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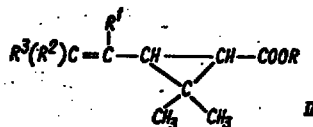


(54) SUBSTITUTED 2,2-DIMETHYL CYCLOPROPANE
CARBOXYLIC ACID ESTERS, PROCESSES FOR THEIR
PREPARATION AND THEIR USE AS INSECTICIDES

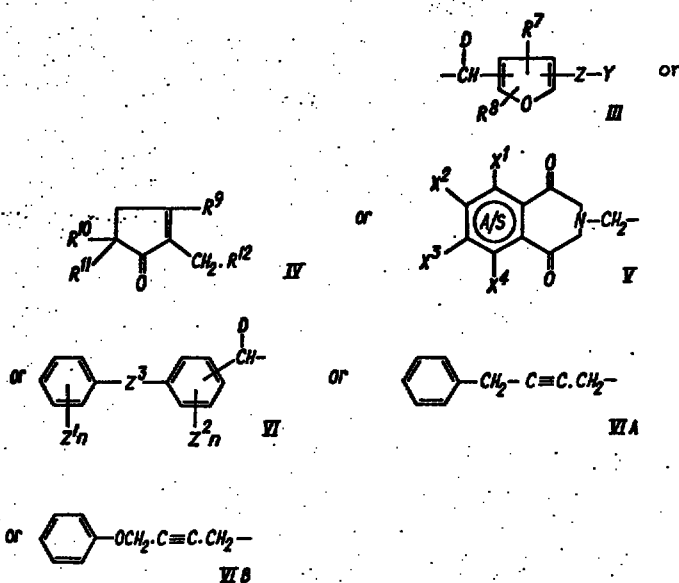
(71) We, NATIONAL RESEARCH DEVELOPMENT CORPORATION, a Corporation established by Statute, of Kingsgate House, 66—74 Victoria Street, London, S.W.1., England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to insecticides and more particularly, to synthetic insecticides of the pyrethrin type, to their preparation, to compositions containing them and to the insecticidal use of the compounds and compositions.

In the Complete Specification of our Application Nos. 24809/72, 24810/72, 30838/72, 59184/72, 20539/73 and 38403/73, now Serial No. 1413491 we have described and claimed esters of the general formula:



wherein R¹ represents hydrogen or a methyl group; R² represents hydrogen or a halogeno or alkyl group; R³ represents hydrogen, or a halogeno, or carboalkoxy group said carboalkoxy group containing at least 2 carbon atoms in the alkoxy residue when R² represents methyl with the proviso that (a) R² and R³ each represent hydrogen only when R¹ represents methyl, (b) when R¹ and R³ represent hydrogen and R² represents alkyl, that alkyl group contains at least 2 carbon atoms and (c) when R² represents an alkyl group, R³ does not represent a halogeno group; and R represents a group of formula:



wherein Z represents O, S, CH₂ or CO, Y represents hydrogen or an alkyl, alkenyl or alkynyl group or an aryl or furyl group which is unsubstituted or substituted in the ring by one or more alkyl, alkenyl, alkoxy or halogeno groups, R⁷ and R⁸, which may be the same or different, each represent hydrogen or an alkyl, or alkenyl group, R⁹ represents hydrogen or a methyl group, R¹⁰ and R¹¹, which may be the same or different, each represent hydrogen or an alkyl group, R¹² represents an organic radical having carbon-carbon unsaturation in a position α to the CH₂ group to which R¹² is attached,

(A/S) indicates an aromatic ring or a dihydro or tetrahydro analogue thereof, X¹, X², X³ and X⁴, which may be the same or different, each represent hydrogen, chlorine or a methyl group,

Z³ represents —CH₂— or —O— or —S— or —CO—, D represents H, CN or —C≡CH, Z¹ and Z², which may be the same or different, each represent chlorine or a methyl group and n=0, 1 or 2, with the proviso that R does not represent hydrogen (or an acid chloride derivative of the acid) or an ethyl or allethronyl group when R¹ represents hydrogen, R² and R³ each represent chlorine and the compound is racemic.

In Example 27 of the above mentioned application, we describe the compound ($\pm$)- α -cyano-3-phenoxybenzyl [1R *cis*]-2,2-dimethyl-3-(2,2-dibromovinyl)-cyclopropane carboxylate. In accordance with one aspect of the present invention, we have been able to separate the above mentioned compound into its component optically active isomers and find, surprisingly, that one of these isomers the one derived from the (–) alcohol is a crystalline compound having more than twice the toxicity to houseflies of the isomer mixture.

In accordance with a further aspect of the present invention, we find, surprisingly, that esters of formula II above in which R² and R³ each represent fluorine, R represents 5-benzyl-3-furylmethyl, 3-phenoxy benzyl or α -cyano-3-phenoxybenzyl and the ester is in the form of a substantially pure optical isomer with respect to the cyclopropane ring and has [R] configuration at the carbon atom of the cyclopropane ring carrying the COOR group, have a useful combination of knock-down and kill properties towards insects. Interest in this series centres on the esters of the [1R, *trans*] and [1R, *cis*] acids.

We also find, in accordance with a still further aspect of the invention, that unexpectedly high toxicity to houseflies and mustard beetles is obtained with esters of formula II above in which R² and R³ each represent chlorine and, R represents 3-phenoxybenzyl and the cyclopropane ring has [1R, *cis*] or [1R, *trans*] configuration or R represents 5-benzyl-3-furylmethyl and the cyclopropane ring has [1R, *cis*] configuration.

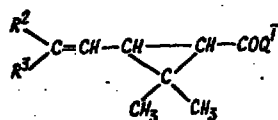
For compounds of the invention which are substantially pure optical isomers, we are using the nomenclature [1R, *cis*] and [1R, *trans*] as a convenient alternative to the strict nomenclature based on the sequence rule (Cahn, RS., Ingold C and Prelog V, Angew. Chem. Int. Ed. 5 385 (1966)) where, for example, dihalovinyl

cyclopropane carboxylates formally derived from (+)-*trans*-[1R,3R]-chrysanthemates by replacement of the vinyl methyl groups would be [1R,3S]. In accordance with our proposal, compounds we previously designated (+)-*cis*-[1R,3S] and (+)-*trans*-[1R,3R] are now designated [1R,*cis*] and [1R,*trans*] respectively.

When the esters are derived from α -cyano-3-phenoxybenzyl alcohol, there is a further site of molecular asymmetry giving rise to a further site of optical activity and these esters are obtainable in the ($\pm$), (+) or (−) forms in relation to the stereochemistry of the "alcohol" part of the molecule.

One of our most toxic compounds to houseflies and mustard beetles is ($\pm$)- α -cyano-3-phenoxybenzyl [1R,*cis*]-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane-carboxylate. This ester has three centres of asymmetry giving rise to optical isomers, two in the carbon atoms of the cyclopropane ring and the other at the carbon atom bearing the α -cyano substituent. Initially, we prepared this ester by the reaction of ($\pm$)- α -cyano-3-phenoxybenzyl alcohol with the acid chloride of the [1R,*cis*]-acid giving an ester in which the configuration at the carbon atoms of the cyclopropane ring is retained but which is still racemic at the carbon atom bearing the α -cyano substituent. This product is a mixture of two stereoisomers and we have now found that one of these stereo isomers can be separated from the racemic mixture and that, surprisingly, the stereo isomer which can be separated is a crystalline isomer which exhibits a higher insecticidal activity than the racemic mixture.

The esters of the present invention may be prepared by the methods disclosed in our earlier mentioned application e.g. wherein a carboxylic acid or esterifiable derivative thereof of formula:

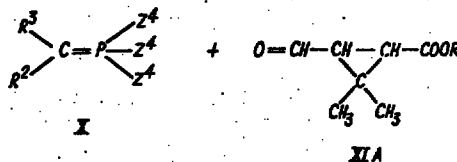


is reacted with a compound of formula RQ, where Q⁺ and Q are functional groups which react together to form an ester linkage and R², R³ and R are as defined above, the resolution into the desired configuration on the cyclopropane ring taking place before or after formation of the ester linkage. When the ester is to be prepared in the form of a pure optical and/or geometrical isomer in relation to the acid part of the molecule, it is preferred to use the ester precursor in the form of the desired optical and/or geometrical isomer rather than to attempt to resolve the ester after its preparation. Thus, in the case where the ester is prepared by the reaction of an alcohol or derivative thereof with the acid or a derivative thereof, the reaction can be carried out using the appropriate isomer of the acid or derivative thereof, e.g. the [1R,*cis*] isomer. The preparation of *trans* isomers of the acids is described in our earlier mentioned application. The *cis*-isomers of the acids can be prepared by modification of the processes described in that complete specification in which the *trans*-chrysanthemates are replaced by *cis*-chrysanthemates.

In order to isolate the stereo isomer of α -cyano-3-phenoxybenzyl [1R,*cis*]-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylate which is optically pure at the carbon atom bearing the α -cyano substituent and which is substantially free from other optical isomers, ($\pm$)- α -cyano-3-phenoxybenzyl [1R,*cis*]-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylate may be dissolved in a solvent, particularly a hydrocarbon solvent such as hexane, at a temperature up to 60°C and the solution then cooled, when one of the stereo isomers, having [S] configuration in the alcohol residue will crystallize out from the solution. The crystalline stereo isomer may be removed from the solution, e.g. by filtration and the solution evaporated to dryness to leave a residue comprising the other stereo-isomer, the [R]-isomer, contaminated with small quantities of the [S]-isomer. Nuclear magnetic resonance indicates that the crystalline isomer is substantially one form while the non-crystalline isomer contains traces of the other stereo isomer i.e. the crystalline stereo isomer. While the insecticidal activity of the crystalline stereo isomer is found to be higher than the racemate, the insecticidal activity of the non-crystalline isomer is found to be less than that of the racemate.

The dextro rotatory stereo isomer which can be readily separated from the racemic mixture is derived from the (−) isomer of the alcohol and the ester has the [S] absolute configuration in the alcohol residue.

The fluorovinyl cyclopropane carboxylic acids and their salts, acid halides and C_1 to C_4 alkyl esters of formula IIA ($R^2 = R^3 = F$, $R = H$ (or a salt or acid halide thereof) or C_1 — C_4 alkyl) are new compounds which can be prepared by the general method described in our above mentioned application. This involves reaction of an aldehyde of formula XIA with a phosphorane or ylide of formula X under the conditions of the Wittig reaction.



In formulae X and XIA, R^2 and R^3 are as defined above and R is a group as defined above which will not interfere in the Wittig reaction such as a methyl or tert. butyl group and Z^4 , which in principle can represent any organic radical, will normally be a phenyl radical since the stability of the trisubstituted phosphorus oxide which is formed as the by-product in the reaction is particularly high. The phosphorane of formula X can be prepared *in situ* by introducing the aldehyde XIA into the reaction mixture together with the triorganophosphine $P(Z^4)_3$ and a salt of the appropriate chlorofluoroacetic acid in accordance with procedures known *per se*.

The isomers of the present invention where R represents a 3-phenoxybenzyl, α -cyano-3-phenoxybenzyl or 5-benzyl-3-furylmethyl group can be prepared directly by the Wittig reaction mentioned above by using a starting aldehyde of appropriate configuration in which R represents the required ester group required in the final product in accordance with the second method disclosed in our earlier mentioned application.

The esters of this invention may be formulated into insecticidal compositions of the type described in our earlier mentioned application and the compounds and the compositions may be used to control insects in the manner described in our earlier mentioned application.

The following examples are given to illustrate the invention: Refractive indices are measured at 20°C.

EXAMPLE 1.

($\pm$)- α -cyano-3-phenoxybenzyl [1R,*cis*]-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylate compound P29B was prepared by the procedure described in Example 27 in our earlier mentioned complete specification. This racemate has the following physical characteristics:

$$[\alpha]_D^{20} = -1^\circ \quad (C=0.4 \text{ in ethanol})$$

$$n_D \quad 1.5732$$

N.M.R. peaks associated with the C—H group (carbon atom bearing the α -cyano substituent) $\tau=3.65$ and 3.72 (equal areas).

0.6 grams of the racemate was dissolved in 25 ml. hexane and maintained at -20°C until precipitation of crystals was complete. The crystals were then filtered off and recrystallised from hexane to give the [1R,*cis*]-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylate of (–)- α -cyano-3-phenoxybenzyl alcohol in 0.25 g yield. This isomer has [S] configuration at the carbon atom carrying the α -cyano group. The physical characteristics of this crystalline isomer are as follows:

$$[\alpha]_D^{20} + 16^\circ \quad (C=0.4 \text{ in ethanol})$$

This isomer has [R] configuration at the carbon atom carrying the α -cyano group.

N.M.R. peaks associated with the C—H group (carbon atom bearing the α -cyano substituent) $\tau=3.65$ but not peak at $\tau=3.72$.

The mother liquors were combined and evaporated to dryness to give 0.32 g of the non-crystalline isomer of the [1R,*cis*]-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylate of (+)- α -cyano-3-phenoxybenzyl alcohol having the following properties:

n_D 1.5749 $[\alpha]_D^{20} - 15^\circ$ (C=0.4 in ethanol)

N.M.R. peaks associated with the C—H bond (carbon atom bearing the α -cyano group) $\tau=3.72$ with a small peak (20% of the 3.72 peak) at $\tau=3.65$ attributable to the crystalline isomer.

In the above examples, temperatures are in degrees centigrade and refractive indices are measured at 20°C.

The insecticidal toxicity of the compounds described in Example 1 was tested against houseflies and mustard beetles by the procedures described in our above identified application and the following relative toxicities were obtained in relation to 5-benzyl-3-furylmethyl (+)-*trans*-chrysanthemate which is arbitrarily assigned a toxicity of 1000.

Compounds	Houseflies	Mustard Beetles
5-benzyl-3-furylmethyl-(+)- <i>trans</i> -chrysanthemate	1,000	1,000
P 29B	10,000	11,000
[S] isomer of Compound P 29B	23,000	14,000
[R] isomer of Compound P 29B	3,500	4,000

EXAMPLE 2.

Experiment A.

[1R,—*Trans*]-3-(2,2-difluorovinyl)-2,2-dimethyl cyclopropane carboxylic acid.

a) A mixture of freshly distilled, dry, dimethyl formamide (20 ml), triphenylphosphine (7.9 g), methyl [1R,—*trans*]-caronaldehyde (3.0 g) and the sodium salt of chlorodifluoro acetic acid (3.6 g) were heated at 90°C with stirring for 20 hours. Water (60 ml) was then added and the solution extracted with 2 × 30 ml portions of diethylether. The combined ethereal extracts were washed with water, saturated sodium carbonate solution, saturated sodium chloride solution, and then dried over sodium sulphate and the ether distilled off. Distillation of the residue gave 2.25 g of methyl [1R,—*trans*]-3-(2,2-difluorovinyl)-2,2-dimethyl cyclopropane carboxylate, b.p. 63°C/20 mm, n_D 1.4209.

b) An alkaline solution was prepared by dissolving sodium hydroxide (200 mg) in water (1 ml) and ethanol (10 ml) was added. The methyl ester described above (0.5 g) was stirred into the alkaline solution and the mixture was refluxed for 1 hour. The solvents were removed under reduced pressure and water (30 ml) added. The solution was washed with 2 × 20 ml portions of diethylether and acidified with concentrated hydrochloric acid. The mixture was extracted with 2 × 30 ml portions of diethylether, washed with saturated sodium chloride solution, dried over sodium sulphate and the solvents evaporated to leave 410 mg of [1R,—*trans*]-3-(2,2-difluorovinyl)-2,2-dimethyl cyclopropane carboxylic acid as an oil having n_D 1.4400.

Experiment B.

[1R,Cis]-3-(2,2-difluorovinyl) 2,2-dimethyl cyclopropane carboxylic acid.

a) The procedure described in Example 2a above was repeated using 1.5 g methyl [1R,—*cis*]-caronaldehyde 2.92 g triphenylphosphine, 1.2 g sodium chlorodifluoro acetate and 7 ml dimethylformamide. The residue obtained after evaporating the final diethyl ether extract was itself extracted with 3 × 40 ml portions of petroleum ether and the petroleum ether evaporated and the residue distilled to give 440 mg of methyl [1R,—*cis*]-3-(2,2-difluorovinyl)2,2-dimethyl cyclopropane carboxylate b.p. 74—78°C/20 mm n_D 1.4288.

b) The methyl ester obtained above (380 mg) was added to a solution of sodium hydroxide (200 mg) in water (1 ml) and ethanol (10 ml). The mixture was refluxed for 1 hour with stirring and the solvents removed under reduced pressure. Water (50 ml) was then added and the solution washed with 20 ml diethylether, acidified with concentrated hydrochloric acid and extracted with diethyl ether. The ethereal extract was washed with saturated sodium chloride, dried over sodium

sulphate and evaporated to give 290 mg of [1R,-*cis*]-3-(2,2-difluorovinyl)-2,2-dimethyl cyclopropane carboxylic acid, n_D 1.4456.

The acids prepared as described in Experiments A and B were then esterified with 5-benzyl-3-furylmethyl alcohol, 3-phenoxybenzyl alcohol and ($\pm$)- α -cyano-3-phenoxybenzyl alcohol by the following procedure. A solution of the acid (110 mg) in benzene (5 ml) was treated with pyridine (50 μ l) and thionyl chloride (45 μ l) and left to stand for three hours at the end of which time, the acid has been converted into its acid chloride. A solution of 3-phenoxybenzyl alcohol (137 mg) or an equivalent quantity of the other alcohols and pyridine (50 μ l) in benzene (5 ml) was added to the acid chloride and the mixture left to stand over night. The desired ester was recovered from the solution by passing it through a column of neutral alumina and eluting the column with benzene. The eluate was evaporated to leave the ester as an oil, the following results being obtained.

Compound	Acid	Alcohol	n_D
P 31A	1R,- <i>trans</i>	5-benzyl-3-furyl methyl	1.5142
P 31B	1R,- <i>trans</i>	3-phenoxy-benzyl	1.5293
P 31C	1R,- <i>trans</i>	($\pm$)- α -cyano-3-phenoxy-benzyl	1.5330
P 31D	1R,- <i>cis</i>	5-benzyl-3-furyl methyl	1.5136
P 31E	1R,- <i>cis</i>	3-phenoxybenzyl	1.5349
P 31F	1R,- <i>cis</i>	($\pm$)- α -cyano-3-phenoxy-benzyl	1.5355

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The insecticidal toxicity of the insecticidal esters described in Example 2 were tested against houseflies and mustard beetles by the procedure described in our above mentioned application and the following results were obtained in relation to 5-benzyl-3-furylmethyl (+)-*trans* chrysanthemate (bioresmethrin) arbitrarily assigned a toxicity of 100.

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Compound	Relative Toxicity	
	Houseflies	Mustard Beetles
bioresmethrin	100	100
P 31A	390	190
P 31B	62	27
P 31C	84	73
P 31D	230	130
P 31E	180	85
P 31F	120	220

EXAMPLE 3.

($\pm$)-*cis-trans*-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic acid, prepared by reacting ethyl diazoacetate with 1,1-dichloro-4-methyl-penta-1,3-diene and hydrolysing the resulting ethyl ester, was separated into the ($\pm$)-*cis* and ($\pm$)-*trans* isomers by selective crystallisation in *n*-hexane, in which the *cis* isomer is more soluble. The substantially pure *cis* and *trans* isomers were then resolved into their individual optical isomers by the following procedure.

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Resolution of (+)-*cis*-2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropanecarboxylic acid. — The (+)-*cis* acid (14.6 g) in benzene (250 ml), and (+)- α -methylbenzylamine (8.47 g) in benzene (30 ml) were mixed at 50°, and allowed to cool to 20° overnight. The precipitate (13.2 g, 58% required isomer) was recrystallised 3 times from benzene to give the (+)- α -methyl benzylamine salt of the [1*S*,*cis*] acid (1.7 g) m.p. 135° [α]_D -17.1° (c, 1.6 in EtOH) was isolated. Repetition, using (-)- α -methylbenzylamine gave, after 3 crystallisations, the (-)- α -methylbenzylamine salt of the [1*R*,*cis*] acid (6.1 g) m.p. 147° [α]_D -26.1° (c, 1.9 in EtOH) and from the mother liquors the (-)- α -methylbenzylamine salt of the [1*S*,*cis*] acid (3.8 g) m.p. 139° [α]_D + 14.8° (c, 2.0 in EtOH).

Each of the four salts was shaken with benzene (50 ml) and 3*N* HCl (50 ml) and the benzene layer processed to give the resolved acids. Thus were obtained [1*S*,*cis*]-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic acid (4.6 g) m.p. 90° [α]_D -26.9° (c, 1.7 in CHCl₃) and [1*R*,*cis*]-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic acid (3.9 g) m.p. 90° [α]_D + 27.2° (c, 2.1 in CHCl₃).

Resolution of (+)-*trans*-2,2-dimethyl-3-(2,2-dichlorovinyl)cyclopropane carboxylic acid. — The (+)-*trans* acid (15.6 g) in benzene (180 ml) and L-(+)-threo-1-p-nitro-phenyl-2-N,N-dimethylaminopropane-1,3-diol (18.0 g) in benzene (180 ml) were mixed at 50° and cooled to 20° during 2 days. The precipitate (14.2 g) was recrystallised 3 times from trichloroethylene to give the L-(+)-threo-1-p-nitro-phenyl-2-N,N-dimethyl-aminopropane-1,3-diol salt of [1*S*,*trans*]-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylic acid (8.9 g) m.p. 129–131° [α]_D + 7.4° (c, 2.1 in EtOH). Correspondingly D-(-)-threo-1-p-nitrophenyl-2-N,N-dimethyl-aminopropane-1,3-diol gave the salt with the [1*R*,*trans*] acid (9.4 g) m.p. 129–131° [α]_D -7.3° (c, 2.0 in EtOH). Decomposition of the salts with 3*N* HCl as described for the *cis* acids gave [1*S*,*trans*]-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic acid (3.8 g) m.p. 68–73° [α]_D -34.6° (c, 1.9 in EtOH) and [1*R*,*trans*]-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic acid (4.1 g) m.p. 69–73° [α]_D + 33.0° (c, 2.0 in EtOH).

The [1*R*,*cis*] and [1*R*,*trans*] acids were converted to their acid chloride and reacted with 3-phenoxybenzyl alcohol by the procedure described in Example 1 to give the 3-phenoxybenzyl ester of [1*R*,*cis*] and of [1*R*,*trans*] 2,2-dimethyl-3-(2,2-dichlorovinyl)-cyclopropane carboxylic acid, compounds P29L and P29M respectively.

The [1*R*,*cis*] acid was also esterified with 5-benzyl-3-furylmethyl alcohol by the same procedure to give compound P29N, 5-benzyl-3-furylmethyl [1*R*,*cis*]-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylate.

The toxicity of these new esters was tested by the procedure described in detail in our above mentioned application and the following results were obtained:

Compounds	Relative Toxicity	
	Houseflies	Mustard Beetles
5-benzyl-3-furylmethyl [1 <i>R</i> , <i>trans</i>]-chrysanthemate (Bioresmethrin)	1,000	1,000
P 29L	1,600	1,400
P 29M	740	2,100
P 29N	2,600	2,200

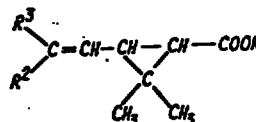
The toxicity of compounds P29L and P29M relative to bioresmethrin was also determined against the American cockroach, *Periplaneta americana* L. with the following results.

Compound	Relative Toxicity
Bioresmethrin	100 *
P 29L	2,100
P 29M	800

* LD₅₀ = 2.5 µg/insect

WHAT WE CLAIM IS:—

1. A compound of the general formula:



5 wherein the compound is in the form of a substantially pure optical isomer with respect to the cyclopropane ring and has [R] configuration at the carbon atom of the cyclopropane ring carrying the COOR group and wherein:

1. the compound is in the form of the crystalline stereoisomer of the compound in which R² and R³ each represent bromine and R represents α-cyano-3-phenoxybenzyl, or
- 10 2. the compound is one in which R² and R³ each represent fluorine and R represents 3-phenoxybenzyl, α-cyano-3-phenoxybenzyl or 5-benzyl-3-furylmethyl, or
- 15 3. the compound is one in which R² and R³ each represent chlorine and R represents 3-phenoxybenzyl when the cyclopropane ring has [1R,cis] or [1R,trans] configuration or R represents 5-benzyl-3-furylmethyl when the cyclopropane ring has [1R,cis] configuration.

2. A compound according to claim 1 in the form of the crystalline stereoisomer in which R² and R³ each represent bromine and R represents α-cyano-3-phenoxybenzyl.

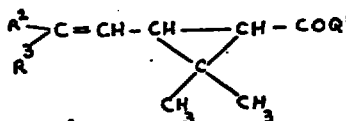
3. [S]-α-cyano-3-phenoxybenzyl [1R,cis]-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylate.

4. A compound according to claim 1 in which R² and R³ each represent fluorine and R represents 3-phenoxybenzyl, α-cyano-3-phenoxybenzyl or 5-benzyl-3-furylmethyl.

5. The 5-benzyl-3-furylmethyl esters of [1R,trans] or [1R,cis] 2,2-dimethyl-3-(2,2-difluorovinyl) cyclopropane carboxylic acid.

6. The 3-phenoxybenzyl ester of [1R,cis] or [1R,trans] 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic acid or 5-benzyl-3-furylmethyl [1R,cis] 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylate.

30 7. A process for the preparation of a compound as defined in claim 1 in which R² and R³ each represent chlorine or each represent fluorine wherein a carboxylic acid or esterifiable derivative thereof of formula:



35 is reacted with a compound of formula RQ where Q' and Q are functional groups which react together to form an ester linkage and R² and R³ each represent chlorine or each represent bromine, the resolution into the desired configuration on the cyclopropane ring taking place before or after formation of the ester linkage.

40 8. A process according to claim 7 substantially as hereinbefore described.

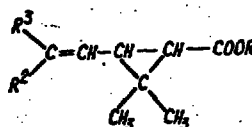
9. A compound as defined in claim 1 in which R² and R³ each represent

Compound	Relative Toxicity
Bioresmethrin	100 *
P 29L	2,100
P 29M	800

* LD₅₀ = 2.5 µg/insect

WHAT WE CLAIM IS:—

1. A compound of the general formula:



wherein the compound is in the form of a substantially pure optical isomer with respect to the cyclopropane ring and has [R] configuration at the carbon atom of the cyclopropane ring carrying the COOR group and wherein:

- the compound is in the form of the crystalline stereoisomer of the compound in which R² and R³ each represent bromine and R represents α-cyano-3-phenoxybenzyl, or
- the compound is one in which R² and R³ each represent fluorine and R represents 3-phenoxybenzyl, α-cyano-3-phenoxybenzyl or 5-benzyl-3-furylmethyl, or
- the compound is one in which R² and R³ each represent chlorine and R represents 3-phenoxybenzyl when the cyclopropane ring has [1R,cis] or [1R,trans] configuration or R represents 5-benzyl-3-furylmethyl when the cyclopropane ring has [1R,cis] configuration.

2. A compound according to claim 1 in the form of the crystalline stereoisomer in which R² and R³ each represent bromine and R represents α-cyano-3-phenoxybenzyl.

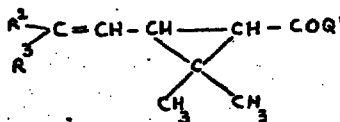
3. [S]-α-cyano-3-phenoxybenzyl [1R,cis]-2,2-dimethyl-3-(2,2-dibromovinyl)cyclopropane carboxylate.

4. A compound according to claim 1 in which R² and R³ each represent fluorine and R represents 3-phenoxybenzyl, α-cyano-3-phenoxybenzyl or 5-benzyl-3-furylmethyl.

5. The 5-benzyl-3-furylmethyl esters of [1R,trans] or [1R,cis] 2,2-dimethyl-3-(2,2-difluorovinyl) cyclopropane carboxylic acid.

6. The 3-phenoxybenzyl ester of [1R,cis] or [1R,trans] 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylic acid or 5-benzyl-3-furylmethyl [1R,cis] 2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropane carboxylate.

7. A process for the preparation of a compound as defined in claim 1 in which R² and R³ each represent chlorine or each represent fluorine wherein a carboxylic acid or esterifiable derivative thereof of formula:



is reacted with a compound of formula RQ where Q' and Q are functional groups which react together to form an ester linkage and R² and R³ each represent chlorine or each represent bromine, the resolution into the desired configuration on the cyclopropane ring taking place before or after formation of the ester linkage.

8. A process according to claim 7 substantially as hereinbefore described.

9. A compound as defined in claim 1 in which R² and R³ each represent



* C L N S *

fluorine or each represent chlorine obtained by a process according to claim 7 or 8.

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10. A process for the preparation of a compound as defined in claim 1 in which R^2 and R^3 each represent bromine in which $(\pm)$ - α -cyano-3-phenoxybenzyl [1R,cis] 2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropane carboxylate is dissolved in a solvent at elevated temperature, the solution is cooled and the precipitate of the isomer having [S]-configuration at the carbon atom carrying the α -cyano group, separated.

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11. A process according to claim 10, substantially as hereinbefore described.
12. A compound as defined in claim 1, in which R^2 and R^3 each represent bromine obtained by a process according to claim 10 or 11.

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13. An insecticidal composition comprising a compound according to any one of claims 1-6, 9 or 12 together with a diluent or carrier.

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14. A composition according to claim 13, wherein R^2 and R^3 each represent bromine.

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15. A composition according to claim 13, wherein R^2 and R^3 each represent fluorine.

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16. A method of insect control which comprises applying to an insect or to an environment susceptible to insect attack a compound according to any one of claims 1-6, 9 or 12 or a composition according to any one of claims 13-15.

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17. A method according to claim 16, wherein R_2 and R_3 each represent bromine.

18. A method according to claim 16, wherein R_2 and R_3 each represent fluorine.

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