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PERSISTENT ATTRACTANTS FOR THE MEDITERRANEAN FRUIT FLY, THE METHOD OF PREPARATION AND METHOD OF USE

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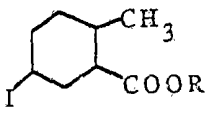
US 3016329

(57) Attacking over 250 varieties of fruits, nuts and vegetables, the Medfly is one of our most serious crop pests. Found predominately in Hawaii, Central America, and subtropical regions of the world, the Medfly has periodically invaded the mainland of the United States causing major economic losses. Consequently, there exists a great need for effective programs to control this pest.

CLAIM

1. An attractant to attract the Mediterranean Fruit Fly comprising an effective amount of a compound of the formula



wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl, and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compound having the iodo atom in the axial position.

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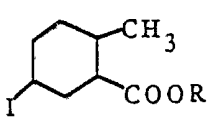
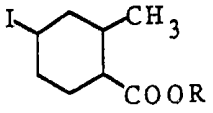
4. A composition to attract the Mediterranean Fruit Fly comprising an attractant having an effective amount of a mixture of compounds of the formulas

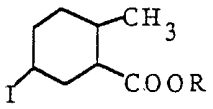


and

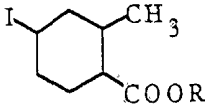


wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compounds having the iodo atom in the axial position, said R in each of the formulas being identical.

7. A composition to attract the Mediterranean Fruit Fly, comprising an attractant having an effective amount of a mixture of compounds of the formulas



and



wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial and axial, but is more than 50% equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, said R in each of the formulas being identical.

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(57) Abstract

Novel attractants for the Mediterranean Fruit Fly, "Medfly", are disclosed. The attractants comprise isomeric blends of esters of iodo-*trans*-2-methylcyclohexanecarboxylic acid. In use, the attractants are competitive in attraction with the "standard" Medfly attractant, Trimedlure, "TML", but are much more persistent than TML.

PERSISTENT ATTRACTANTS FOR THE MEDITERRANEAN FRUIT FLY, THE METHOD OF PREPARATION AND METHOD OF USE

Background of the Invention

Field of the Invention

This invention relates to novel attractants for the Mediterranean Fruit Fly, Ceratitis capitata Wiedmann, hereinafter referred to as the "Medfly." More particularly, the present invention relates to novel isomeric blends of aliphatic esters of iodo-trans-2-methylcyclohexanecarboxylic acid, the method of their preparation and the method of use thereof to attract the Medfly for prolonged periods of time.

Description of the Prior Act

Attacking over 250 varieties of fruits, nuts and vegetables, the Medfly is one of our most serious crop pests. Found predominately in Hawaii, Central America, and subtropical regions of the world, the Medfly has periodically invaded the mainland of the United States causing major economic losses. Consequently, there exists a great need for effective programs to control this pest.

Several attractants for the Medfly are known. Siglure (1-methylpropyl trans-6-methyl-3-cyclohexenecarboxylate) was the first synthetic lure found to have significant attraction to the Medfly. Medlure (1-methylpropyl 4(and 5)-chloro-trans-2-methylcyclohexanecarboxylate),

hereinafter referred to as "TML," were later reported to be greatly superior as Medfly attractants.

Currently, TML is the "standard" attractant most widely used in traps for survey and detection of the Medfly. TML evaporates rapidly during hot weather thereby necessitating frequent and costly rebaiting of the traps. Further, the short residual life of TML (as well as Medlure and Siglure) mitigates against the development of an economical male-annihilation formulation of attractant plus insecticide. TML also forms crystals during cold-weather storage so that the amount of the attractant is reduced in the supernatant. Because these crystals do not readily redissolve, special storage problems can occur in large volume programs.

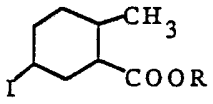
Summary of the Invention

An object of this invention is to provide novel attractants which are highly attractive to the Medfly for prolonged periods of time.

Another object of this invention is to provide persistent Medfly attractants which are comparable in attraction with TML but do not possess the deficiencies associated with TML.

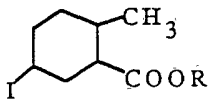
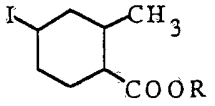
We have accomplished the aforementioned objects by providing certain isomeric blends of lower alkyl esters of 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylic acid which when applied in an amount sufficient to attract the Medfly are highly effective for prolonged periods of time. In addition to being much more persistent than TML, the esters of the invention are not prone to crystallization as is TML, and may be more facilely and economically produced than TML.

According to a first embodiment of this invention, there is provided an attractant to attract the Mediterranean Fruit Fly comprising an effective amount of a compound of the formula



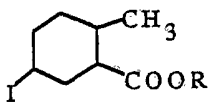
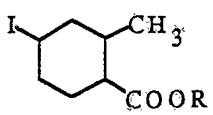
wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl, and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compound having the iodo atom in the axial position.

According to a second embodiment of this invention, there is provided a composition to attract the Mediterranean Fruit Fly comprising an attractant having an effective amount of a mixture of compounds of the formulas

 and 

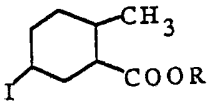
wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compounds having the iodo atom in the axial position, said R in each of the formulas being identical.

According to a third embodiment of this invention, there is provided a composition to attract the Mediterranean Fruit Fly, comprising an attractant having an effective amount of a mixture of compounds of the formulas

 and 

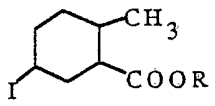
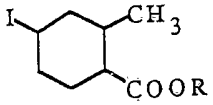
wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial and axial, but is more than 50% equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, said R in each of the formulas being identical.

According to a fourth embodiment of this invention, there is provided a method of attracting the Mediterranean Fruit Fly, comprising the step of subjecting the fly for an extended period of time to a composition having an attractant with an effective amount of a compound of the formula



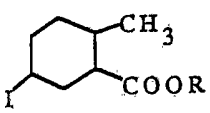
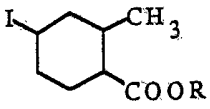
wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compounds having the iodo atom in the axial position.

According to a fifth embodiment of this invention, there is provided a method of attracting the Mediterranean Fruit Fly, comprising the step of subjecting the fly for an extended period of time to a composition having an attractant with an effective amount of a mixture of compounds of the formulas

 and 

wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compounds having the iodo atom in the axial position, said R in each of the formulas being identical.

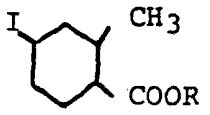
According to a sixth embodiment of this invention, there is provided a method of attracting the Mediterranean Fruit Fly, comprising the step of subjecting the fly for an extended period of time to a composition having an attractant with an effective amount of a mixture of compounds of the formulas

 and 

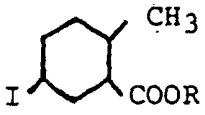
wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial and axial, but is more than 50% equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, said R in each of the formulas being identical.

Detailed Description of the Invention

In general, esters useful in the present invention are represented by the general formulae



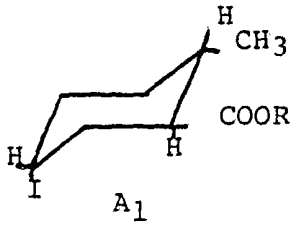
I



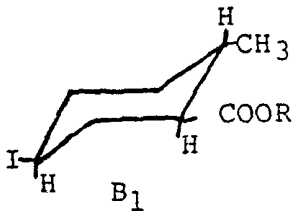
II

wherein $-CH_3$ and -COOR are in the trans-configuration and I is in both the equatorial and axial conformation; and wherein R is an aliphatic radical having from 1-5 carbon atoms and is selected from the group consisting of lower alkyls and fluoro-substituted lower alkyls, said R in each of formulae I and II being identical.

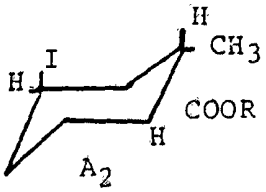
For purposes of the invention, the term "4 and 5" is used herein to designate a mixture of the 4- and 5-iodo isomers wherein the iodo atoms of the invention esters are in both an equatorial and axial conformation, thus providing a blend of four stereoisomers for each ester. The four stereoisomers are herein designated A_1, A_2, B_1 and B_2 as follows:



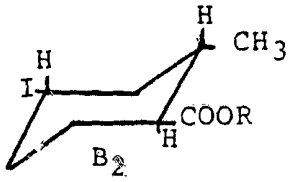
A_1



B_1



A_2



B_2

Examples of esters useful in the present invention are methyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate; ethyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate; propyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate; 1-methylpropyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate; 2,2,2-trifluoroethyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate; 1-methyl-2,2,2-trifluoroethyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate; 2,2,3,3,3-pentafluoro-1-methylpropyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate; and 2,2,3,3,4,4,4-heptafluoro-1-methylbutyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate.

Esters useful in the present invention may be prepared as follows: The corresponding trans-6-methyl-3-cyclohexenecarboxylic acid (as prepared by a Diels-Alder reaction) is heated in a pressure vessel for 3 to 6 hours at elevated temperatures with aqueous hydriodic acid in the presence of an organic solvent, such as dioxane. The resultant iodo-trans-2-methylcyclohexanecarboxylic acid is a mixture of the 4- and 5-iodo isomers and is converted to the corresponding acid halide by reacting with a suitable halogenating agent, such as thionyl chloride, phosphorus trichloride or phosphorus tribromide under mild conditions, preferably at room temperature. The acid halide is then reacted with the appropriate alcohol in a suitable solvent such as benzene or anhydrous ethyl ether in the presence of a hydrochloric acid scavenger, such as pyridine, to yield the ester.

Isolation of the ester is accomplished by sequentially washing the crude reaction mixture with dilute acid, dilute base and saturated salt solutions. The crude product is thereafter dried over a suitable drying agent, filtered and the solvent removed. Final purification is accomplished by

fractional distillation under high vacuum. Individual stereoisomers of the esters can be separated by high-performance liquid chromotography.

The stereoisomeric content of the esters can be easily varied by changing the reaction temperature during preparation of the ester. For example, invention esters synthesized by the addition of hydrogen iodide to the Diels-Alder acid adduct at moderately elevated temperatures, i.e., from about 65°C to 80°C, consist of a isomeric blend which has isomers A_1 and A_2 as its major components, with isomers B_1 and B_2 comprising about 10% to 20% of the blend. Esters synthesized by the addition of hydrogen iodide to the Diels-Alder acid adduct at about 95°C to 130°C consist of an isomeric blend which consists of greater than 50% of isomers B_1 and B_2. Consequently, the higher the temperature the greater the B_1/B_2 isomeric content in the resulting ester.

Of the four stereoisomers, the most attractive isomer is isomer B_1 having an equatorial iodo atom attached at the 5 carbon atom. For commercial practicalness, it is preferred to use a blend of isomers consisting predominately of isomers B_1 and B_2. Preferably, the blend comprises an isomeric content of from about 50% to 100% of isomers B_1 and B_2 with isomers A_1 and A_2 comprising from about 0% to 50% of the blend.

The esters may be used as is or they may be dissolved in volatile inert solvents such as liquid hydrocarbons, emulsified in water, or admixed with any other solid or inert liquid carrier. When used in actual practice in the field, the compounds may be impregnated on a solid carrier such as paper, cloth, sawdust, wood chips, or other absorbent material. The attractants may also be dispersed into the atmosphere by spraying or by dipping wicks into containers holding the ester composition. Further, the

attractants may be used in bait traps usually provided with means to prevent the exit of insects so that the size and location of infestations may be ascertained.

For optimum results, the esters of the invention should be used in a substantially pure form, that is, the esters must be free of undesirable contaminants that tend to mask or otherwise inhibit their effectiveness as an attractant. It is within the compass of the invention to use the esters either individually or in combination. The invention esters may also be used with other Medfly attractants or control agents, such as insecticides, chemosterilants or the like. When used, however, these agents should be used in an amount which, as readily determined by one skilled in the arts, will not interfere with the effectiveness of the invention esters.

Although the preparative procedures described above are the preferred synthesis for the compounds of the invention, it is within the scope of this invention to prepare the esters using any suitable hydriodic acid addition and esterification procedures.

The invention is further demonstrated by the following examples which are intended only to further illustrate the invention and not to limit the scope of the invention as defined by the claims.

Example 1

The preparation of a blend of ethyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate comprising more than 50% of isomers B_1 and B_2 using the Diels-Alder acid adduct intermediate is hereinafter illustrated.

21 g of trans-6-methyl-3-cyclohexenecarboxylic acid (0.15 mole) were added to a pressure bottle along with 60 ml of 57% hydriodic acid and 30 ml of p-dioxane. The pressure bottle was equipped with a magnetic stirrer,

securely capped, and placed in an oil bath held at 115 to 125°C. The reaction mixture was stirred vigorously while being held in the bath for 3 hours. After cooling, the reaction mixture was poured into water and the organic layer was taken up in ether. The ether layer was washed 2 times with water, then the organic acid was extracted from the crude reaction mixture with 10% aqueous sodium hydroxide. The alkaline portion was strongly acidified. The released organic acid was taken up in ether and was washed 3 times with water, then with dilute sodium bisulfite solution, again with water, dried over anhydrous magnesium sulfate and filtered. After removal of the solvent the crude iodo acid (ca 36 g) was used directly in the acid chloride synthesis. 26.8 g of the iodo acid (0.1 mole) was dissolved in 25 ml of benzene and 9 ml of thionyl chloride (0.125 mole) was added dropwise at room temperature. The reaction mixture was stirred overnight and the excess thionyl chloride and benzene were removed under vacuum with slight warming (40°C). The crude acid chloride was added dropwise to an excess of ethanol (12 ml) and 8 ml of pyridine in anhydrous ether. After standing overnight, the reaction mixture was extracted sequentially with water, dilute aqueous hydrochloric acid and sodium hydroxide and finally with saturated salt solution. After drying over anhydrous magnesium sulfate, the crude product was isolated and purified by fractional distillation under high vacuum, b.p. 81°C/ 0.15mm Hg, n^{25}_{D} 1.5130, recovered yield 15.0 g, approximately 67% of which consisted of isomers B_1 and B_2 and 33% of isomers A_1 and A_2 (from gc peak height measurement). If the product darkens excessively after distillation, the excessive color can be removed by washing the product with dilute sodium bisulfite solution.

Example 2

An isomeric blend of propyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate was synthesized in a 0.02 mole reaction in accordance with the procedure described in Example 1, and purified by distillation under high vacuum, b.p. 85°C 0.15 mm, n^{25}_D 1.5065, recovered yield 2.67 g (about 67% isomers B_1 and B_2 and about 33% isomers A_1 and A_2 from gc peak height measurement).

Example 3

To determine the effectiveness of the blends of the invention a field test was conducted in a macadamia nut orchard at Keaau, Hawaii, in October 1987.

Medfly captures using isomeric blends of methyl, propyl, 1-methylethyl, 1-methyl-2,2,2-trifluoroethyl and 2,2,2-trifluoroethyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate were compared with those captures obtained by using TML. The ester blends used were (1) blends which consisted of about 100% B_1 and B_2 isomers; and/or (2) normal blends, that is, blends comprising isomers A_1, and A_2, B_1 and B_2 wherein isomers A_1 and A_2 comprise more than 50% of the blend.

Treatments were applied to cotton wicks (9.5 mm diam. x 12.7 mm length; Johnson and Johnson No. 2) in standard Jackson sticky traps. Each attractant was applied in a 0.025 ml dosage undiluted to a wick. Six replicates were used. The TML wick was allowed to age along with the other attractants. Sterile laboratory-reared medflies were released throughout the test plot in a uniform manner at 0, 1, 2, 3, 4, 8, 10 and 13 days posttreatment. Fresh sticky inserts were placed in the traps prior to each release and remained in the trap throughout the test interval.

The TML used in the tests was obtained commercially from UOP in East Rutherford, N.J.

Data was analyzed by analysis of variance, and means were separated by Duncan's multiple range test at the P = 0.05 level (Duncan 1951). The results are recorded in Table I.

Table I clearly shows the high attraction and superior persistence of ester blends comprising only isomers B_1 and B_2 over the normal blends. All of the B_1B_2 blends were significantly more attractive than their corresponding normal blends. In no case throughout the test did the catch of the normal mixture equal the catch obtained with the corresponding B_1B_2 blend. Of the ester blends tested, the B_1B_2 isomeric blend of the ethyl ester was the most attractive. Although not as initially attractive as the ethyl ester blend, the B_1B_2 isomeric blends of the propyl and the 1-methylethyl esters showed significant persistence over TML. After 2 days TML began to fail while the propyl and 1-methylethyl esters were effective up to 13 and 8 days, respectively. Further, the propyl and 1-methylethyl blends outlasted the ethyl ester up to 5 and 2 days, respectively.

Example 4

The relative attractiveness of the four stereoisomers of ethyl 4(and 5)-iodo-trans-2-methylcyclohexanecarboxylate, and mixtures thereof, were determined in a field test conducted in a macadamia nut orchard at Keaau, Hawaii, in February 1988.

Medfly captures obtained with fresh and aged TML was compared to captures obtained using the ethyl ester having the following isomeric content: (1) high A_1 and A_2, that is, more than 50% of isomers A_1 and A_2; (2, isomer A_2; (3) isomers B_1 and B_2; (4) isomer B_1 and (5) isomer B_2 with ca. 2.5% of isomer B_1.

The bioassay was the same as described in Example 4 except that a freshly baited TML wick was added to the test prior to each fly release and medflies were released at 0, 1, 3, 4, 8, 9, 10, 11 and 14 days postreatment.

Data were analyzed in accordance with Example 4. The results are reported in Table II.

Table II shows that of the four stereoisomers of the ethyl ester, the most attractive isomer was the B_1 isomer. Traps with the B_1 isomer had higher mean catches than those of fresh TML in the first 6 test periods and in 7 of the 9 test periods overall, Medfly captures with blends comprising the B_1 isomer were significantly as attractive as fresh TML up to 10 days. All isomeric mixtures of the ethyl ester tested were more persistent than aged TML which began to fail between days 1 and 3.

It is understood that modifications and variations may be made to the foregoing disclosure without departing from the spirit and scope of the invention.

TABLE I

Attraction of the Mediterranean Fruit Fly to Esters of 4(and 5)-Iodo-trans-2-methylcyclohexane-1-carboxylic Acid When Compared With Trimedlure (TML), October, 1987, Keaau, Hawaii

Ester	Isomer blend[a]	Weighted mean catch/trap after indicated days of exposure in the field[b] [c]							
		0	1	2	3	4	8	10	13
TML-aged		162a	176a	122bc	14f	0f	0e	0d	0c
Methyl	Normal	5f	5e	6f	9f	7ef	0e	0d	0c
	B_1B_2	31de	38d	45de	49de	48d	0e	0d	0c
Ethyl	B_1B_2	157a	216a	190ab	200a	229a	93b	0d	0c
Propyl	Normal	33de	62cd	56de	97bc	91cd	52c	23b	6b
	B_1B_2	69bc	143ab	12bc	147ab	165ab	146a	65a	49a
1-Methylethyl	Normal	12ef	36d	49de	58cde	90cd	19d	7c	0c
	B_1B_2	47cd	84c	94cd	93bc	125bc	34cd	8c	0c
1-Methyl-2,2,2-trifluoroethyl	Normal	16ef	39d	33e	29ef	14e	0e	0d	0c
	B_1B_2	49cd	102bc	52de	64cd	65d	0e	0d	0c
2,2,2-Trifluoroethyl	Normal	107b	197a	207a	167a	144bc	0e	0d	0c

[a] Normal blend is composed of 4 isomers, A_1, A_2, B_1, and B_2 wherein isomers A_1 and A_2 are more than 50% of the blend

[b] 6 replicates; 0.025 ml dosage

[c] Catches followed by the same letter within a column are not significantly different ($P > 0.05$; Duncan's [1951] multiple range test).

TABLE II

Attraction Of The Mediterranean Fruit Fly To Varying Isomeric Blends Of Ethyl 4(and 5)-iodo-trans-2-methyl-cyclohexanecarboxylate And To Its Individual Isomers A_2, B_1, AND B_2 When Compared With Trimedlure (TML).

Isomer Content[a]	Weighted mean catch/trap after indicated days in the field[b]								
	0	1	3	4	8	9	10	11	14
TML-(fresh)	152a	44ab	63a	92a	136a	130ab	125a	52b	119a
TML-(aged)	78bc	19b	10b	0c	0c	0d	0e	0d	0c
High A_1A_2[c]	19de	2c	5b	23b	15b	15c	12d	2cd	3b
A_2	4e	0c	0c	0c	0c	0d	0e	0d	0c
High B_1B_2[c]	113ab	40ab	50a	109a	96a	91b	41bc	7c	0c
B_1B_2	135ab	60a	65a	123a	126a	109ab	28cd	6c	0c
B_1	172a	63a	73a	121a	139a	144a	103a	85a	116a
B_2[d]	40cd	3c	8b	22b	15b	12c	1e	0d	0c

[a] The 4 isomers that compose the trans blend are designated A_1, A_2, B_1 and B_2.

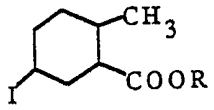
[b] Catches followed by the same letter within a column are not significantly different ($P > 0.05$; Duncan's [1951] multiple range test); 0.02 ml dosage; 6 replicates.

[c] High A_1/A_2 consists of isomers A_1, A_2, B_1 and B_2 wherein isomers A_1 and A_2 are more than 50% of the blend.
High B_1/B_2 consists of isomers A_1, A_2, B_1 and B_2 wherein isomers B_1 and B_2 are more the 50% of the blend.

[d] Contained ca. 2.5% isomer B1.

The claims defining the invention are as follows:

1. An attractant to attract the Mediterranean Fruit Fly comprising an effective amount of a compound of the formula

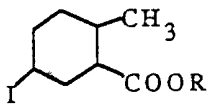
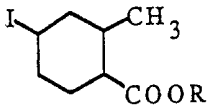


wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl, and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compound having the iodo atom in the axial position.

2. A composition to attract the Mediterranean Fruit Fly comprising the attractant of claim 1, and an inert carrier for said compound.

3. The composition of claim 2, further comprising a control agent for the Mediterranean Fruit Fly.

4. A composition to attract the Mediterranean Fruit Fly comprising an attractant having an effective amount of a mixture of compounds of the formulas

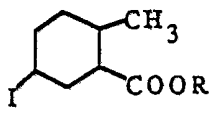
 and 

wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compounds having the iodo atom in the axial position, said R in each of the formulas being identical.

5. The composition of claim 4, further comprising an inert carrier for said compounds.

6. The composition of claim 4 or claim 5, further comprising a control agent for the Mediterranean Fruit Fly.

7. A composition to attract the Mediterranean Fruit Fly, comprising an attractant having an effective amount of a mixture of compounds of the formulas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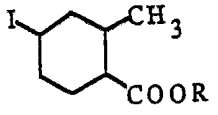


wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial and axial, but is more than 50% equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, said R in each of the formulas being identical.

8. The composition of claim 7, wherein R is ethyl.

9. The composition of claim 7, wherein R is propyl.

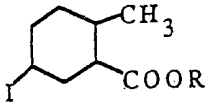
10. The composition of claim 7, wherein R is 2,2,2-trifluoroethyl.

11. The composition of any one of claims 7 to 10, further comprising an inert carrier for said compounds.

12. The composition of any one of claims 7 to 11, further comprising a control agent for the Mediterranean Fruit Fly.

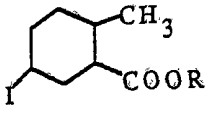
13. The composition of claim 12, wherein said control agent is an insecticide.

14. A method of attracting the Mediterranean Fruit Fly, comprising the step of subjecting the fly for an extended period of time to a composition having an attractant with an effective amount of a compound of the formula



wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compounds having the iodo atom in the axial position.

15. A method of attracting the Mediterranean Fruit Fly, comprising the step of subjecting the fly for an extended period of time to a composition having an attractant with an effective amount of a mixture of compounds of the formulas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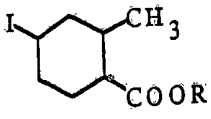
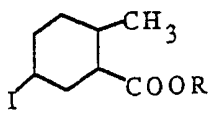
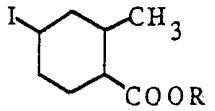


wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, wherein said composition essentially is free of isomers of said compounds having the iodo atom in the axial position, said R in each of the formulas being identical.

16. A method of attracting the Mediterranean Fruit Fly, comprising the step of subjecting the fly for an extended period of time to a composition having an attractant with an effective amount of a mixture of compounds of the formulas



and



wherein $-CH_3$ and -COOR are in the trans-configuration and the iodo atom is equatorial and axial, but is more than 50% equatorial, and wherein R is selected from the group consisting of ethyl, 2,2,2-trifluoroethyl, propyl, 1-methylethyl and 1-methyl-2,2,2-trifluoroethyl, said R in each of the formulas being identical.

17. The method of claim 16, wherein R is ethyl.

18. The method of claim 16, wherein R is propyl.

19. A composition to attract the Mediterranean Fruit Fly, which composition is substantially as hereinbefore described with reference to Example 1 or Example 2.

20. A method of attracting the Mediterranean Fruit Fly, comprising the step of subjecting the fly for an extended period of time to the composition of claim 19.

DATED this EIGHTEENTH day of APRIL 1991
The United States of America, as represented by the
Secretary, US Department of Commerce

Patent Attorneys for the Applicant
SPRUSON & FERGUSON

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US89/01501

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [5]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(4): A01N 25/00

U.S.Cl.: 424/84

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	424/84

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

Chemical Abstracts - Subject 1909-1988
alkyl and haloalkyl esters of 2-methyl cyclohexanecarboxylic acid

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
&, Y	US, A, 4,764,366 (McGOVERN ET AL) published 16 August 1988, see abstract and column 2, lines 15-49.	1-12
A	US, A, 4,152,422 (OHINATA ET AL) published 1 May 1979, see abstract.	1-12
Y	US, A, 3,016,329 (BEROZA ET AL) published 9 January 1962, see column 1, lines 44-68; column 4, lines 9-59; and column 6, lines 17-65.	1-12
A	N, Gertler et al, "Esters of 6-methyl-3-Cyclohexene-1-carboxylic acid as Attractants for the Mediterranean Fruit Fly", Agricultural and Food Chemistry, Vol. 6, No. 8 pp. 592-594, August 1958, see table I, on page 593.	1-12
A	N, Beroza et al, "New Attractants for the Mediterranean Fruit Fly", Agricultural and Food Chemistry, Vol. 9, No. 5, pp. 361-365, Sept/Oct. 1961, see table 1, on page 352.	1-12

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
6 JULY 1989	26 JUL 1989
International Searching Authority	**Signature of Authorized Officer**
ISA/US	ALLEN J. ROBINSON