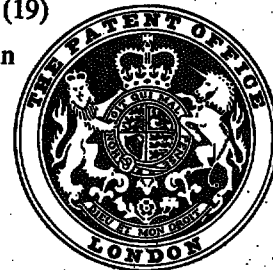


PATENT SPECIFICATION

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(54) CYCLOPROPANE CARBOXYLIC ACID ESTERS

(71) We, ROUSSEL UCLAF, a French Body Corporate of 35 Boulevard des Invalides, Paris 7^{ème}, France, 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 new cyclopropane carboxylic acid esters and insecticidal compositions containing them.

According to the present invention there are provided (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate and (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate.

The first of these compounds, that is to say the (S) alcohol ester, is particularly well suited for use in the control of insects in the field of agriculture.

For example it permits effective control of aphids, the larvae of Lepidoptera, and Coleoptera. It can also be used as an insecticide in the domestic field (flies and moquitos).

Tests given in the experimental portion illustrate the separate insecticidal activity of this compound with respect to the domestic fly and against the larvae of Spodoptera Littoralis.

(R) α -cyano 3-phenoxybenzyl 2,2-dimethyl 3R-(2,2-dichlorovinyl) cyclopropane-1R carboxylate is endowed with a useful insecticidal activity but which is less potent than that of the corresponding (S) alcohol ester.

According to a further feature of the invention there are provided insecticidal compositions comprising, as active ingredients, (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate and insecticidal compositions comprising, as active ingredient (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate, each active ingredient being in association with a carrier or excipient.

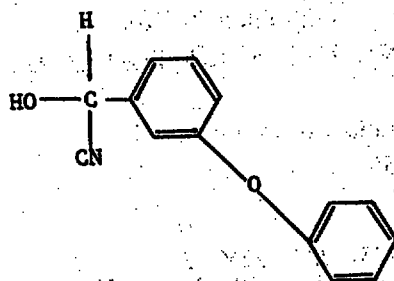
In these compositions the active material can optionally be mixed with one or more other pesticidal agents. These compositions can be presented in the form of powders, granules suspensions, emulsions, solutions, solutions for aerosols, combustible strips, baits or other preparations normally employed for the use of this kind of compound.

In addition to the active ingredient these compositions generally contain a vehicle and/or a non-ionic surface-active agent ensuring uniform dispersion of the substances constituting the mixture. The vehicle used can be a liquid such as water, alcohol, hydrocarbons or other organic solvents, a mineral, animal or vegetable oil, a powder such as talc, clays, silicates, kieselguhr or a combustible solid such as tabu powder (pyrethrum marc).

In order to increase the insecticidal activity of the compounds of the invention they can be mixed with standard synergists used in a similar case such as 1-(2,5,8-trioxa dodecyl 2-propyl 4,5-methylenedioxy) benzene (or piperonyl butoxide), N-(2-ethyl heptyl) bicyclo [2,2,1]-5-heptene-2,3-dicarboximide or piperonylbis-2-(2'-n-butoxy ethoxy) ethyl acetal (or tropical).

The insecticidal compositions according to the invention preferably contain from 0.005% to 10% by weight of active ingredient.

(S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate can be prepared for example, starting with (R) or racemic (R,S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate of formula (B):



(B)

(R) or (R,S)

or a mixture, in non-equimolecular proportions, of (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate and (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate, a mixture denoted hereinafter as "(R + S) dichloro ester", as described and claimed in our British Patent Application No. 16866/77 (Serial No. 1582595). As described therein (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate or a mixture thereof with (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate is reacted with a basic agent selected from ammonia, a primary, secondary or tertiary amine, a quaternary ammonium compound, a basic ion exchange resin, a high molecular weight liquid amine and a catalytic amount of a strong base, in the presence of a solvent in which (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate is insoluble and (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate is soluble and then precipitated (S) α -cyano-3-phenoxybenzyl ester is isolated from the reaction medium.

Starting with racemic (R,S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate, (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate can be isolated by chromatography.

The following non-limiting examples illustrate the invention:

EXAMPLE 1:

Conversion of (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate into (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate.

a) Preparation of the (R) alcohol ester:

10 g of racemic (R,S) alcohol ester, of $[\alpha]_D^{20} = +16.5^\circ$ ($c = 10\%$, benzene) are chromatographed on silica gel eluting with a mixture of petroleum ether (B.Pt. $40^\circ - 70^\circ\text{C}$) and diisopropyl ether (85/25), and one obtains 3 g of (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate of $[\alpha]_D^{20} = -31^\circ$ ($c = 1\%$, benzene) or $[\alpha]_D^{20} = -21.5^\circ$ ($c = 1\%$, chloroform).

b) Conversion into (S) alcohol ester:

To 60 of (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate $[\alpha]_D^{20} = -31^\circ$ ($c = 1\%$, benzene) or $[\alpha]_D^{20} = -21.5^\circ$ ($c = 1\%$, chloroform) obtained in paragraph a) one adds 120 cm³ of isopropanol then 9 cm³ of an aqueous solution of 22° Bé ammonia, cools to 0°C , agitates for forty-eight hours to 0°C , isolates by vacuum-filtration the precipitate formed, washes it with 30 cm³ of isopropanol at -20°C , dries it and obtains 48.5 g of (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate. M.Pt. = 60°C , $[\alpha]_D^{20} = +66^\circ$ ($c = 1\%$, benzene) or $[\alpha]_D^{20} = +34^\circ$ ($c = 1\%$, chloroform).

EXAMPLE 2:

Conversion of (R,S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate into (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate.

To 600 g of racemic (R,S) alcohol ester, $[\alpha]_D^{20} = +16.5^\circ$ ($c = 10\%$, benzene), one adds 1200 cm³ of isopropanol then introduces into the solution obtained 90 cm³ of an aqueous solution of 22° Bé ammonia, cools to 0°C , agitates for forty-eight hours at this temperature,

isolates by vacuum-filtration the precipitate formed, washes it with 300 cm³ of isopropanol at -20°C, dries it and obtains 485 g of (S) α-cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate. M.Pt. = 60°C [α_D^{20} = + 66° (c = 1%, benzene) or [α_D^{20} = + 34° (c = 1%, chloroform).

Analysis.	C ₂₂ H ₁₉ O ₃ NCl ₂	(416.28)	Cl%
	C%	H%	N%
Calculated:	63.48	4.60	3.36
Found:	63.7	4.6	3.4
			17.03
			17.1

EXAMPLE 3:

Composition based upon (S) α-cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate.

One mixes:

- (S) α-cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate	: 25 g/l
- 2,6-diterbutyl paracresol	: 10 g/l
- "EMCOL" [Registered Trade Mark] H 300 B *	: 50 g/l
- "EMCOL" H 500 B *	: 20 g/l
- "SUPERSOL" [Registered Trade Mark] **	: 786 g/l

* These surface-active agents are mixtures of calcium salts of alkyl benzene sulphonates (anionic portion) and of polyoxyethylenated ethers (non-anionic portion) sold by the company WITE.

** "Supersol" is a mixture of aromatic solvents sold by the company B.P. (SHELL).

Study of the insecticidal activity of (S) α-cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-1R-carboxylate (compound A).

A) Study of the insecticidal activity with respect to the domestic fly:

The test insects are domestic flies of mixed sexes. One operates by topical applications of 1 μl of an acetonic solution to the dorsal thorax of the insects. One uses 50 individuals per treatment. One carries out a mortality check twenty-four hours after treatment and determines the lethal dose (LD 50) of the test compound.

The experimental results obtained are summarised in the following table:

Dose (ng)	% mortality at 24 hours	LD 50
5	93.3	
3.75	83.2	
2.5	68.0	1.6 nanogram per insect.
1.25	34.5	
0.625	10.0	

Conclusion: Compound A is endowed with a very high insecticidal activity with respect to the domestic fly.

B) Study of the insecticidal activity with respect to the larvae of *Spodoptera Littoralis*:

The tests are carried out by topical application. One deposits 1 μl of an acetonic solution of the product to be tested upon the dorsal thorax of each individual. One uses 15 *Spodoptera Littoralis* caterpillars at the fourth larval stage for each dose employed. After treatment the individuals are placed on an artificial nutrient medium (Piotot medium). One carries out an efficiency check (percentage mortality bearing in mind an un-treated control) twenty-four hours then forty-eight hours after treatment and one determines the lethal dose (LO 50) in nanograms per caterpillar.

The experimental results are summarised in the following table:

Dose (ng)	% mortality		LD 50 at 48 hours
	24 hours	48 hours	
1.25	95.6	97.8	0.3 nanogram per caterpillar
0.625	80.0	82.2	
0.3125	48.9	62.2	
0.1562	20.5	27.3	

WHAT WE CLAIM IS:

1. (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-IR-carboxylate.

2. (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-IR-carboxylate.

3. Insecticidal compositions comprising, as active ingredient, a compound as claimed in claim 1 in association with a carrier or excipient.

4. Insecticidal compositions comprising, as active ingredient, a compound as claimed in claim 2 in association with a carrier or excipient.

5. Compositions as claimed in claim 3 or claim 4 in the form of powders, granules, suspensions, emulsions, solutions, aerosols, combustible strips or baits.

6. Compositions as claimed in any of claims 3 to 5 further containing a synergist.

7. Compositions as claimed in claim 6 wherein the synergist is 1-(2,5,8-trioxadodecyl-2-propyl-4,5-methylenedioxy)-benzene, N-(2-ethylheptyl)-bicyclo[2,2,1]-5-heptene-2,3-dicarboximide or piperonylbis-2-(2'-n-butoxyethoxy)-ethyl acetal.

8. Compositions as claimed in any of claims 3 to 7 containing from 0.005 to 10% by weight of active ingredient.

9. Insecticidal compositions substantially as herein described.

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The experimental results are summarised in the following table:

	Dose (ng)	% mortality		LD 50
		24 hours	48 hours	at 48 hours
5	1.25	95.6	97.8	
	0.625	80.0	82.2	0.3 nanogram
				per caterpillar
	0.3125	48.9	62.2	
10	0.1562	20.5	27.3	

WHAT WE CLAIM IS:

1. (S) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-IR-carboxylate.
- 15 2. (R) α -cyano-3-phenoxybenzyl 2,2-dimethyl-3R-(2,2-dichlorovinyl)-cyclopropane-IR-carboxylate.
3. Insecticidal compositions comprising, as active ingredient, a compound as claimed in claim 1 in association with a carrier or excipient.
4. Insecticidal compositions comprising, as active ingredient, a compound as claimed in
- 20 claim 2 in association with a carrier or excipient.
5. Compositions as claimed in claim 3 or claim 4 in the form of powders, granules, suspensions, emulsions, solutions, aerosols, combustible strips or baits.
6. Compositions as claimed in any of claims 3 to 5 further containing a synergist.
7. Compositions as claimed in claim 6 wherein the synergist is 1-(2,5,8-trioxadodecyl-2-propyl-4,5-methylenedioxy)-benzene, N-(2-ethylheptyl)-bicyclo[2,2-1]-5-heptene-2,3-
- 25 dicarboximide or piperonylbis-2-(2'-n-butoxyethoxy)-ethyl acetal.
8. Compositions as claimed in any of claims 3 to 7 containing from 0.005 to 10% by weight of active ingredient.
9. Insecticidal compositions substantially as herein described.

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