29) from the emulsifiable concentrates obtained Examples 39 and 40, and emulsions obtained by diluting 100 times with water the wettable powders obtained in Examples 51 and 52, were sprayed in an amount of 10 ml/pot. The whole was covered with a wire net and about 30 adult green rice leafhoppers were introduced therein. After one day 80% or more of the adult leafhoppers were dead.

Test Example 6.

200 Mg of each of the dusts obtained in Examples 44 and 45 was mixed with 100 g of unhulled rice with stirring, and the mixture was introduced into a 100 ml glass Erlenmeyer flask. About 50 rice weevils were introduced therein and the flask was covered. After a week, 80% or more of the rice weevils were dead.

Test Example 7.

About 50 adult houseflies were introduced into a (70 cm³) glass chamber, and a battery-driven small motor fan (13 cm blade diameter) was placed in the chamber and rotated. Subsequently, the fibrous mass impregnated with the insecticidal fumigant obtained in Example 54 was placed on an electrically heated plate and vaporized in the chamber. As a result, 80% or more of the flies were knocked down within 20 minutes.

Test Example 8.

Onto the bases of glass Petri dishes of 14 cm diameter, were uniformly dusted each of the dusts obtained in Examples 44 and 45 respectively in a proportion of 2 g/m², and butter was coated on the lower part of the dishes leaving an uncoated portion of 1 cm, in width. Subsequently, a group of about 10 adult German cockroaches was introduced into each of the dishes and contacted with the dust for 30 minutes. As a result, 80% or more of the cockroaches were knocked down, and 70% or more of the knocked-down insects were dead on the third day after contact.

Test Example 9.

Into each of a series of 14 l polythene buckets were introduced 10 l of water, and 2 g of one of each of the dusts obtained in Example 53 were added thereto. After one day, about 100 fully grown larvae of the northern house mosquito were introduced into each bucket, and it found that 90% or more of the larvae were dead.

Test Example 10.

Into each of a series of (70 cm³) glass chambers, a group of about 20 adult northern house mosquitoes were introduced, and a battery-driven small motor fan (13 cm blade diameter) was placed in each of the chambers and was rotated. Mosquito coils each consisting of 1 G one of each of the mosquito coils which were obtained in Examples 41, 42, 43 and 56 were ignited at both ends and one of each of said coils was placed in each chamber. As a result, 90% or more of mosquitoes were killed within 20 minutes by each of the mosquito coils.

Test Example 11.

Two open glass cylinders each having a diameter of 20 cm and being 40 cm in height were placed one upon another, and one of the fibrous masses impregnated with an insecticidal fumigant from those obtained in Examples 57 and 62 was placed on an electric heating plate in the bottom of the lower cylinder. Another glass cylinder having a diameter of 20 cm and being 20 cm in height, both ends of which were covered with a net, and in which 20 adult houseflies were introduced was then placed on top of the above mentioned cylinders, and an electric current was then passed through the plate, when 100% of the adult houseflies were knocked down within 20 minutes by the fumigant. This procedure was repeated for each of the other impregnated fibrous masses obtained in Examples 57 and 62 with the same result.

Test Example 12.

The effects of the insecticidal fumigants obtained in Examples 57 and 62, on german cockroaches were examined using a procedure similar to that described in Test Example 11, and it was found that 100% of the cockroaches were knocked down within 30 minutes by each of the fumigants.

Test Example 13.

Using the same apparatus as that described in Test Example 11 and 1 g of the mosquito coil obtained in Example 61, one side of which was ignited, the smoking effect on adult northern house mosquitoes was examined, and it was found that 100% of the mosquitoes were knocked down within 20 minutes of smoking.

Test Example 14.

A glass cylinder having a 20 cm diameter and 20 cm height, both ends of which were covered with a wire net and in which 20 adult German cockroaches were introduced, was placed on top of another glass cylinder having a diameter of 20 cm and being 40 cm in height. A further glass cylinder having a diameter of 20 cm diameter and being 40 cm in height was then placed thereon. Aerosols obtained in Examples 58 and 59 were respectively sprayed downwardly from the upper side of the cylinder for one second. As a result, 100% of the cockroaches were knocked down within 20 minutes, and the cockroaches knocked down were, 20 minutes thereafter, taken out and allowed to stand at room temperature, when 90% or more of the cockroaches were killed after 2 days.

Test Example 15.

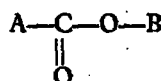
Tomato plants which had been grown for one month after sowing, were dipped for one minute into one of each of the emulsion prepared by diluting 50 and 500 times with water the emulsifiable concentrates obtained in Examples 39, 60 and 63. They were then subjected to air-drying, and transferred to a plastic vessel equipped with a cover. Into the vessel were introduced 28-spotted lady beetles (*Epilachna vigintioctopunctata*) and 80% or more thereof were killed after 5 days by each of the 50 times diluted emulsions. A repellent effect was also confirmed by the fact that almost no damage to the tomato plants treated with the 500 times diluted emulsions was observed, though the beetles were alive.

Test Example 16.

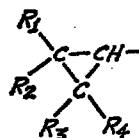
Ten 3rd to 4th instar larvae of the tobacco cutworm (*Prodenia litura*) were introduced into each of a series of glass Petri dishes each 14 cm in diameter, and one ml of one of each of the emulsions prepared by diluting 200 times with water the emulsifiable concentrates obtained in Examples 39, 60 and 63 was sprayed from a spray tower. The cutworms were then transferred to another of a series of Petri dishes in which a bait was placed, and allowed to stand, when 90% or more of the cutworms were dead after 2 days.

WHAT WE CLAIM IS:—

1. A cyclopropanecarboxylate of the formula,



wherein A is a group of the formula



wherein R_1 is a hydrogen atom or a methyl or ethyl group, R_2 is a methyl, ethyl, 2-methyl-1-propenyl or 2-methoxycarbonyl-1-propenyl group when R_1 is a hydrogen atom, or R_2 is a methyl or ethyl group when R_1 is a methyl or ethyl group, and R_3 and R_4 are each independently a hydrogen atom or a methyl or ethyl group, provided that



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Test Example 12.

The effects of the insecticidal fumigants obtained in Examples 57 and 62, on german cockroaches were examined using a procedure similar to that described in Test Example 11, and it was found that 100% of the cockroaches were knocked down within 30 minutes by each of the fumigants.

Test Example 13.

Using the same apparatus as that described in Test Example 11 and 1 g of the mosquito coil obtained in Example 61, one side of which was ignited, the smoking effect on adult northern house mosquitoes was examined, and it was found that 100% of the mosquitoes were knocked down within 20 minutes of smoking.

Test Example 14.

A glass cylinder having a 20 cm diameter and 20 cm height, both ends of which were covered with a wire net and in which 20 adult German cockroaches were introduced, was placed on top of another glass cylinder having a diameter of 20 cm and being 40 cm in height. A further glass cylinder having a diameter of 20 cm diameter and being 40 cm in height was then placed thereon. Aerosols obtained in Examples 58 and 59 were respectively sprayed downwardly from the upper side of the cylinder for one second. As a result, 100% of the cockroaches were knocked down within 20 minutes, and the cockroaches knocked down were, 20 minutes thereafter, taken out and allowed to stand at room temperature, when 90% or more of the cockroaches were killed after 2 days.

Test Example 15.

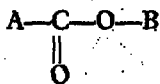
Tomato plants which had been grown for one month after sowing, were dipped for one minute into one of each of the emulsion prepared by diluting 50 and 500 times with water the emulsifiable concentrates obtained in Examples 39, 60 and 63. They were then subjected to air-drying, and transferred to a plastic vessel equipped with a cover. Into the vessel were introduced 28-spotted lady beetles (*Epilachna vigintioctopunctata*) and 80% or more thereof were killed after 5 days by each of the 50 times diluted emulsions. A repellent effect was also confirmed by the fact that almost no damage to the tomato plants treated with the 500 times diluted emulsions was observed, though the beetles were alive.

Test Example 16.

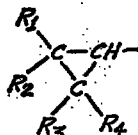
Ten 3rd to 4th instar larvae of the tobacco cutworm (*Prodenia litura*) were introduced into each of a series of glass Petri dishes each 14 cm in diameter, and one ml of one of each of the emulsions prepared by diluting 200 times with water the emulsifiable concentrates obtained in Examples 39, 60 and 63 was sprayed from a spray tower. The cutworms were then transferred to another of a series of Petri dishes in which a bait was placed, and allowed to stand, when 90% or more of the cutworms were dead after 2 days.

WHAT WE CLAIM IS:—

1. A cyclopropanecarboxylate of the formula,



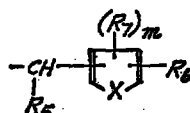
wherein A is a group of the formula



wherein R_1 is a hydrogen atom or a methyl or ethyl group, R_2 is a methyl, ethyl, 2-methyl-1-propenyl or 2-methoxycarbonyl-1-propenyl group when R_1 is a hydrogen atom, or R_2 is a methyl or ethyl group when R_1 is a methyl or ethyl group, and R_3 and R_4 are each independently a hydrogen atom or a methyl or ethyl group, provided that



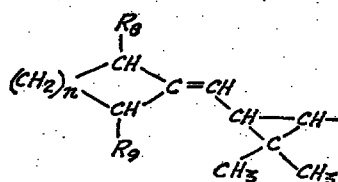
R_1 , R_3 and R_4 are not each simultaneously a hydrogen atom, and B is a group of the formula



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wherein R_5 is a C_{2-5} alkynyl or a C_{2-5} alkenyl group, R_6 is a C_{2-5} alkynyl, a C_{2-5} alkenyl or a C_{1-5} alkoxy- C_{1-5} alkyl group, R_7 is a C_{1-5} alkyl or a C_{1-5} alkoxy group or a halogen atom, m is 0, 1 or 2, and X is an oxygen or sulphur atom, or A is a group of the formula,

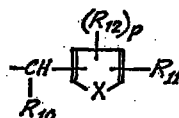
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wherein R_8 and R_9 are each independently a hydrogen atom or a C_{1-5} alkyl group and n is 1, 2 or 3, and B is a group of the formula,

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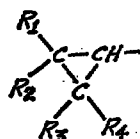


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wherein R_{10} is a C_{1-5} alkyl, a C_{2-5} alkynyl, a C_{2-5} alkenyl or a phenyl group, which phenyl group is unsubstituted, or substituted by a halogen atom or a C_{1-5} alkyl or C_{1-5} alkoxy group, R_{11} is a C_{1-5} alkyl, a C_{2-5} alkenyl, a C_{2-5} alkynyl, a C_{1-5} alkoxy- C_{1-5} alkyl, benzyl, furylmethyl or thenyl group, R_{12} is a C_{1-5} alkyl or C_{1-5} alkoxy group or a halogen atom, p is 0, 1 or 2, and X is as defined above.

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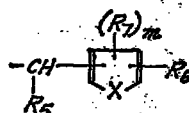
2. A cyclopropanecarboxylate according to claim 1, wherein A is the group of the formula



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wherein R_1 , R_2 , R_3 and R_4 are as defined in claim 1, and B is the group of the formula,

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wherein R_5 , R_6 , R_7 , X and m are as defined in Claim 1.

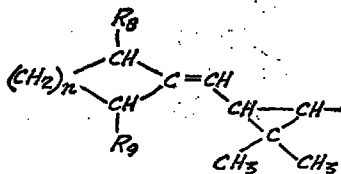


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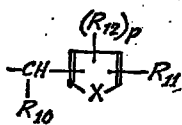
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3. A cyclopropanecarboxylate according to Claim 1, wherein A is the group of the formula

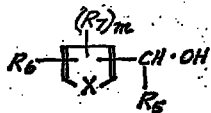


wherein R_8 , R_9 and n are as defined in Claim 1, and B is the group of the formula

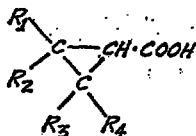


wherein R_{10} , R_{11} , R_{12} and p are as defined in Claim 1.

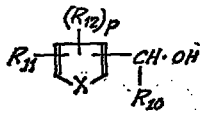
4. A process for the production of a cyclopropanecarboxylate represented by the formula given and defined in Claim 1 which includes reacting an alcohol of the formula



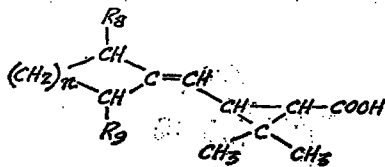
wherein R_6 , R_7 , R_8 , X and m are as defined in Claim 1, with a cyclopropanecarboxylic acid of the formula,



wherein R_1 , R_2 , R_3 and R_4 are as defined in Claim 1, or a reactive derivative thereof as hereinbefore defined, or reacting an alcohol of the formula,



wherein R_{10} , R_{11} , R_{12} , X and p are as defined in Claim 1, or a reactive derivative thereof as hereinbefore defined, with a cyclopropanecarboxylic acid of the formula,



wherein R_8 , R_9 and n are as defined in Claim 1, or a reactive derivative thereof as hereinbefore defined, optionally in the presence of a suitable solvent, a reaction promoting agent and an esterification catalyst.



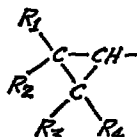
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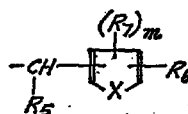
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5. A process according to Claim 4, wherein A is a group of the formula



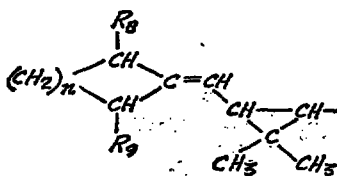
wherein R_1 , R_2 , R_3 and R_4 are as defined in Claim 1, and B is a group of the formula



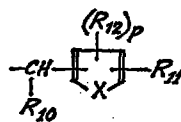
5 wherein R_5 , R_6 , R_7 , X and m are as defined in Claim 1.

5

6. A process according to Claim 4, wherein A is a group of the formula



wherein R_8 , R_9 and n are as defined in Claim 1, and B is a group of the formula

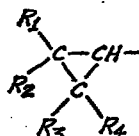


10 wherein R_{10} , R_{11} , R_{12} and p are as defined in Claim 1.

10

7. An insecticidal composition containing as an active compound a cyclopropane-carboxylate of the formula given and defined in Claim 1, and an inert carrier.

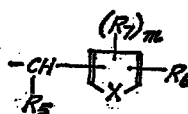
8. An insecticidal composition according to Claim 7, wherein A is a group of the formula



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wherein R_1 , R_2 , R_3 and R_4 are as defined in Claim 1, and B is a group of the formula



wherein R_5 , R_6 , R_7 , X and m are as defined in Claim 1.



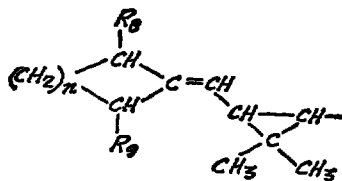
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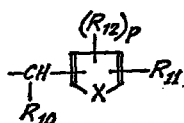
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9. An insecticidal composition according to Claim 7, wherein A is a group of the formula,



wherein R_8 , R_9 and n are as defined in Claim 1, and B is a group of the formula



wherein R_{10} , R_{11} , R_{12} and p are as defined in Claim 1.

10. An insecticidal composition according to Claim 7, wherein the composition further contains at least one other cyclopropanecarboxylate insecticide, organic chlorine containing insecticide, organic phosphorus containing insecticide, carbamate insecticide, or other insecticide, or a fungicide, acaricide, herbicide, or fertilizer.

11. An insecticidal composition according to Claim 7, wherein the composition further contains a synergist.

12. An insecticidal composition according to Claim 7, in the form of an oil spray, emulsifiable concentrate, wettable powder, dust, aerosol, mosquito coil, fumigant, granules, or a dust or solid combined with an attractant or bait.

13. A process for knocking down or killing an insect which includes contacting the insect with an effective amount of a compound of the formula given and defined in Claim 1, optionally in admixture with an inert carrier substance.

14. Cyclopropanecarboxylates of the formula given and defined in claim 1 which are specifically disclosed herein.

15. Processes for producing a carboxylate of the formula given and defined in claim 1 substantially as herein described and exemplified.

16. Cyclopropanecarboxylates of the formula given and defined in claim 1 when ever prepared by a process according to any one of claims 4 to 6 and 15.

17. Insecticidal compositions according to claim 7 substantially as herein described and exemplified.

18. Processes for preparing insecticidal compositions according to claim 7 substantially as herein described and exemplified.

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