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Synthesis and Biological Activity of Permethrin Analogs Containing Various Substituents in Position *2* of the Cyclopropane Ring

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Abstract—A number of permethrin derivatives having various substituents (Me, Et, Pr, Ph, $PhCH_2$, $PhCH_2CH_2$) in position *2* of the cyclopropane ring were synthesized and assayed for insecticidal activity against typhoid flies, rice weevils, and black bean aphid and juvenile hormone activity against flour beetle chrysalises. The examined compounds showed a weak insecticidal activity. Some derivatives were found to exert knockdown effect analogous to that of commercial pyrethroid tetramethrin; however, unlike permethrin, they exhibited pronounced juvenile hormone activity.

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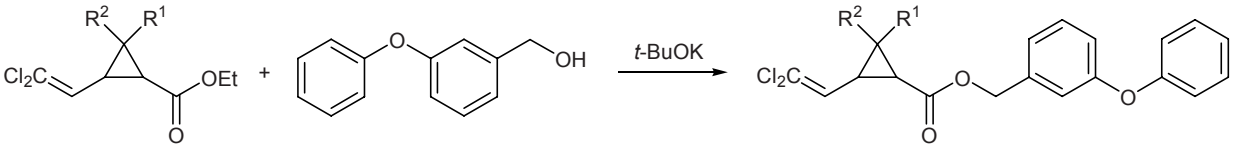
Pyrethroids constitute a new generation of highly active synthetic insecticides. Studies performed nowadays in the field of pyrethroids include synthesis of new compounds and investigations of mechanisms of their action, metabolism, and effect on humans [1–6]. We previously synthesized analogs of permethric acid ethyl ester, which contained alkyl and aryl substituents in position *2* of the cyclopropane ring, and tested them for biological activity [7].

In continuation of our studies on structure–activity relations in the pyrethroid series, in the present work we synthesized permethrin analogs, 3-phenoxybenzyl esters of 2,2-disubstituted permethric acid, analyzed their stereoisomeric composition, and examined side processes accompanying their formation. For this purpose, 2,2-disubstituted 3-(2,2-dichloroethenyl)cyclopropanecarboxylic acid ethyl esters were subjected to transesterification with 3-phenoxybenzyl alcohol in the presence of potassium *tert*-butoxide at 100–105°C (Scheme 1). Analysis of the reaction mixture obtained from ethyl 2-benzyl-2-methyl-3-(2,2-dichloroethenyl)-cyclopropane-1-carboxylate showed that, apart from the target product, 3-phenoxybenzyl 2-benzyl-2-methyl-3-(2,2-dichloroethenyl)cyclopropane-1-carboxylate (**IIa**), it contained a minor product, 3-phenoxybenzyl 2-benzyl-2-methyl-3-(chloroethynyl)cyclopropane-1-carboxylate (**III**) (Scheme 2).

Compounds **II** were isolated from the reaction mixtures and separated into particular stereoisomers by column chromatography on silica gel, and their yields were no less than 60%. Compounds **II** are light yellow oily liquids which are insoluble in water and readily

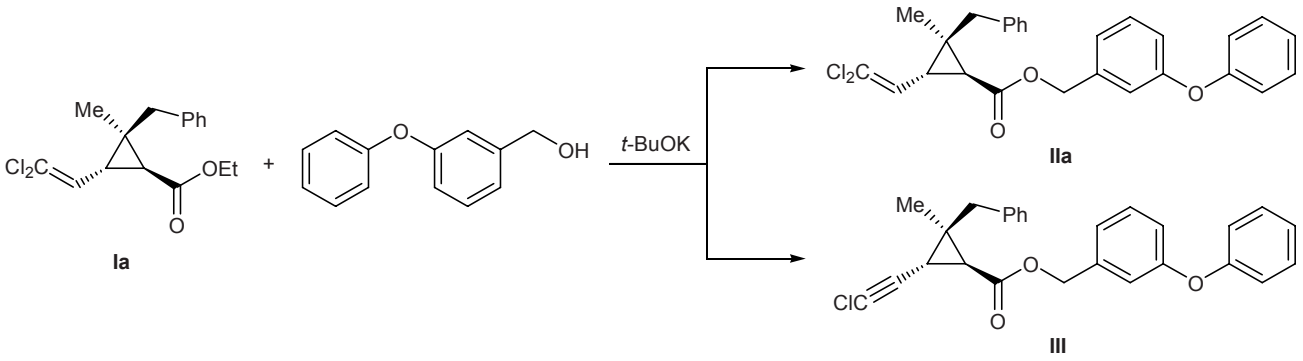
Scheme 1.



Ia–Ih **IIa–IIh**

R^1 = Me, R^2 = $PhCH_2$ (**a**); R^1 = Et, R^2 = $PhCH_2$ (**b**); R^1 = Me, R^2 = $PhCH_2CH_2$ (**c**); R^1 = Me, R^2 = Ph (**d**); R^1 = R^2 = Et (**e**); R^1 = Et, R^2 = Pr (**f**); R^1 = Me, R^2 = Et (**g**); R^1 = R^2 = Pr (**h**).

Scheme 2.



soluble in common organic solvents. Their purity was checked by TLC, HPLC, and spectral measurements, and the structure was confirmed by IR and NMR spectroscopy, mass spectrometry (GC–MS), and elemental analysis. The mass spectra of the new pyrethroids contained the molecular ion peaks, and their IR spectra displayed absorption bands at about 1735 and 1650 cm^{-1}, which are typical of ester carbonyl group and double C=C bond, respectively.

The stereoisomeric structure of the products was determined by ^{1}H and ^{13}C NMR spectroscopy. Signals were assigned to particular diastereoisomers on the basis of their position, multiplicity, and intensity, as well as of the data of two-dimensional ^{1}H–^{1}H COSY [8] and ^{1}H–^{13}C HSQC experiments [9]. Steric configuration of phenoxybenzyl esters **II** was established using two-dimensional ROESY spectra [10]. The presence in the ROESY spectra of cross peaks between protons in particular substituents unambiguously indicated their *cis* or *trans* (no cross peak) orientation with respect to the cyclopropane ring plane. The data in table show the presence or absence of cross peaks between protons in the 2-benzyl fragment, 2-methyl group, and 3-dichlorovinyl substituent and 1-H and 3-H protons in the ROESY spectra of different diastereoisomers of 3-phenoxybenzyl 2-benzyl-3-(2,2-dichlorovinyl)-2-methylcyclopropane-1-carboxylate (the complete spectra are available from the authors upon request by e-mail: *nsm21@yandex.ru*).

Biological assay of the synthesized compounds by the complete screening procedure [11, 12] revealed their weak insecticidal activity against test insects. The mode of action (knockdown effect) of some derivatives, namely of compounds **IIa**–**IIc** and **IIg**, was analogous to that of commercial pyrethroid tetramethrin. On the other hand, biological tests showed that the new compounds acquired some specific properties which distinguish them from permethrin. Although neither high insecticidal nor acaricidal activity was found, compounds **II** exhibited pronounced juvenile hormone activity (score 7–8 according to Schmialek). They also showed weak phytotoxicity against plant leaves.

Using PASS software [13] we analyzed the possibility of using the newly synthesized permethrin analogs in pharmacology. It was found with a probability of 50% that some of the obtained compounds possessing no appreciable insecticidal activity (toxicity) should act as fibrinogen receptor antagonists and agents for the treatment of Alzheimer disease, inhibit synthesis of cholesterol, stimulate synthesis of acetylcholine, and exhibit estrogenic and antiestrogenic activity.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded at 300±1 K on a Bruker Avance-300 spectrometer at 300.13 and 75.47 MHz, respectively, using $CDCl_3$ as

Cross peaks in the ROESY spectra of different diastereoisomers of 3-phenoxybenzyl 2-benzyl-2-methyl-3-(2,2-dichlorovinyl)cyclopropane-1-carboxylate (**IIa**)

Diastereoisomer	PhC**H**$_2$/HC=CCl	PhC**H**$_2$/1-H	PhC**H**$_2$/3-H	2-CH$_3$/HC=CCl	2-CH$_3$/1-H	2-CH$_3$/3-H
(1*R**,2*R**,3*R**)	–	+	+	+	–	–
(1*R**,2*S**,3*S**)	–	–	+	+	+	–
(1*R**,2*R**,3*S**)	+	+	–	–	–	+
(1*R**,2*S**,3*R**)	+	–	–	–	+	+

solvent and tetramethylsilane as internal reference. The one- and two-dimensional experiments were performed according to standard procedure [8–10]. The IR spectra were measured on a Perkin–Elmer 1720 spectrometer from solutions in carbon tetrachloride or neat substances (film). The mass spectra (electron impact) were obtained on a Fisons Trio 1000 GC–MS system with a quadrupole mass analyzer. HPLC analysis was performed on a Millikhrom AO-2 liquid chromatograph equipped with a UV detector and a C18 reversed-phase column; eluents: A (aqueous phase): 90% buffer (100 ml of distilled water, 0.2 ml of 10% trimethylamine, and 100 μg of heptanesulfonic acid) + 10% acetonitrile or distilled water without ionogenic compounds (constant pH value); B (organic phase): 90% acetonitrile + 10% distilled water. The progress of reactions was monitored by TLC on Silica gel 60 F254 plates (Merck) using hexane–benzene (1:1) or benzene–diethyl ether (9:1) as eluent; spots were visualized under UV light or by treatment with a solution of phosphomolybdic acid. The products were isolated from the reaction mixtures by column chromatography on silica gel 60 (0.040–0.063 mm; Merck) using Kontes glass columns and the same eluents as indicated above.

3-Phenoxybenzyl alcohol and potassium *tert*-butoxide were commercial products, and initial 2,2-disubstituted permethric acid ethyl esters were synthesized according to the procedure described in. [7].

3-Phenoxybenzyl 2,2-disubstituted-3-(2,2-dichlorovinyl)cyclopropane-1-carboxylates IIa–IIh (*general procedure*). A mixture of 10 mmol of ethyl ester **Ia**–**Ih**, 12 mmol of 3-phenoxybenzyl alcohol, and 1 mmol of potassium *tert*-butoxide was stirred for 4–6 h at 100–105°C under reduced pressure (1–2 mm). The light yellow oily product was subjected to column chromatography on silica gel. The purity of the products was checked by HPLC.

3-Phenoxybenzyl 2-benzyl-3-(2,2-dichlorovinyl)-2-methylcyclopropane-1-carboxylate (IIa). Yield 83% (61% after chromatographic separation); the product contained 96% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1620 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,2*S**,3*R**) isomer: 1.04 s (3H, CH_3), 1.89 d (1H, CH), 2.08 q (1H, CH), 2.90 d.d (1H, CH_2), 3.08 m (1H, CH_2), 4.95 m (2H, CH_2), 6.49 d (1H, CH), 6.98–7.46 m (14H, H_{arom}); (1*R**,2*R**,3*R**) isomer: 1.13 s (3H, CH_3), 1.93 d (1H, CH), 2.15 q (1H, CH), 2.61 d.d (1H, CH_2), 2.71 m (1H, CH_2), 5.05 m (2H, CH_2), 6.29 d (1H, CH), 7.00–7.43 m (14H, H_{arom}); (1*R**,2*R**,3*S**) isomer: 1.08 s (3H, CH_3), 1.85 d (1H, CH), 2.27 d (1H, CH), 2.60 m (1H, CH_2), 2.67 m (1H, CH_2), 5.04 m (2H, CH_2), 5.69 d (1H, CH), 7.00–7.40 m (14H, H_{arom}); (1*R**,2*S**,3*S**) isomer: 1.00 s (3H, CH_3), 1.66 d (1H, CH), 2.48 q (1H, CH), 2.84 d.d (1H, CH_2), 2.95 m (1H, CH_2), 4.95 m (2H, CH_2), 5.53 d (1H, CH), 6.98–7.46 m (14H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,2*S**,3*R**) isomer: 25.72, 29.13, 31.81, 32.84, 34.01, 65.65, 118.25, 118.41, 119.03, 121.00, 122.04, 122.77, 123.49, 124.80, 127.03, 128.34, 129.89, 129.93, 137.85, 141.65, 156.90, 157.52, 171.5; (1*R**,2*R**,3*R**) isomer: 13.02, 30.23, 30.72, 31.05, 47.10, 65.50, 118.30, 118.44, 119.11, 120.84, 122.04, 122.69, 123.40, 124.80, 127.01, 128.83, 129.81, 129.88, 137.94, 141.65, 156.92, 157.50, 170.74; (1*R**,2*R**,3*S**) isomer: 17.42, 32.20, 32.80, 34.54, 42.02, 65.65, 118,35, 118.44, 119.13, 122.04, 122.21, 122.77, 123.49, 126.60, 127.03, 128.34, 129.89, 129.93, 137.85, 141.65, 156.90, 157.62, 171.50; (1*R**,2*S**,3*S**) isomer: 19.92, 32.40, 33.41, 34.72, 38.90, 65.68, 118.29, 118.42, 119.09, 122.02, 122.20, 122.79, 123.47, 126.00, 127.13, 128.34, 129.89, 129.93, 137.92, 141.95, 156.88, 157.60, 171.30. Mass spectrum: *m/z* 466 $[M]^+$. Found, %: C 69.05; H 4.39; Cl 14.79. $C_{27}H_{23}Cl_2O_3$. Calculated, %: C 69.53; H 4.98; Cl 15.20. *M* 466.40.

3-Phenoxybenzyl 2-benzyl-3-(2,2-dichlorovinyl)-2-ethylcyclopropane-1-carboxylate (IIb). Yield 85% (65% after chromatographic separation); the product contained 95% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1620 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,2*S**,3*R**) isomer: 0.83 t (3H, CH_3), 1.07 m (1H, CH_2), 1.38 m (1H, CH_2), 1.85 d (1H, CH), 2.06 d.d (1H, CH), 2.92 d (1H, CH_2), 3.02 d (1H, CH_2), 5.05 q (2H, CH_2), 6.45 d (1H, CH), 7.02–7.42 m (14H, H_{arom}); (1*R**,2*R**,3*R**) isomer: 0.85 t (3H, CH_3), 1.44 m (1H, CH_2), 1.50 m (1H, CH_2), 1.83 d (1H, CH), 2.12 m (1H, CH), 2.60 d (1H, CH_2), 2.77 d (1H, CH_2), 5.02 q (2H, CH_2), 6.33 d (1H, CH), 7.09–7.25 m (14H, H_{arom}); (1*R**,2*R**,3*S**) isomer: 0.82 t (3H, CH_3), 1.35 m (1H, CH_2), 1.42 m (1H, CH_2), 1.80 d (1H, CH), 2.25 d.d (1H, CH), 2.66 d (1H, CH_2), 2.68 d (1H, CH_2), 5.08 q (2H, CH_2), 5.65 d (1H, CH), 7.09–7.23 m (14H, H_{arom}); 1*R**,2*S**,3*S**) isomer: 0.90 t (3H, CH_3), 1.20 m (1H, CH_2), 1.25 m (1H, CH_2), 1.68 d (1H, CH), 2.49 m (1H, CH), 2.90 d (1H, CH_2), 2.98 d (1H, CH_2), 4.98 m (2H, CH_2), 5.57 d (1H, CH), 7.10–7.23 m (14H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,2*S**,3*R**) isomer: 10.37, 30.28, 31.04, 31.25, 31.59, 36.74, 65.65, 118,25, 118.41, 119.03, 120.61, 122.04, 122.67, 123.45, 124.91, 127.02, 128,42, 129.79, 129.90, 137.95, 138.73, 156.90,

157.52, 171.5; (1*R**,2*R**,3*R**) isomer: 10.31, 18.46, 29.72, 31.04, 36.60, 42.63, 65.50, 118.30, 118.44, 119.11, 120.50, 122.07, 122.69, 123.40, 124.59, 127.07, 128.39, 129.81, 129.88, 137.59, 137.94, 156.92, 157.50, 170.74; (1*R**,2*R**,3*S**) isomer: 10.80, 22.36, 31.66, 34.70, 37.89, 38.36, 65.84, 118.28, 118.40, 119.09, 122.05, 122.40, 122.65, 123.43, 126.25, 127.11, 128.43, 129.78, 129.92, 137.96, 138.08, 156.89, 157.54, 170.74; (1*R**,2*S**,3*S**) isomer: 10.64, 25.47, 32.71, 34.26, 34.48, 38.51, 65.90, 118.27, 118.42, 119.06, 122.06, 122.30, 122.68, 123.44, 126.92, 127.08, 128.39, 129.77, 129.93, 137.94, 138.13, 156.92, 157.50, 170.82. Mass spectrum: *m*/*z* 480 $[M]^+$. Found, %: C 69.64; H 4.87; Cl 14.12. $C_{28}H_{25}Cl_2O_3$. Calculated, %: C 69.98; H 5.26; Cl 14.76. *M* 480.43.

3-Phenoxybenzyl 3-(2,2-dichlorovinyl)-2-methyl-2-(2-phenylethyl)cyclopropane-1-carboxylate (IIc). Yield 83% (67% after chromatographic separation); the product contained 95% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1621 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,2*S**,3*S**) isomer: 1.07 s (3H, CH_3), 1.62 d (1H, CH), 1.65 m (1H, CH_2), 1.80 m (1H, CH_2), 2.27 t (1H, CH), 2.68 d.d (2H, CH_2), 5.07 s (2H, CH_2), 5.58 d (1H, CH), 6.90–7.37 m (14H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,2*S**,3*S**) isomer: 17.39, 33.18, 33.19, 33.29, 34.50, 39.34, 65.58, 118.27, 118.40, 119.12, 122.09, 122.38, 122.80, 123.37, 126.90, 127.03, 128.40, 129.89, 129.83, 137.95, 138.95, 156.98, 157.59, 170.81. Mass spectrum: *m*/*z* 480 $[M]^+$. Found, %: C 69.72; H 4.91; Cl 14.27. $C_{28}H_{25}Cl_2O_3$. Calculated, %: C 69.98; H 5.26; Cl 14.76. *M* 480.43.

3-Phenoxybenzyl 3-(2,2-dichlorovinyl)-2-methyl-2-phenylcyclopropane-1-carboxylate (IId). Yield 87% (65% after chromatographic separation); the product contained 94% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1621 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,2*R**,3*R**) isomer: 1.29 s (3H, CH_3), 1.76 d (1H, CH), 2.24 t (1H, CH), 4.99 q (2H, CH_2), 6.29 d (1H, CH), 6.98–7.38 m (14H, H_{arom}); (1*R**,2*S**,3*S**) isomer: 1.11 s (3H, CH_3), 1.65 d (1H, CH), 1.97 t (1H, CH), 4.98 q (2H, CH_2), 5.60 d (1H, CH), 6.88–7.41 m (14H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,2*R**,3*R**) isomer: 17.85, 30.52, 31.61, 33.94, 65.78, 118.26, 118.42, 119.05, 120.57, 122.69, 123.43, 124.73, 125.01, 126.25, 127.31, 129.78, 129.92, 137.96, 138.08, 156.89, 157.54, 170.37; (1*R**,2*S**,3*S**) isomer: 20.40, 32.41, 33.56, 35.54, 67.80, 118.42, 118.58, 119.06, 122.62, 122.83, 123.44, 126.25, 126.33, 128.34, 128.40, 129.14, 129.82, 137.50, 138.41, 156.99, 157.41, 171.25. Mass spectrum: *m*/*z* 452 $[M]^+$. Found, %: C 68.77; H 4.12; Cl 15.26. $C_{26}H_{21}Cl_2O_3$. Calculated, %: C 69.03; H 4.69; Cl 15.67. *M* 452.37.

3-Phenoxybenzyl (2,2-dichlorovinyl)-2,2-diethylcyclopropane-1-carboxylate (IIe). Yield 83% (67% after chromatographic separation); the product contained 96% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1619 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,3*R**) isomer: 0.71 t (3H, CH_3), 0.75 t (3H, CH_3), 1.19 m (1H, CH_2), 1.44 m (1H, CH_2), 1.58 q (2H, CH_2), 1.76 d (1H, CH), 1.95 t (1H, CH), 4.99 q (2H, CH_2), 6.31 d (1H, CH), 6.30–7.20 m (9H, H_{arom}); (1*R**,3*S**) isomer: 0.76 t (3H, CH_3), 0.86 t (3H, CH_3), 1.20 m (1H, CH_2), 1.39 m (1H, CH_2), 1.42 m (1H, CH_2), 1.51 m (1H, CH_2), 1.59 d (1H, CH), 2.19 d.d (1H, CH), 5.01 d (2H, CH_2), 5.54 d (1H, CH), 6.87–7.26 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,3*R**) isomer: 10.16, 10.24, 17.13, 30.48, 31.03, 31.95, 37.36, 65.78, 118.33, 118.41, 119.04, 120.57, 122.68, 123.46, 124.73, 129.78, 129.94, 137.95, 156.90, 157.58, 170.37; (1*R**,3*S**) isomer: 10.45, 10.62, 21.80, 25.20, 32.96, 34.40, 39.57, 66.04, 118.34, 118.40, 119.05, 121.84, 122.68, 123.47, 126.97, 129.78, 129.94, 137.95, 156.89, 157.58, 170.87. Mass spectrum: *m*/*z* 418 $[M]^+$. Found, %: C 65.54; H 5.17; Cl 16.34. $C_{23}H_{23}Cl_2O_3$. Calculated, %: C 66.03; H 5.55; Cl 16.95. *M* 418.36.

3-Phenoxybenzyl 3-(2,2-dichlorovinyl)-2-ethyl-2-propylcyclopropane-1-carboxylate (IIf). Yield 80% (64% after chromatographic separation); the product contained 94% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1619 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,2*R**,3*R**) isomer: 0.73 t (3H, CH_3), 0.76 t (3H, CH_3), 1.15 m (2H, CH_2), 1.40 m (1H, CH_2), 1.54 q (1H, CH_2), 1.52 m (2H, CH_2), 1.64 d (1H, CH), 1.86 t (1H, CH), 5.07 q (2H, CH_2), 6.24 d (1H, CH), 6.90–7.28 m (9H, H_{arom}); (1*R**,2*S**,3*S**) isomer: 0.70 t (3H, CH_3), 0.76 t (3H, CH_3), 1.19 m (2H, CH_2), 1.35 m (1H, CH_2), 1.42 m (1H, CH_2), 1.43 m (1H, CH), 1.48 m (2H, CH_2), 2,03 d.d (1H, CH), 5.06 q (2H, CH_2), 5.45 d (1H, CH), 6.90–7.28 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,2*R**,3*R**) isomer: 10.14, 10.26, 17.50, 19.43, 30.48, 31.03, 31.95, 37.36, 65.43, 118.46, 118.98, 119.15, 120.17, 122.68, 123.55, 124.85, 129.90, 130.01, 132.57, 156.88, 157.53, 170.54; (1*R**,2*S**,3S*) isomer: 10.28, 10.96, 19.49, 25.10, 32.23, 32.55, 34.50, 39.05, 67.12, 118.25, 118.42, 121.38, 121.57, 122.67, 123.46, 127.09, 129.67, 129.90, 138.21, 156.89, 157.52, 170.87. Mass spectrum: *m*/*z* 432 $[M]^+$. Found, %: C 66.21; H 5.38; Cl 16.07. $C_{24}H_{25}Cl_2O_3$. Calculated, %: C 66.67; H 5.84, Cl 16.40. *M* 432.39.

3-Phenoxybenzyl 3-(2,2-dichlorovinyl)-2-ethyl-2-methylcyclopropane-1-carboxylate (IIg). Yield 77% (62% after chromatographic separation); the product contained 96% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1619 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,2*R**,3*R**) isomer: 0.83 t (3H, CH_3), 1.19 s (3H, CH_3), 1.44 m (1H, CH_2), 1.58 q (1H, CH_2), 1.76 d (1H, CH), 2.24 t (1H, CH), 4.99 q (2H, CH_2), 6.29 d (1H, CH), 6.30–7.55 m (9H, H_{arom}); (1*R**,2*S**,3*S**) isomer: 0.91 t (3H, CH_3), 1.05 s (3H, CH_3), 1.29 m (1H, CH_2), 1.32 q (1H, CH_2), 1.65 d (1H, CH), 1.97 t (1H, CH), 4.98 q (2H, CH_2), 5.60 d (1H, CH), 6.48–7.44 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,2*R**,3*R**) isomer: 10.35, 19.85, 30.52, 31.13, 32.29, 37.83, 65.78, 118.33, 118.41, 119.05, 121.44, 122.67, 123.45, 124.73, 129.78, 129.90, 137.96, 156.79, 156.99, 170.37; (1R*,2S*,3S*) isomer: 10.40, 19.53, 28.35, 28.82, 33.56, 35.54, 67.80, 118.26, 118.48, 119.04, 121.44, 122.71, 123.50, 124.97, 129.81, 130.01, 136.50, 156.94, 157.36, 171.25. Mass spectrum: *m*/*z* 404 $[M]^+$. Found, %: C 65.03; H 4.84; Cl 17.05. $C_{22}H_{21}Cl_2O_3$. Calculated, %: C 65.35; H 5.25; Cl 17.54. *M* 404.33.

3-Phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dipropylcyclopropane-1-carboxylate (IIh). Yield 63% (52% after chromatographic separation); the product contained 95% of the main substance. IR spectrum, ν, cm^{-1}: 1735 (C=O), 1619 (C=C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: (1*R**,3*R**) isomer: 0.73 t (3H, CH_3), 0.75 t (3H, CH_3), 1.18 m (4H, CH_2), 1.51 m (2H, CH_2), 1.55 m (2H, CH_2), 1.60 d (1H, CH), 1.86 t (1H, CH), 5.07 s (CH_2), 6.24 d (1H, CH), 6.90–7.32 m (9H, H_{arom}); (1*R**,3*S**) isomer: 0.70 t (6H, CH_3), 1.19 m (4H, CH_2), 1.43 d (1H, CH), 1.48 m (4H, CH_2), 2.03 d.d (1H, CH), 5.02 s (CH_2), 5.45 d (1H, CH), 6.91–7.36 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: (1*R**,3*R**) isomer: 10.29, 13.95, 19.27, 19.50, 30.51, 31.03, 31.94, 33.59, 37.38, 65.43, 118.35, 118.41, 119.15, 120.17, 122.50, 123.70, 124.85, 129.12, 129.79, 137.57, 156.89, 157.34, 170.59; (1*R**,3*S**) isomer: 10.28, 13.96, 19.31, 25.10, 31.30, 32.28, 32.55, 34.50, 39.05, 67.12, 118.42, 119.12, 121.38, 121.57, 122.75, 123.58, 127.09, 129.93, 130.02, 138.21, 156.91, 157.62, 170.87. Mass spectrum: *m*/*z* 446 $[M]^+$. Found, %: C 66.86; H 5.74; Cl 15.21. $C_{25}H_{27}Cl_2O_3$. Calculated, %: C 67.26; H 6.11; Cl 15.88. *M* 446.42.

Estimation of insecticidal and acaricidal activity. Tests were performed under laboratory conditions on standard sensitive laboratory strains of typhoid fly *Musca domestica* L., rice weevils *Calandra oryzae* L., bean aphides *Aphis fabae* Scop., and twospotted spider mite *Tetranychus urticae* Koch. Tests for juvenile hormone activity were performed on chrysalises of flour beetle *Tenebrio molitor L*. The acute phytotoxicity was studied on hydrangea or cucumber leaves. All experiments were carried out in triplicate.

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