

AN OPTICALLY ACTIVE PYRETHROID COMPOUND AND PREPARATION PROCESS AND USE THEREOF

Technical field of the invention

[0001] The present invention relates to a pyrethroid compound, especially relates to an optically active pyrethroid compound, and a safe and high-yield process for preparing the compound and the use thereof.

Background of the invention

[0002] Pyrethroid compounds can be used to control mosquitoes, and have a high pesticidal activity, which has been well known. The US Patent US4370346 described that a racemic compound of formula (A), wherein R_1 and R_2 are chlorine at the same time, may be used as a pest control agent, and the Chinese patent CN1669429 and CN1669419 also described that the racemic compound can be made into a pesticide. However, in the course of the study, we found that the resolved single optical isomer has higher pesticidal activity, after further exploration, we found that when R_1 and R_2 , which may be identical or different, are chlorine or bromine, the single optically active compound represented by formula (A) had a high pesticidal activity. With increasing demands on environmental protection, the high biological activity isomer of pesticides has drawn increasing attention, the pyrethroid usually has 2 to 8 optical isomers, the biological activity difference between each isomer is very large, so it needs to study the preparation of an isomer which has the highest activity. From an environmental point of view, the use of a single optical isomer having high activity can reduce the amount of the pesticide to be applied without reducing the efficacy of same, which results in reduction of toxicity to non-target organisms, improving safety, and reducing environmental pollution of residues.

[0003] The purpose of the present invention is to provide a new pyrethroid compound, which is a single optical activity isomer, while the present invention also provides a process for preparing the compound and the use thereof.

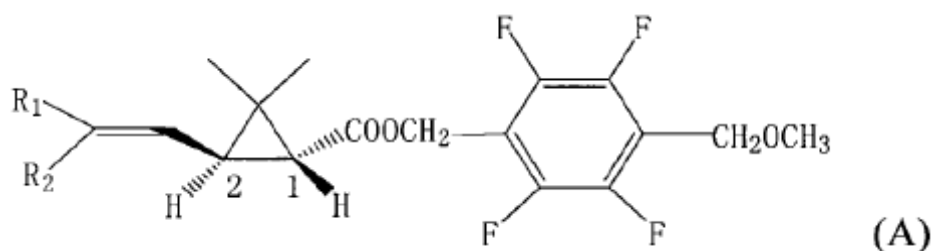
Summery of the invention

[0004] The purpose of the present invention is to provide a pyrethroid compound which shows better pesticidal effect than the pyrethroid compound of the prior art.

[0005] The purpose of the present invention achieved by the following technical

solutions:

[0006] Provides a pyrethroid compound according to the following formula (A),



[0007] The compound is a dextro single optical isomer, wherein R_1 and R_2 , which may be identical or different, represent halogen.

[0008] Among the compounds, such a compound is preferred, wherein R_1 and R_2 , which may be identical or different, represent fluorine, chlorine or bromine; and the following compound is further preferred:

[0009] Compound I, wherein R_1 and R_2 are chlorine at the same time, the compound is 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester.

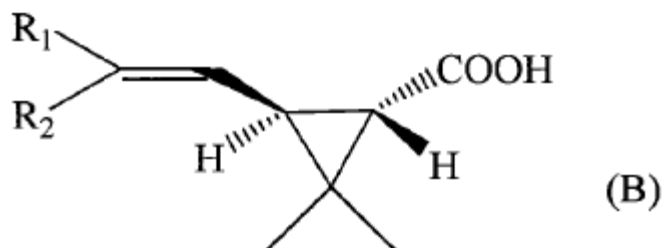
[0010] Compound II, wherein R_1 and R_2 are bromine at the same time, the compound is 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester.

[0011] Compound III, wherein R_1 and R_2 are fluoride at the same time, the compound is 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-difluorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester, or

[0012] Compound IV, wherein R_1 is chlorine and R_2 is bromine, the compound is 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2-chloro-2-bromovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester.

[0013] The present invention also provides a process for preparing the compound, which contains the following steps:

[0014] 1) resolving a racemic trans-chrysanthemum acid with a chemical resolving agent to obtain the corresponding D-trans-chrysanthemum acid, wherein the racemic trans-chrysanthemum acid is the compound according to the following formula (B), wherein R_1 and R_2 , which may be identical or different, represent halogen; the molar ratio of the chemical resolving agent to the racemic trans-chrysanthemum acid is 0.2:1-4:1;



[0015] 2) acyl-chlorinating the D-trans-chrysanthemum acid got from the step 1) with an acyl-chlorination reagent to obtain the corresponding D-trans-acyl chloride; wherein the molar ratio of the acyl-chlorination reagent to the D-trans-chrysanthemum acid is 0.2:1-4:1; the acyl-chlorination reagent is one selected from the group consisting of phosphorus trichloride, thionyl chloride, and bis (trichloromethyl) carbonate;

[0016] 3) esterifying the D-trans-acyl chloride got from the step 2) with 2,3,5,6-tetrafluoro-4-methoxy methyl benzyl alcohol to obtain the pyrethroid compound of the formula (A); wherein the molar ratio of the D-trans-acyl chloride to 2,3,5,6-tetrafluoro-4-methoxy methyl benzyl alcohol is 0.2:1-4:1,

[0017] wherein the chemical resolving agent in the step 1) is a dextro chiral organic amine compound, which is one selected from the group consisting of D-chloramphenicol amine ((+) N, N-dimethyl-para-nitrophenyl-1,3-propanediol), D-PTE ((+) β -p-methyl-phenyl- α -phenylethylamine) or D- α -phenylethylamine.

[0018] The present invention also provides use of the compound for preventing and treating hygiene pests.

[0019] In the use, the hygiene pests are mosquitoes, flies or *blattela germanicas* and so on.

[0020] Compared with the prior art, the present invention has the following beneficial effects:

[0021] 1. The process for preparing the compound provided by the present invention shows high quality, high yield, process safety, and ease to control.

[0022] 2. Biological efficacy test results show that the compound of the invention has a significant preventing and treating effect on *Musca domestica*, *Culex pipiens*, *Culex pipiens fatigans*, *Blattela germanicas* et al., the pesticidal activity of the optically active isomer of which is much higher than the corresponding racemic body. Furthermore, the results of the efficacy test between the compound and a commonly used hygiene pesticide allethrin show the efficacy of the present compound is 20 times higher than that of allethrin. If using the compound instead of allethrin, to achieve the same effect, the amount of the compound to be applied is only about 5%

of allethrin, which greatly reduces the environmental pollution.

Detailed description of the invention

[0023] Hereinafter combine with some examples to illustrate the present invention. It should be understood that these examples are only for illustration but not to limit the scope of the present invention. In the following examples, any experimental method which does not indicate the specific condition, was conducted under a condition which is usually used in this field or recommended by the manufacturer.

Preparation Example 1: Resolution of trans-2,2-dimethyl-3-(2,2-dichlorovinyl) cyclopropanecarboxylic acid (trans-dichloro-chrysanthemic acid)

[0024] Trans-dichloro-chrysanthemic acid (100.0g) and D-chloramphenicol amine (100.0g) were put into a four-neck flask (1000ml), dissolved in toluene (500ml), followed with agitating, the mixture was heated to 110°C and reacted under reflux for 1 hour, and then cooled to 40°C within 3 hours, kept at same temperature for 1 hour, then cooled to 10°C within 2 hours, and kept at same temperature for 0.5 hours, and at this time a large amount of crystal was precipitated. Then the reaction mixture was filtrated, 10% hydrochloric acid (100g) was added to the obtained mother liquors to adjust the pH to 2-3. After layer separation, the oil layer was washed with water until it was nearly neutral, and heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then (R)-2,2-dimethyl-3-trans-(2,2-dichlorovinyl) cyclopropane carboxylic acid was obtained (46.5g), wherein the ee value of the dextro isomer was 97%.

Preparation Example 2: Resolution of trans-dichloro-chrysanthemic acid

[0025] Trans-dichloro-Chrysanthemic acid (100.0g) and D-PTE (125.0g) were put into a four-neck flask (1000ml), dissolved in toluene (400ml), followed with agitating, the mixture was heated to 110°C and reacted under reflux for 1 hour, and then cooled to 60°C within 3 hours, kept at same temperature for 1 hour, then cooled to 20°C within 2 hours, and kept at same temperature for 1 hours, and at this time a large amount of crystal was precipitated. After filtration, crystal was obtained, 5% hydrochloric acid (200g) was added thereto for acidating and at the same time toluene (400 ml) was added thereto for extracting. After layer separation, the oil layer was washed with water until it was nearly neutral, heated to 100°C to evaporate off the

toluene solvent under reduced pressure (10mmHg), then (R)-2,2-dimethyl-3-trans-(2,2-dichlorovinyl) cyclopropane carboxylic acid was obtained (45.2g), wherein the ee value of the dextro isomer was 96%.

Preparation Example 3: Acyl-chlorination of D-trans-dichloro chrysanthemic acid

[0026] D-trans-dichloro-chrysanthemic acid (209g, 1mol, ee value of 97%) got from Preparation Example 1 was put into a four-neck flask (1000ml), dissolved in toluene (600ml), followed with agitating, the mixture was heated to 50°C, and SOCl₂ (142g, 1.2mol) was dropwise added thereto within 2 hours. The resultant was heated to 60°C and kept at same temperature for reaction. After the reaction finished, the resultant was heated to 80°C to evaporate off the toluene solvent under reduced pressure (30mmHg), then rectified under reduced pressure (10mmHg), the fraction between 60-75°C was collected, then (R)-2,2-dimethyl-3-trans-(2,2-dichlorovinyl) cyclopropane carboxylic acid acyl chloride was obtained (216.1g), wherein the yield was 95.1%, the ee value of the dextro isomer was 97%.

Preparation Example 4: Acyl-chlorination of D-trans-dichloro chrysanthemic acid

[0027] Trans-dichloro-D-chrysanthemic acid (209g, 1mol, ee value of 97%) got from Preparation Example 1 was put into a four-neck flask (1000ml), dissolved in toluene (600ml), followed with agitating, the mixture was heated to 50°C, and a toluene solution (200 ml) containing triphosgene (118.7g, 0.4mol) was dropwise added thereto within 2 hours. The resultant was heated to 60°C and kept at same temperature for reaction. After the reaction finished, the resultant was heated to 80°C to evaporate off the toluene solvent under reduced pressure (30mmHg), then rectified under reduced pressure (10mmHg), the fraction between 60-75°C was collected, then (R)-2,2-dimethyl-3-trans-(2,2-dichlorovinyl) cyclopropane carboxylic acid acyl chloride was obtained (214.1g), wherein the yield was 94.3%, the ee value of the dextro isomer was 97%.

Preparation Example 5: Resolution of trans-2,2-dimethyl-3-(2,2-dibromovinyl) cyclopropanecarboxylic acid (trans-dibromo-chrysanthemic acid)

[0028] Trans-dibromo-chrysanthemic acid (100.0g) and D-chloramphenicol amine

(80.0g) were put into a four-neck flask (1000ml), dissolved in toluene (500ml), followed with agitating, the mixture was heated to 110°C and reacted under reflux for 1 hour, and then cooled to 40°C within 3 hours, kept at same temperature for 1 hour, then cooled to 10°C within 2 hours, and kept at same temperature for 0.5 hours, and at this time a large amount of crystal was precipitated. After filtration, 10% hydrochloric acid (100g) was added to the obtained mother liquors to adjust the pH to 2-3. After layer separation, the oil layer was washed with water until it was nearly neutral, heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then (R)-2,2-dimethyl-3-trans-(2,2-dibromovinyl) cyclopropane carboxylic acid was obtained (44.7g), wherein the ee value of the dextro isomer was 95%.

Preparation Example 6: Acyl-chlorination of D-trans-dibromo chrysanthemic acid

[0029] Trans-dibromo-D-chrysanthemic acid (298g, 1mol, ee value of 95%) got from Preparation Example 5 was put into a four-neck flask (1000ml), dissolved in toluene (600ml), followed with agitating, the mixture was heated to 50°C, and SOCl₂ (142g, 1.2mol) was dropwise added thereto within 2 hours. The resultant was heated to 60°C and kept at same temperature for reaction. After the reaction finished, the resultant was heated to 80°C to evaporate off toluene the solvent under reduced pressure (30mmHg), then rectified under reduced pressure (10mmHg), the fraction between 60-75°C was collected, then (R)-2,2-dimethyl-3-trans-(2,2-dibromovinyl) cyclopropane carboxylic acid acyl chloride was obtained (305.4g), wherein the yield was 94.7%, the ee value of dextro isomer was 95%.

Preparation Example 7: Resolution of trans-2,2-dimethyl-3-(2,2-difluorovinyl) cyclopropanecarboxylic acid (trans-difluoro-chrysanthemic acid)

[0030] Trans-difluoro-chrysanthemic acid (100.0g) and D-chloramphenicol amine (120.0g) were put into a four-neck flask (1000ml), dissolved in toluene (500ml), followed with agitating, the mixture was heated to 110°C and reacted under reflux for 1 hour, and then cooled to 40°C within 3 hours, kept at same temperature for 1 hour, then cooled to 10°C within 2 hours, and kept at same temperature for 0.5 hours, and at this time a large amount of crystal was precipitated. After filtration, 10% hydrochloric acid (100g) was added to the obtained mother liquors to adjust the pH to 2-3. After

layer separation, the oil layer was washed with water until it was nearly neutral, heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then (R)-2,2-dimethyl-3-trans-(2,2-difluorovinyl) cyclopropane carboxylic acid was obtained (45.2g), wherein the ee value of the dextro isomer was 96%.

Preparation Example 8: Acyl-chlorination of D-trans-difluoro chrysanthemic acid

[0031] Trans-difluoro-D-chrysanthemic acid (176g, 1mol, ee value of 96%) got from Preparation Example 7 was put into a four-neck flask (1000ml), dissolved in toluene (600ml), followed with agitating, the mixture was heated to 50°C, and SOCl₂ (142g, 1.2mol) was dropwise added thereto within 2 hours. The resultant was heated to 60°C and kept at same temperature for reaction. After the reaction finished, the resultant was heated to 80°C to evaporate off toluene the solvent under reduced pressure (30mmHg), then rectified under reduced pressure (10mmHg), the fraction between 60-75°C was collected, then (R)-2,2-dimethyl-3-trans-(2,2-difluorovinyl) cyclopropane carboxylic acid acyl chloride was obtained (180.1g), wherein the yield was 93.3%, the ee value of the dextro isomer was 96%.

Preparation Example 9: Resolution of trans-2,2-dimethyl-3-(2-chloro-2-bromovinyl) cyclopropane carboxylic acid

[0032] Trans-2,2-dimethyl-3-(2-chloro-2-bromovinyl) cyclopropane carboxylic acid (100.0g) and D-chloramphenicol amine (90.0g) were put into a four-neck flask (1000ml), dissolved in toluene (500ml), followed with agitating, the mixture was heated to 110°C and reacted under reflux for 1 hour, and then cooled to 40°C within 3 hours, kept at same temperature for 1 hour, then cooled to 10°C within 2 hours, and kept at same temperature for 0.5 hours, and at this time a large amount of crystal was precipitated. After filtration, 10% hydrochloric acid (100g) was added to the obtained mother liquors to adjust the pH to 2-3. After layer separation, the oil layer was washed with water until it was nearly neutral, heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then (R)-2,2-dimethyl-3-trans-(2-chloro-2-bromovinyl) cyclopropane carboxylic acid was obtained (44.9g), wherein the ee value of the dextro isomer was 95%.

Preparation Example 10: Acyl-chlorination of D-trans-2,2-dimethyl-3-(2-chloro - 2-bromovinyl) cyclopropane carboxylic acid

[0033] (R)-2,2-dimethyl-3-trans-(2-chloro-2-bromovinyl) cyclopropane carboxylic acid (253.5g, 1mol, ee value of 95%) got from Preparation Example 9 was put into a four-neck flask (1000ml), dissolved in toluene (600ml), followed with agitating, the mixture was heated to 50°C, and SOCl₂ (142g, 1.2mol) was dropwise added thereto within 2 hours. The resultant was heated to 60°C and kept at same temperature for reaction. After the reaction finished, the resultant was heated to 80°C to evaporate off toluene the solvent under reduced pressure (30mmHg), then rectified under reduced pressure (10mmHg), the fraction between 60-75°C was collected, then (R)-2,2-dimethyl-3-trans-(2-chloro-2-bromovinyl) cyclopropane carboxylic acid acyl chloride was obtained (258.6g), wherein the yield was 94.2%, the ee value of the dextro isomer was 95%.

Preparation Example 11: Synthesis of 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester (compound I)

[0034] Tetrafluoro-p-methoxy-methyl benzyl alcohol (112.0g) and pyridine (50.0g) were put into a four-neck flask (2000ml), dissolved in toluene (800ml), followed with agitating, and (R)-2,2-dimethyl-3-trans-(2,2-dichlorovinyl) cyclopropane carboxylic acid acyl chloride (114.0g, prepared according to Preparation Example 3) was dropwise added thereto under 0-5°C. After that, the mixture was heated to 20°C for 4 hours to react. The resultant was washed with 5% hydrochloric acid (400ml), then washed with 5% NaHCO₃ (400ml). After layer separation, the oil layer was heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester was obtained (203.3g, pale yellow solid), wherein the purity was 97.8%, the yield was 95.8 %. Chemical formula: C₁₇H₁₇Cl₂F₄O₃, Molecule Weight: 416.2, Rotation [α] = -9.32, which can dissolve in toluene, benzene, xylene and other organic solvents, IR: 3020, 2950, 2840, 1750, 1640, 1580, 1240, 1050 cm⁻¹, NMRS: (1H (ppm) CDCl₃) 1.11 (m, 6H); 1.06-1.41 (m, 2H); 3.24 (s, 3H); 4.63 (m, 2H); 5.34 (m, 2H); 5.63 (d, 1H).

Preparation Example 12: Synthesis of 2,3,5,6-tetrafluoro-4-methoxy-methyl

benzyl (1R, 3S)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester (compound II)

[0035] Tetrafluoro-p-methoxy-methyl benzyl alcohol (56.0g), pyridine (25g) and toluene (400ml) were put into a four-neck flask (1000ml), followed with agitating for 15 min, and (R)-2,2-dimethyl-3-trans-(2,2-dibromovinyl) cyclopropane carboxylic acid acyl chloride (79.4g, prepared according to Preparation Example 6) was dropwise added thereto under 0-5°C. After that, the mixture was heated to 10°C for 1 hours. The oil layer was washed with 5% hydrochloric acid (150ml), and then with 5% NaHCO₃ (100ml), and washed with water until it was nearly neutral. The oil layer was heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester was obtained (125.1g, pale white solid), wherein the purity was 97.1%, the yield was 96.2 %. Chemical formula: C₁₇H₁₇Br₂F₄O₃, Molecule Weight: 505.1, Rotation [α] = -7.63, which can dissolve in toluene, benzene, xylene and other organic solvents, IR: 3020, 2940, 2840, 1750, 1630, 1580, 1240, 1040 cm⁻¹, NMRS: (1H (ppm) CDCl₃) 1.11 (m, 6H); 1.06-1.41 (m, 2H); 3.24 (s, 3H); 4.63 (m, 2H); 5.34 (m, 2H); 6.32 (d, 1H).

Preparation Example 13: Synthesis of 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-difluorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester (compound III)

[0036] Tetrafluoro-p-methoxy-methyl benzyl alcohol (112.0g) and pyridine (50.0g) were put into a four-neck flask (2000ml), dissolved in toluene (800ml), followed with agitating, and (R)-2,2-dimethyl-3-trans-(2,2-difluorovinyl) cyclopropane carboxylic acid acyl chloride (97.5g, prepared according to Preparation Example 8) was dropwise added thereto under 0-5°C. After that, the mixture was heated to 20°C for 4 hours to react. The resultant was washed with 5% hydrochloric acid (300ml), then washed with 5% NaHCO₃ (300ml), the oil layer was heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-difluorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester was obtained (196.3g, pale yellow solid), wherein the purity was 96.9%, the yield was 93.8 %. Chemical formula: C₁₇H₁₇F₆O₃, Molecule Weight: 383.2, Rotation [α] = -4.51, IR: 3010, 2950, 2840, 1750, 1640, 1580, 1240, 1050 cm⁻¹, NMRS: (1H (ppm) CDCl₃) 1.11 (m6H); 1.06-1.41 (m, 2H); 3.24 (s, 3H); 4.63 (m,

2H); 5.34 (m, 2H); 4.72 (d, 1H).

Preparation Example 14: Synthesis of 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2-chloro-2-bromovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester (compound IV)

[0037] Tetrafluoro-p-methoxy-methyl benzyl alcohol (112.0g) and pyridine (50.0g) and toluene (800ml) were put into a four-neck flask (2000ml), agitating and dissolving, and (R)-2,2-dimethyl-3-trans-(2-chloro-2-bromovinyl) cyclopropane carboxylic acid acyl chloride (136.2g, prepared according to Preparation Example 10) was dropwise added thereto under 0-5°C. After that, the mixture was heated to 10°C for 4 hours to react. The resultant was washed with 5% hydrochloric acid, and then with 5% NaHCO₃, then the oil layer was washed with deionized water (200 ml) for twice. The oil layer was heated to 100°C to evaporate off toluene the solvent under reduced pressure (10mmHg), then 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2-chloro-2-bromovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester was obtained (229.8g, pale white solid), wherein the purity was 98.2%, the yield was 98.1 %. Chemical formula: C₁₇H₁₇BrClF₄O₃, Molecule Weight: 460.7, IR: 3020, 2950, 2840, 1760, 1640, 1580, 1240, 1050 cm⁻¹, NMRS: (¹H (ppm) CDCl₃ 1.11 (m, 6H); 1.06-1.41 (m, 2H); 3.24 (s, 3H); 4.63 (m, 2H); 5.34 (m, 2H); 6.05 (d, 1H).

Test Example 1

[0038] In accordance with GB13917.4-92, the compound I, compound II and compound III of the present invention were compared with D-allethrin which is one of the most commonly used pesticides at present for testing the pesticidal efficacy. The compound I (0.014g) was dissolved in kerosene (1g), which was dropwise added onto a blank mosquito-coil fan (35g) to make a mosquito-repellent incense which contains 0.04% compound I; The compound II (0.014g) was dissolved in kerosene (1g), which was dropwise added onto a blank mosquito-coil fan (35g) to make a mosquito-repellent incense which contains 0.04% compound II; The compound III (0.014g) was dissolved in kerosene (1g), which was dropwise added onto a blank mosquito-coil fan (35g) to make a mosquito-repellent incense which contains 0.04% compound III; D-allethrin (0.28g) was dissolved in kerosene (1g), which was dropwise added onto a blank mosquito-coil fan (35g) to make a mosquito-repellent incense which contains 0.8% D-allethrin. The four mosquito-repellent incenses were

tested for their pesticidal efficacy respectively. The specific process for the test is that 20 female *Culex pipiens fatigans* were sucked by a suction tube, and put into a sealed drum which was the test device, any section of the tested mosquito-repellent incense was taken and placed on racks, then the mosquito-repellent incense was lighted up and the time was recorded, after 1min, the mosquito-repellent incense was removed, the number of mosquitoes knocked down was recorded at a determined time interval. After 20min, all tested mosquitoes were transferred to a clean rearing cage, the number of dead mosquitoes was checked after 24hrs. The results were shown in Table 1.

Table 1. The comparison of the efficacy for preventing and treating mosquitoes between compounds of the present invention and D-allethrin

mosquito-repellent incenses type	Concentration(m/m)	KT50(min)	Death Rate (24h)
Compound I	0.04%	4.32	100%
Compound II	0.04%	7.23	100%
Compound III	0.04%	10.50	95%
D-allethrin	0.8%	4.17	95%

[0039] The results showed that the relative effectiveness of compounds I was 20 times higher than that of D-allethrin, the relative effectiveness of compounds II was 10 times higher than that of D-allethrin propylene, the relative effectiveness of compounds III was 3 times higher than that of D-allethrin.

Test Example 2

[0040] Compounds I of the present invention and compounds (RS) 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester (the racemic body of compound I without resolving) were made into 0.08% mosquito-repellent incenses by the same method of Test Example 1, in accordance with GB13917.4-92 to test the pesticidal efficacy, the results were shown in Table 2:

Table 2. Comparison of the efficacy for preventing and treating mosquitoes between a single optically active compound of the present invention and its racemic body

mosquito-repellent incenses type	Concentration(m/m)	KT50(min)	Death Rate % (24h)
Compound I	0.08%	3.43	100%

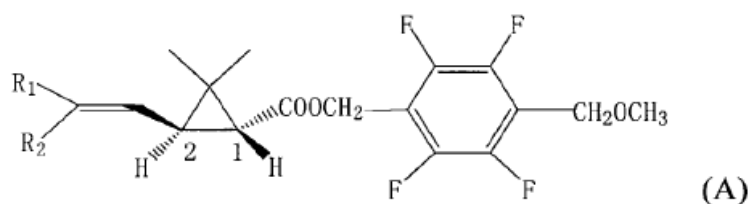
mosquito-repellent incenses type	Concentration(m/m)	KT50(min)	Death Rate % (24h)
The racemic body of Compound I	0.08%	5.80	100%

[0041] The results showed that the relative effectiveness of the single dextro trans-isomer of compounds I was 1.7 times higher than that of its racemic body.

[0042] All of the reference documents cited in this specification are herein incorporated by reference separately. Furthermore, it should also be understood, after reading the contents of the present invention, persons of ordinary skill in the art can make various changes or modifications to the invention, while the resultant equivalent belongs to the limited scope of the claims attached to this specification in each case.

Claims:

1. A pyrethroid compound according to the following formula (A),



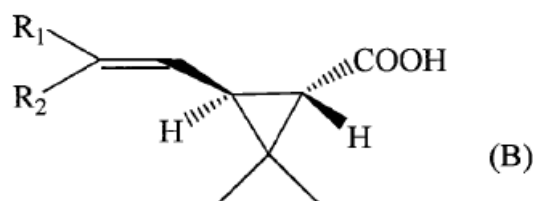
wherein the compound is a dextro single optical isomer,

wherein R1 and R2 are both chlorine and the compound is 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-dichlorovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester,

wherein R1 and R2 are both bromine and the compound is 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl (1R, 3S)-3-(2,2-Dibromovinyl)-2,2-dimethyl cyclopropane carboxylic acid ester.

2. A process for preparing the pyrethroid compound according to claim 1, which contains the following steps:

1) resolving a racemic trans-chrysanthemum acid with a chemical resolving agent to obtain the corresponding D-trans-chrysanthemum acid, wherein the racemic trans-chrysanthemum acid is the compound according to the following formula (B), wherein R1 and R2 are the same halogen atoms selected from chlorine or bromine; the molar ratio of the chemical resolving agent to the racemic trans-chrysanthemum acid is 0.2:1-4:1;



2) acyl-chlorinating the D-trans-chrysanthemum acid got from the step 1) with an acyl-chlorination reagent to obtain the corresponding D-trans-acyl chloride; wherein the molar ratio of the acyl-chlorination reagent to the D-trans-chrysanthemum acid is 0.2:1-4:1; the acyl-chlorination reagent is one selected from the group consisting of phosphorus trichloride, thionyl chloride, and bis (trichloro methyl) carbonate;

3) esterifying the D-trans-acyl chloride got from the step 2) with 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl alcohol to obtain the pyrethroid compound of the formula (A), wherein the molar ratio of the D-trans-acyl chloride to 2,3,5,6-tetrafluoro-4-methoxy-methyl benzyl alcohol is 0.2:1-4:1.

3. The process according to claim 2, wherein the chemical resolving agent in the step 1) is a dextro chiral organic amine compound selected from the group consisting of D-chloramphenicol amine ((+) N, N- dimethyl-para nitrophenyl -1,3-propanediol), D-PTE ((+) β -p-methyl-phenyl- α -phenylethylamine) or D- α -phenylethylamine.

4. Use of the compound according to claim 1 for preventing and treating hygiene pests.

5. Use according to claim 4, wherein the hygiene pests are selected from mosquitoes, flies or blattela germanicas.

Abstract

Disclosed is an optically active pyrethroid compound represented by general formula (A), preparation process thereof and use thereof for preventing and treating hygiene pests. The compound is dextro simple optical isomer, wherein R_1 and R_2 is respectively same or different halogen. The present compound shows better pesticidal effect compared with that of the prior art.

