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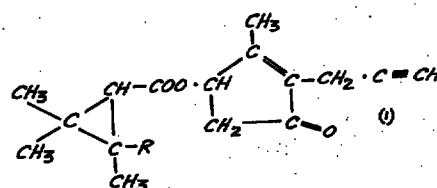


(54) CYCLOPROPANECARBOXYLATES, PROCESSES FOR
 PRODUCING THEM AND COMPOSITIONS CONTAINING
 THEM

(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:—

This invention relates to novel cyclopropanecarboxylic acid esters, to processes for preparing them, and to insecticidal compositions containing them.

More particularly, the present invention provides a cyclopropanecarboxylic acid ester represented by the formula (I),



wherein R is a hydrogen atom or a methyl group.

Specific examples of the cyclopropanecarboxylate (I) are shown in Table 1.

TABLE 1

Compound No.	Name	Formula
1	2-propargyl-3-methyl-2-cyclopentene-1-on-4-yl 2',2',3'-trimethyl-cyclopropanecarboxylate	
2	2-propargyl-3-methyl-2-cyclopentene-1-on-4-yl 2',2',3',3'-tetramethyl-cyclopropanecarboxylate	

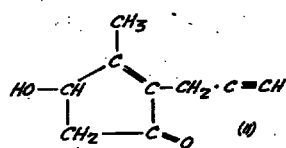
Various insecticides of the cyclopropanecarboxylic acid ester type, such as pyrethrin or allethrin are known and have been widely used for the control of harmful insanitary insects and insects harmful to agricultural and horticultural plants because of their excellent insecticidal properties, e.g., high insecticidal activity, low toxicity to mammals and rapid knock-down effect on such harmful insects.

Recently, it has been found that one of the most important problems concerns control of mosquitoes carrying encephalitis, filariasis or other infection diseases prevalent among harmful, insanitary household insects. Until now, the commercially available insecticides most suitable for use as fumigants incorporated in, for example, mosquito coils and electric mosquito killer mats are pyrethrin and allethrin. They are easy to use, low in cost and easy to prepare.

We have conducted a great deal of research into synthesizing various cyclopropanecarboxylic acid esters and examining the biological activities thereof. As a result, we have found that the compounds within the formula (I) hereinafter called "the present compounds" have excellent insecticidal activities when used in the form of oil sprays, emulsifiable concentrates, aerosols, and particularly fumigants.

Thus, the present invention provides an insecticidal composition containing at least one inert carrier and, as an active ingredient, at least one carboxylic acid ester of the formula (I).

The insecticidal effects of the ester compound obtained by reacting 2-propargyl-3-methyl-4-hydroxy-2-cyclopentene-1-one (alcohol moiety of the present ester compound) represented by the formula (II),



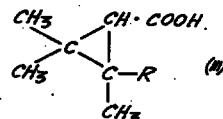
with chrysanthemic acid have been reported by Gersdorff and Piquett [(Gersdorff, Piquett; J. Econ. Entomol 54, 1250 (1961))].

According to the report, the effect of this chrysanthemic acid ester on house flies was only 64% of that of the composition containing allethrin when determined by the turn table method for oil sprays. We prepared homologues of this chrysanthemic acid ester and examined the insecticidal effects of these, which are hereinafter called "the present compounds". As a result, we have found that the present compounds have a more excellent knock down effect and killing effect than that of allethrin, and moreover the vapour pressure of present compounds is higher than that of allethrin. Thus, we have found, in

particular, that the present compounds exhibit even better insecticidal effects when used as fumigants.

2,2,3-Trimethylcyclopropanecarboxylic acid and 2,2,3,3-tetramethylcyclopropanecarboxylic acid (the acid moiety of the present ester compound) can be prepared by the method of Matsui and Kitahara [described in "Agr. Biol. Chem. 31, 1143 (1967)"], and these acids can easily be synthesized and at low cost. As a result, we have found that the present compounds can be also obtained at far lower cost and are far more applicable in practice than known insecticides of the pyrethroid type.

The present compounds are novel compounds and can be obtained by a process of the present invention which includes reacting 2-propargyl-3-methyl-4-hydroxy-2-cyclopentene-1-one with a cyclopropanecarboxylic acid represented by the formula (III),



wherein R is as defined above, or a reactive derivative thereof, optionally in the presence of a reaction assistant, such as a dehydrating agent or hydrogen halide acceptor.

The above-mentioned reactive derivative may, for example, be an acid halide or acid anhydride.

In accordance with a process within the present invention, when a carboxylic acid of the formula (III) is used, the reaction is carried out under conditions which promote dehydration. Thus, the acid is reacted at room temperature or at an elevated temperature with the cyclopenten-1-one of the formula (II) in a suitable inert solvent in the presence of a dehydrating agent, for example, dicyclohexyl carbodiimide, when a desired ester can be obtained in a high yield.

When an acid halide is used as a reactive derivative of the carboxylic acid of the general formula (III), the reaction can be sufficiently accomplished at room temperature by reacting the acid halide with a cyclopenten-1-one of the formula (II), using as a hydrogen halide acceptor for example, an organic tertiary base, e.g. pyridine or triethylamine. The acid halide used in this case may be any halide, but is preferably an acid chloride. In the reaction, the use of a solvent is desirable for smooth progress of the reaction, and an inert solvent, for example, benzene, toluene or petroleum benzene is preferably used. The acid halide of the formula (III) which is used in a process within the present invention may easily be prepared by a conventional procedure comprising halogenating the carboxylic

acid with a thienyl halide or phosphorous polyhalide.

When an acid anhydride is used as a reactive derivative of the carboxylic acid of the formula (III), no particular reaction assistant is required, and the reaction can be effected by treating the acid anhydride with a cyclopenten-1-one of the formula (II). In this case, the elevation of temperature is preferable for acceleration of the reaction, and the use of an inert solvent, for example, toluene or xylene is preferable for smooth progress of the reaction, though this is not always required.

The acid anhydrides which are used in processes within the present invention may easily be prepared by refluxing the carboxylic acid of the formula (III) with, for example, acetic acid anhydride with heating, and the carboxylic acid recovered in the esterification reaction can be used repeatedly with the acid anhydride.

Compounds within the present invention and processes for preparing them are illustrated with reference to the following Examples.

Example 1.

A solution of 5.3 g of 2-propargyl-3-methyl-4-hydroxy-2-cyclopentene-1-one and 4.2 g of pyridine in 25 ml of dry benzene was cooled with ice, and a solution of 5.3 g of 2,2,3-trimethylcyclopropanecarbonyl chloride in 15 ml of dry benzene was added dropwise thereto. The resulting reaction mixture was sealed and left overnight. The reaction mixture was then poured into ice water, and the organic layer was separated and washed with 5% (by weight) aqueous hydrochloric acid solution, 5% (by weight) aqueous sodium carbonate solution and an aqueous solution saturated with sodium chloride, and then dried over anhydrous magnesium sulfate. Benzene was evaporated off to obtain 9.1 g of a yellowish oil. Distillation under a reduced pressure gave 7.9 g of a yellowish oil of 2-propargyl-3-methyl-2-cyclopentene-1-one-4-yl-2,2',3,3'-trimethylcyclopropanecarboxylate (n_D^{25} : 1.4988).

Elemental Analysis

	C%	H%
Found	73.91%	7.74%
Calculated	73.82%	7.74%

Example 2.

A solution of 5.3 g of 2-propargyl-3-methyl-4-hydroxy-2-cyclopentene-1-one and 2,2,3-trimethylcyclopropanecarboxylic anhydride dissolved in 60 ml of toluene was refluxed for 4 hours. After cooling, the resulting reaction mixture was washed with 5% aqueous sodium carbonate and an aqueous solution saturated with sodium chloride. The organic layer was dried over anhydrous magnesium sulfate and distilled under reduced pressure.

The crude oily product was purified by silica gel column chromatography to obtain 8.9 g of the same ester compound as that obtained in Example 1.

Example 3.

To a solution of 5.3 g of 2-propargyl-3-methyl-4-hydroxy-2-cyclopentene-1-one and 4.5 g of 2,2,3-trimethylcyclopropanecarboxylic acid dissolved in 100 ml of methylenechloride, 7.9 g of dicyclohexycarbodiimide was added thereto. The resulting reaction mixture was stirred at room temperature for 24 hours and heated for 3 hours to complete the reaction. After cooling, the dicyclohexylurea thus deposited was separated and then a procedure similar to that described in Example 1 was effected to obtain 7.6 g of the same ester compound as that obtained in Example 1.

Example 4.

A solution of 5.3 g of 2-propargyl-3-methyl-4-hydroxy-2-cyclopentene-1-one and 4.2 g of pyridine in 25 ml of dry benzene was cooled with ice, and a solution of 5.9 g of 2,2,3,3-tetramethylcyclopropanecarbonyl chloride in 15 ml of dry benzene was added thereto. The resulting reaction mixture was sealed and left overnight. The reaction mixture was then poured into ice water, and the organic layer was separated and washed with 5% (by weight) aqueous hydrochloric acid solution, 5% (by weight) aqueous sodium carbonate solution and an aqueous solution saturated with sodium chloride and then dried over anhydrous magnesium sulfate. Benzene was evaporated off to obtain 9.6 g of a yellowish oil. Distillation under a reduced pressure gave 8.5 g of a yellowish oil of 2-propargyl-3-methyl-2-cyclopentene-1-on-4-yl-2',2',3',3'-tetramethylcyclopropanecarboxylate (n_D^{25} : 1.5011).

Elemental Analysis

	C%	H%
Found	74.49	8.10
Calculated	74.42	8.08

Example 5.

To a solution of 5.3 g of 2-propargyl-3-methyl-4-hydroxy-2-cyclopentene-1-one and 5.9 g of 2,2,3,3-tetramethylcyclopropanecarboxylic acid in 100 ml of methylenechloride, 7.9 g of dicyclohexycarbodiimide was added thereto and the resulting mixture was left overnight. The dicyclohexyl urea thus deposited was then filtered off, and a procedure similar to that described in Example 4 gave 8.3 g of the same ester compound as that obtained in Example 4.

In order to show clearly that the present compounds are superior in their insecticidal effect to commercially available allethrin and the corresponding chrysanthemic acid ester, comparisons in the effectiveness of these

insecticides are shown below with reference to Experimental Examples.

Experimental Examples.

5 A series of mosquito coils each containing 0.3% and a series each containing 0.6% by weight of single active ingredient were prepared by a conventional procedure. The following active ingredients were used to make up the series:—the present compound (1), 10 the present compound (2), the chrysanthemic acid ester corresponding to compound (1) and technical allethrin.

15 Into a (70 cm)³ glass chamber were introduced about 20 adults of the Northern house mosquito. 1G of each of the mosquito coils

prepared as described above was ignited at both ends and placed at the centre of the bottom of the chamber. After ignition of the mosquito coil, the number of knocked down mosquitoes was counted at intervals of 24 minutes to calculate the knock down ratio after each interval. The 50% knock down time (KT₅₀) was also calculated.

After each interval of 24 minutes knocked down mosquitoes were taken out, fed and allowed to stand for one day in the room for observation, and the numbers of alive and dead mosquitoes were observed to calculate the ratio of killed insects.

The results obtained are shown in Table 1.

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TABLE 1

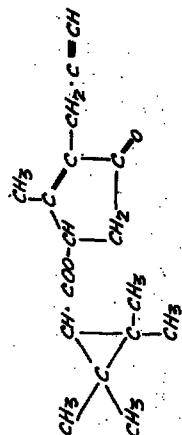
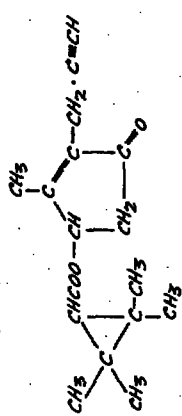
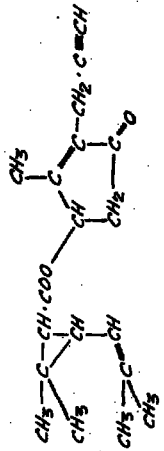
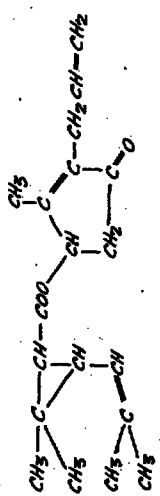
Test compound			0.3% mosquito coil		0.6% mosquito coil	
No.	No.	Formula	KT ₅₀ (min. sec)	Killing ratio (%)	KT ₅₀ (min. sec)	Killing ratio (%)
1	Present compound (1)		4' 42"	96	2' 30"	100
2	Present compound (2)		3' 12"	100	2' 00"	100
3	Corresponding chrysanthemic acid ester of the present compound (1)		9'	72	6' 06"	93

TABLE 1 (cont.)

Test compound			0.3% mosquito coil		0.6% mosquito coil	
No.	No.	Formula	KT ₅₀ (min. sec)	Killing ratio (%)	KT ₅₀ (min. sec)	Killing ratio (%)
4	Allethrin		10' 48"	31	7' 36"	77

As can be seen from the above-mentioned Experimental Examples, the present compounds exhibit a more rapid knock down effect than that of allethrin (which is widely used as fumigant), and have an excellent killing effect. The present compounds show much better insecticidal effects than those of the corresponding chrysanthemic acid esters.

A compound of the formula (I) which is an active ingredient in a composition within the present invention, may be used alone, or may be incorporated with suitable amounts of phenol or bisphenol derivatives, for example, BHT, or arylamines, for example, phenyl- α -naphthylamine, phenyl- β -naphthylamine or the condensation product of phenetidine with acetone, when compositions which are more stabilized in their insecticidal effects can be obtained. Further, the compositions may be increased in insecticidal activity by incorporation of synergists for pyrethroid type

insecticides, for example, N-(2-ethyl-hexyl)-bicyclo[2,2,1]hepta-5-ene-2,3-dicarboximide (hereinafter referred to as "MGK-264"), octachlorodipropyl ether [hereinafter referred to as "S-421"], α [2-(2-butoxyethoxy)ethoxy]-4,5-methylenedioxy-2-propyl toluene (hereinafter referred to as "piperonylbutoxide"), 4-(3,4-methylenedioxyphenyl)-5-methyl-1,3-dioxane (hereinafter referred to as "Sufropane"), and other known synergists.

Furthermore, the present compounds can display wider insecticidal activities when two or more such compounds are used in admixture, and can be enhanced in their insecticidal effect when used in admixture with other physiologically active materials, e.g. pyrethrin, allethrin, d-trans-allethrin, N-(chrysanthemoxymethyl)-3,4,5,6-tetrahydrophthalimide, dimethylmaleimidomethyl chrysanthemate, 5-benzyl-3-furylmethyl chrysanthemate, 5-propargyl-furfuryl chrysanthemate, 5-prop-

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argyl-2-methyl-3-furylmethyl chrysanthemate, 3-phenoxybenzyl chrysanthemate, and optical isomers thereof or derivatives, for example, the corresponding tetra- or tri-methylcyclopropane carboxylic acid esters, of the above-

- 5 mentioned chrysanthemic acid esters, other insecticides of the pyrethroid type, and other types of insecticides, for example, BHC, Diazinone, phenitrothion and DDVP.
- 10 In preparing insecticidal compositions within the present invention, the present compounds may be formulated into oil sprays, emulsifiable concentrates, dusts, aerosols, wettable powders, granulates, mosquito coils
- 15 and other fumigants (effective with or without heating thereof) using well known procedures, using diluting adjuvants for general insecticides as in the case of the conventional pyrethroids. Alternatively, they may be formulated
- 20 into death-inducing powders or solid preparations incorporated with baits or other substances attractive to harmful insects.

- Procedures for the preparation of the present compositions and biological effects thereof are illustrated below with reference
- 25 to Blending Examples and Test Examples, but the scope of the present invention is not limited to these Examples.

Blending Example 1.

- 30 A 0.3 g sample of present compound (1) and a 0.3 g sample of the present compound (2) are each dissolved in separate aliquots of 5 ml of methanol and each mixture is well mixed with 60 g of pyrethrum marc, 30 g
- 35 of Tabu powder (Tabu is a registered Trade Mark) and 9.7 g of wood flour. Each mixture is then well kneaded with 100 ml of water, and shaped and dried to obtain two 100 g mosquito coils.

- 40 The mosquito coil may optionally be coloured by the addition of 5% of a dye such as Malachite Green or may have incorporated therein a phenol or p-hydroxybenzoic acid ester.

- 45 **Blending Example 2.**

- To separate 0.25 g samples of each of the present compounds (1) and (2) are added 0.1 g of one of each of allethrin, d-trans allethrin, dimethylmaleimidomethyl chrysanthemate, dimethylmaleimidomethyl, 2,2,3,3-
- 50 tetramethylcyclopropanecarboxylate or 5-propargylfulfuryl chrysanthemate, and each mixture is dissolved in 5 ml of methanol.

- These mixtures are treated in the same manner as that described in the Blending
- 55 Example 1 to obtain a series of combined mosquito coils.

Blending Example 3.

- 60 A 0.2 g sample of the present compound (1) and a 0.2 g sample of the present compound (2) are each mixed with 0.5 g of S-421 and dissolved in chloroform. Each of

these solutions is uniformly absorbed onto the surface of one of two asbestos sheets of 2.5 cm x 1.5 cm in area and 0.3 cm in thickness. Onto each of the asbestos surfaces is pasted another asbestos sheet identical in size therewith to obtain two fibrous beds containing insecticidal fumigant compositions for use on an electrically heated plate. As the fibrous carrier, there may be used, in addition, or as an alternative to asbestos, a pulp sheet which is identical in effectiveness therewith.

Blending Example 4.

75 A mixture comprising 0.2 g of the present compound (2) and 0.05 g of DDVP is dissolved in chloroform. This solution is treated in the same manner as that described in Blending Example 3 to obtain a fibrous bed containing an insecticidal fumigant composition for use on an electrically heated plate.

Blending Example 5.

To a series of 0.2 g samples of the present compound (2) is added 0.1 g of one of each of 5-benzyl-3-furylmethyl chrysanthemate, 5-benzyl-3-furylmethyl-2',2',3'-trimethylcyclopropanecarboxylate or 3-phenoxybenzyl-2',2',3',3'-tetramethylcyclopropanecarboxylate, and in addition 0.6 g of BHT is added to each mixture and each resulting mixture is dissolved in separate aliquots of 5 ml of methanol. 60 G of pyrethrum marc, 30 g of Tabu powder and 9.1 g of wood flour are added to each methanolic mixture and well mixed. These mixtures are formulated in the same manner as that described in Blending Example 1 to obtain a series of combined mosquito coils, one of each mixture.

Blending Example 6.

100 A mixture comprising 0.1 part by weight of the present compound (2) and 0.5 part by weight of piperonyl butoxide was dissolved in deodorized kerosene to make the total amount up to 100 parts, when an oil spray was obtained.

Blending Example 7.

A mixture comprising 20 parts by weight of the present compound (2), 10 parts by weight of Sorpol SM-200 (registered trade mark of Toho Chemical Co.) and 70 parts by weight of xylene was thoroughly stirred to obtain an emulsifiable concentrate.

Blending Example 8.

A mixture comprising 0.4 part by weight of the present compound (1), 2 parts by weight of p,p'-dichlorodiphenyl trichloroethane, 6 parts by weight of xylene and 6.6 parts by weight of deodorized kerosene was mixed and packed in an aerosol container.

After attaching a valve portion to the con-

5 tainer, 85 parts by weight of a propellant (e.g. Freon (Freon is a registered Trade Mark), vinyl chloride monomer, or liquefied petroleum gas) was introduced under pressure through the said valve portion into the container to obtain an aerosol.

Blending Example 9.

10 0.3 Part by weight of the present compound (1) was dissolved in deodorized kerosene to make the total amount up to 100 parts, when an oil spray was obtained.

Blending Example 10.

15 A mixture comprising 0.4 part by weight of the present compound (2), 0.3 part by weight of 0,0-dimethyl-0-(3-methyl-4-nitrophenyl)thiophosphate, 6 parts by weight of xylene and 8.3 parts by weight of deodorized kerosene was mixed and treated in the same manner as that described in Blending Example 20 8 to obtain an aerosol.

Blending Example 11.

25 A mixture comprising 5 parts by weight of the present compound (2), 5 parts by weight of Toyolignin CT (registered trade mark of Toyo Spinning Co.) and 90 parts by weight of GSM clay (registered trade mark of Zieglite Mining Co.) was thoroughly stirred in a mortar. Subsequently, the mixture was kneaded with 10% by weight, based on 30 the amount of the said mixture, of water and granulated by means of a granulator, followed by air-drying, to obtain a granulate.

Blending Example 12.

35 A mixture comprising 25 parts by weight of the present compound (1), 1.5 parts by weight of Sorpol 5029—O (registered trade mark of Toho Chemical Co.) and 3.5 parts by weight of lignin was made up and 70 parts by weight of diatomaceous earth were added thereto. The resulting mixture was 40 thoroughly stirred in a mortar to obtain a wettable powder.

Blending Example 13.

45 To a solution of 1 part by weight of the present compound (2) in 20 parts by weight of acetone was added 99 parts by weight of diatomaceous earth capable of passing through a sieve having 300 apertures per square inch (i.e. aperture size 46μ). The 50 resulting mixture was thoroughly stirred in a mortar, and the acetone was then vaporized to obtain a dust.

55 Insecticidal effects of the compositions within the present invention thus obtained are as shown in the Test Examples given below.

Test Example 6.

Into a (70 cm)³ glass chamber were introduced about 50 adults of the Northern house

60 mosquito. 0.2 Grams of each of the mosquito coils obtained in Examples 1, 2 and 5 was ignited at both ends, and placed at the centre of the bottom of the chamber. The smoke inside the chamber was stirred by means of 65 a small motor fan (blade diameter 13 cm). As a result, each mosquito coil knocked down more than 90% of the adult mosquitoes within 20 minutes and killed more than 80% of the insects by the next day.

Test Example 7.

70 Into a (70 cm)³ glass chamber were introduced about 50 adult house flies. 0.2 Grams of each of the mosquito coils obtained in Examples 2 and 5 was ignited at both ends 75 and placed at the centre of the bottom of the chamber. The smoke inside the chamber was stirred by means of a small motor fan (blade diameter 13 cm). As a result, each mosquito coil knocked down more than 80% 80 of the adult mosquitoes within 20 minutes and killed more than 60% of the insects by the next day.

Test Example 8.

85 Into a (70 cm)³ glass chamber were introduced about 50 adults of the Northern house mosquito. Each of the fibrous beds containing insecticidal fumigant compositions obtained in Examples 3 and 4 was placed on an 90 electric heater, which was then placed at the centre of the bottom of the chamber. Subsequently, an electric current was applied to the heater, and the interior of the chamber was stirred by means of a small motor fan (blade diameter 13 cm). As a result, each 95 composition killed more than 90% of the adult mosquitoes within 20 minutes, and killed more than 80% of the insects by the next day.

Test Example 9.

100 Using Campbell's turn table method [disclosed in "Soap & Sanitary Chemicals", Vol. 14, No. 6, page 119 (1938)], 5 ml of each of the oil sprays obtained in Blending Example 9 was sprayed using 0.3% oil spray, 0.15% oil spray diluted with deodorised kerosene and 0.075% oil diluted with deodorized 105 kerosene. Adult house flies (a group of about 100 flies) were exposed to the settling mist for 10 minutes. Thereafter, the flies were taken out, fed and allowed to stand in a 110 constant temperature room at 27°C and the numbers of alive and dead were observed after 24 hours to calculate the ratio of killed insects.

115 The insecticidal effect of the oil spray obtained in the above Blending Example 9 on adults of the house fly was measured by determining the LC₅₀ value (50% lethal concentration). The result obtained is shown in Table 2, in which the results obtained when 120 using allethrin and pyrethrin are also given for comparison.

TABLE 2

	Insecticidal composition (oil spray)	LC ₅₀ (%)
1	Present compound (1)	0.047
2	Allethrin	0.095
3	Pyrethrin	0.052

Test Example 10.

5 About 20 adult house flies were introduced in a (70 cm)³ glass chamber, and 0.7 ml of one of each of the oil sprays obtained in Blending Example 9 and oil sprays of allethrin and pyrethrin was sprayed into the chamber under a pressure of 20 pounds/in² by use

of a glass-made atomizer.

10 Thereafter, the number of knocked down house flies were counted to calculate the KT₅₀ value (50% knock down time) for each compound. This result obtained is shown in Table 3.

TABLE 3

	Insecticidal composition (oil spray)	KT ₅₀ (second)
1	Present compound (1)	105
2	Allethrin (0.2%)	130
3	Pyrethrin (0.2%)	120

Test Example 11.

20 About 20 adults of the Northern house mosquito were introduced in a (70 cm)³ glass chamber, and 0.7 ml of one of each of the oil sprays obtained in Blending Example 9, and oil sprays of allethrin and pyrethrin all of which were further diluted with deodorized kerosene to give a composition con-

25 taining 0.1% by weight of active ingredient, was sprayed into the chamber under a pressure of 20 pound/in² using a glass-made atomizer. Thereafter, the numbers of knocked down Northern house mosquitoes were counted to calculate the KT₅₀ value (50% knock down time). The results obtained are shown in Table 4.

TABLE 4

	Insecticidal composition (oil spray)	KT ₅₀ (second)
1	Present compound (1)	70
2	Allethrin (0.1%)	125
3	Pyrethrin (0.1%)	105

Test Example 12.

Using Campbell's turn table method [described in Example 9], 5 ml of the oil spray obtained in Blending Example 6 was sprayed, and adult house flies (a group of about 100 flies) were exposed to the settling mist for

10 minutes. Thereafter, the flies were taken out, fed and allowed to stand in a constant room temperature at 27°C, and the numbers of alive and dead were observed after 24 hours to calculate the ratio of killed insects. The results obtained are shown in Table 5.

TABLE 5

Insecticidal composition	Knock down ratio (%)	
	After 10 min.	After 1 day
Present compound (2)	100	100

Test Example 13.

About 20 adult house flies were introduced in a (70 cm)³ glass chamber, one of each of the aerosols obtained in Blending Examples 8 and 10 was sprayed for one second, and the knocked-down flies were observed after

15 minutes. The knocked down flies only were collected, removed to a new observation cage, fed and the numbers of alive and dead were observed after one day. The results obtained are shown in Table 6.

TABLE 6

	Insecticidal composition	Knock down ratio (%) After 15 minutes	Ratio of killed insects (%) After 1 day
1	Aerosol of Blending Example 8	100	86
2	Aerosol of Blending Example 10	100	72

Test Example 14.

Into three 300 milliliter-glass beakers, one containing a 200 ml solution of the emulsifiable concentrate obtained in Blending Example 7, another containing a 200 ml solution of the wettable powder obtained in Blending Example 12, and a third heater containing a 200 ml solution of allethrin, each solution

having been diluted to the tested concentration with water, were introduced about 30 full-grown larvae of the Northern house mosquito. The numbers of alive and dead were observed after one day to calculate the LC₅₀ value (50% lethal concentration). The results obtained are shown in Table 7.

TABLE 7

Insecticidal composition	LC ₅₀ (p.p.m.)
Emulsifiable concentrate of Blending Example 7	0.02
Wettable powder of Blending Example 12	0.09
Wettable powder of Allethrin	0.10

Test Example 15.

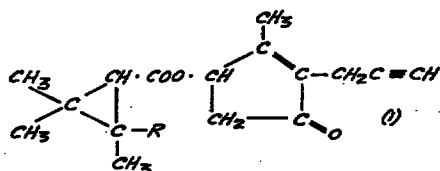
Into a 14 litre-polyethylene bucket containing 10 litres of water were placed 400 mg. of the granulate obtained in Blending Example 11. After 1 day, full-grown larvae of the Northern house mosquito were immersed in the water, and the numbers of alive and dead larvae were then observed. As a result, more than 90% of the larvae were killed within 24 hours.

Test Example 16.

Onto the bottom of a glass Petri dish of 14 cm in diameter and 7 cm in height was uniformly dusted 2 g/in² of the dust obtained in Blending Example 13, and the dish was coated on its inner wall with butter, leaving at the lower part an uncoated portion of about 1 cm in width. Subsequently, a group of 10 German cockroaches were introduced into the dish and contacted with the dust for 30 minutes. As a result, all of the cockroaches were knocked down, and all of the knocked down cockroaches were killed by the third day after the contact.

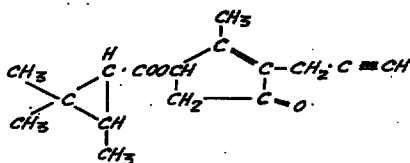
25 WHAT WE CLAIM IS:—

1. A cyclopropanecarboxylic acid ester of the formula (I),

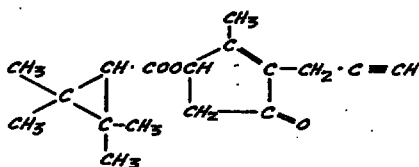


wherein R is a hydrogen atom or a methyl group.

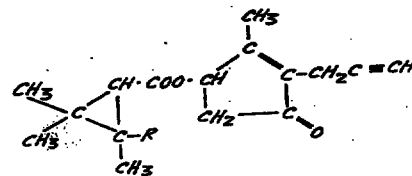
2. A compound of the formula,



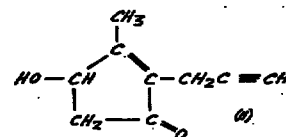
3. A compound of the formula,



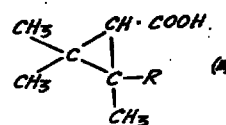
35 4. A process for preparing a cyclopropanecarboxylic acid ester of the formula (I),



wherein R is a hydrogen atom or a methyl group, which includes reacting a compound of the formula (II),



with a compound of the formula (III),



wherein R is as defined above, or a reactive derivative thereof.

5. A process according to Claim 4, wherein the reaction is carried out in an inert solvent optionally at an elevated temperature.

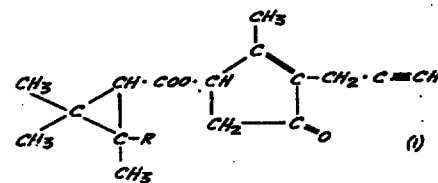
6. A process according to Claim 4 or Claim 5, wherein the reaction is carried out in the presence of a dehydrating agent.

7. A process according to Claim 6, wherein the dehydrating agent is dicyclohexylcarbodiimide.

8. A process according to Claim 4, wherein a reactive derivative of the acid is used, the said reactive derivative being an acid halide or an acid anhydride.

9. A process according to Claim 8, wherein the reaction is carried out in the presence of a hydrogen halide acceptor in an inert solvent.

10. An insecticidal composition containing at least one inert carrier and as an active ingredient at least one compound of the formula (I)



wherein R is a hydrogen atom or a methyl group.

Test Example 15.

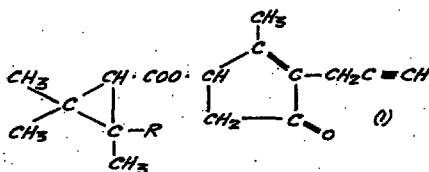
Into a 14 litre-polyethylene bucket containing 10 litres of water were placed 400 mg. of the granulate obtained in Blending Example 11. After 1 day, full-grown larvae of the Northern house mosquito were immersed in the water, and the numbers of alive and dead larvae were then observed. As a result, more than 90% of the larvae were killed within 24 hours.

Test Example 16.

Onto the bottom of a glass Petri dish of 14 cm in diameter and 7 cm in height was uniformly dusted 2 g/in² of the dust obtained in Blending Example 13, and the dish was coated on its inner wall with butter, leaving at the lower part an uncoated portion of about 1 cm in width. Subsequently, a group of 10 German cockroaches were introduced into the dish and contacted with the dust for 30 minutes. As a result, all of the cockroaches were knocked down, and all of the knocked down cockroaches were killed by the third day after the contact.

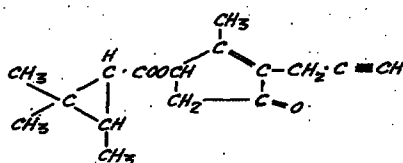
WHAT WE CLAIM IS:—

1. A cyclopropanecarboxylic acid ester of the formula (I),

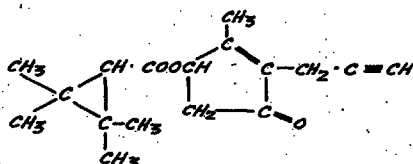


wherein R is a hydrogen atom or a methyl group.

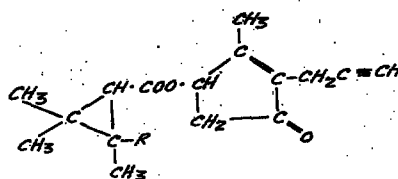
2. A compound of the formula,



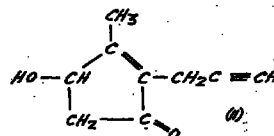
3. A compound of the formula,



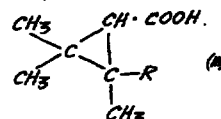
4. A process for preparing a cyclopropanecarboxylic acid ester of the formula (I),



wherein R is a hydrogen atom or a methyl group, which includes reacting a compound of the formula (II),



with a compound of the formula (III),



wherein R is as defined above, or a reactive derivative thereof.

5. A process according to Claim 4, wherein the reaction is carried out in an inert solvent optionally at an elevated temperature.

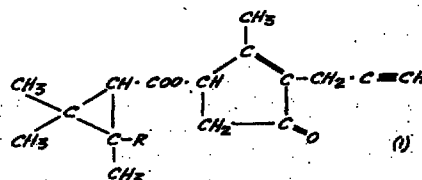
6. A process according to Claim 4 or Claim 5, wherein the reaction is carried out in the presence of a dehydrating agent.

7. A process according to Claim 6, wherein the dehydrating agent is dicyclohexylcarbodiimide.

8. A process according to Claim 4, wherein a reactive derivative of the acid is used, the said reactive derivative being an acid halide or an acid anhydride.

9. A process according to Claim 8, wherein the reaction is carried out in the presence of a hydrogen halide acceptor in an inert solvent.

10. An insecticidal composition containing at least one inert carrier and as an active ingredient at least one compound of the formula (I)



wherein R is a hydrogen atom or a methyl group.



11. A composition according to Claim 10, wherein the composition is in the form of an oil spray, emulsifiable concentrate, dust, aerosol, wettable powder, granulate, mosquito coil, fumigant or a bait.
12. A method of knocking down or killing insects which includes contacting the insects with a compound according to Claim 1.
13. Processes for producing a cyclopropanecarboxylic acid ester of the formula (I), given and defined in Claim 1, substantially as herein described and exemplified.
14. A cyclopropanecarboxylic acid ester of the formula (I), given and defined in Claim 1, whenever prepared by a process according to any one of claims 4 to 9 and 13.
15. Insecticidal compositions according to claim 10 substantially as herein described and exemplified.

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