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Synthesis of Allyl Esters of Fatty Acids and Their Ovicidal Effect on *Cydia pomonella* (L.)

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Eight allyl esters of fatty acids were synthesized in moderate to high yields with a novel two-step procedure using glycerol as a starting material. The two-step methodology avoids the use of allyl alcohol. The first step consisted of heating at 80 °C for 48 h a 2:1:5 mmol mixture of glycerol, a fatty acid, and chlorotrimethylsilane in a solvent-free medium. The crude compound was then dissolved in butanone and heated at 115 °C in the presence of NaI. A tandem Finkelstein rearrangement−elimination reaction occurs, producing the corresponding allyl ester. The activity of these esters against *Cydia pomonella* (L.) (Lepidoptera: Tortricidae) eggs was tested in the laboratory by topical application of one 0.1 μL drop. All of the compounds showed a concentration−mortality response and caused 100% mortality at the highest concentration tested (10 mg/mL). There was an inverse relationship between the alkyl chain length and the ovicidal activity of the allyl ester; the LC_{50} and the LC_{90} of the two compounds that have the longer alkyl chains were significantly higher than those of the rest of the compounds. The ovicidal and IGR activities of this kind of compound appear to be unprecedented.

KEYWORDS: Allyl esters; codling moth; *Cydia pomonella*; insecticide; ovicide

INTRODUCTION

Economic losses caused by the codling moth [*Cydia pomonella* (L.), Lepidoptera: Tortricidae], a major pest of apple, pear, and walnut crops, demand effective control methods against it. Damage is caused by the larvae, which enter into the fruits, feed on them, and cause their fall and depreciation. Of Euroasiatic origin, it is nowadays a key pest almost everywhere that apple and pear trees are grown (*1*); therefore, many control methods have been developed to reduce its population, chemical control and mating disruption being the most important methods. Many synthetic and natural chemicals show insecticidal activity against this pest, although resistant populations against different chemical pesticides have been reported in many countries (*2*, *3*). It is necessary, then, to find compounds with new modes of action, such as molting accelerator compounds (e.g., methoxyfenozide) or activators of insect ryanodine receptors (e.g., chlorantraniliprole) (*4*), and to restrict their use to those modes that are more environmentally friendly.

The search for new compounds active against *C. pomonella* eggs began in our laboratory with the synthesis of *N*-(4-phenoxyphenyl)-2-pyridinecarboxamide, designed with reference to the phenoxyphenyl moiety, which is supposed to be responsible for juvenilizing activity in insects, and adding a pyridine ring to it. This compound showed ovicidal activity on codling moth and juvelinization effects on *Tribolium confusum* duVal (Coleoptera: Tenebrionidae) (*5*). The activity of 13 phenoxyphenyl pyridine and pyrazine carboxamides on eggs of *C. pomonella* was tested afterward. Six compounds showed ovicidal activity (their efficacy ranged from 26 to 50%), and they also produced a significant increase in the length of the development period of the eggs (from 1 to 2 days) (*6*). Moreover, the insecticidal activity of extracts of *Maytenus* species against the same pest has also been studied (*7*).

It is also well-known that diverse compounds containing the allyl group, such as the pyrethroid allethrin, 4-allylanisole, or allyl isothiocyanate, have a high activity as insecticides, acaridides, and insect repellents (*8*−*10*). Allyl esters of fatty acids have been proposed as wood preservatives, allyl pentanoate having the highest activity on termites (*11*). Moreover, allyl formate has been tested against several pest species (*12*), and allyl alcohol itself is used as a herbicide manufactured by the Shell Chemical Co., Washington, DC, and Haco, Inc., Madison, WI. According to these references and our previous experience, we hypothesize that allyl esters could have ovicidal activity. Furthermore, many of these esters have been used as aromas and in cosmetic formulations for a long time (*13*−*16*), so low or no human toxicity is expected, which is a desirable characteristic of new insecticidal compounds.

With this aim, we have developed an easy synthesis of allyl esters of fatty acids. Starting from glycerol, a fatty acid and chlorotrimethylsilane (CTMS) 1,3-dichloropropyl esters are obtained. 1,3-Dichloropropyl esters lead to allyl esters in high yields

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in a tandem Finkelstein transposition−elimination reaction promoted by NaI in a further step. This process allows the use of glycerol as a starting material, avoiding the use of reagents such as allylic alcohol, an irritant compound, and fatty acid acyl chlorides. The synthesis of the intermediate compounds can also be carried out by an alternative synthesis. Researchers from Dow Global Technologies recently described its synthesis starting from glycerol, carboxylic acids, and hydrogen chloride with a partial pressure of > 15 psi (*17*). A mixture of glycerol, carboxylic acid, and metal halide in an ionic liquid leads also to the same intermediates (*18*). Nevertheless, using CTMS results in obtaining the allyl ester precursors in high purity. Yields were also high in most of the reactions assayed. Once the allyl esters of medium- and long-chain fatty acids were obtained, their ovicidal activity against eggs of *C. pomonella* was tested. A set of experiments using different concentrations of each allyl ester was carried out to evaluate the efficacy and the growth regulator activity on *C. pomonella* eggs.

MATERIALS AND METHODS

Chemicals. Butanone was purchased from Acros and dried over molecular sieves (3 Å) according to the conventional method prior to use. Sodium iodide was purchased from Riedel-de Haën and dried by heating at 110 °C for 24 h. Chlorotrimethylsilane (CTMS), glycerol, and the other fatty acids were purchased from Fluka (Sigma-Aldrich Química, S.A., Madrid, Spain) and used as received. *t*-Butyl methyl ether was purchased from J. T. Baker (Quimega, Lleida, Spain). Anhydrous magnesium sulfate ($MgSO_4$) was purchased from Panreac (Barcelona, Spain).

Apparatus. NMR spectra were recorded on a Varian 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). Chemical shifts are reported in delta units (δ), parts per million (ppm) relative to the singlet at 7.26 ppm of $CDCl_3$ for ^1H and the center line of the triplet at 77.00 ppm for ^{13}C NMR: The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; m, multiplet. GC-MS was performed in an Agilent 6890N GC coupled to a 5973 mass selective detector (Agilent Technologies España, S.L., Las Rozas, Spain) and equipped with a DB5-MS column (J&W, Anorsa, Barcelona, Spain) (30 m × 0.25 mm × 0.25 μm). The following chromatographic conditions were used: injection volume, 1 μL; constant flow, 2 mL/min with He as the carrier gas; split injection ratio, 20:1 at 280 °C. The oven temperature program started at 50 °C for 5 min; the temperature was increased at 5 °C/min to 110 °C and then increased at 10 °C/min until holding at the final temperature of 260 °C for 15 min. MS acquisition parameters were scan mode from m/z 50 to 600, 280 °C interface temperature, and 1200 V resulting EM voltage.

Synthesis of Allyl Esters (General Procedure). Carboxylic acid (1 mmol) **2a**−**h**, glycerol (2 mmol), and CTMS (5 mmol) were mixed in a 15 mL reaction vial fitted with a PTFE-lined cap. The mixture was heated at 80 °C for 48 h in a digestion stirrer block. After cooling, *t*-butyl methyl ether was added, and the mixture was washed three times with water. The organic layer was dried ($MgSO_4$), filtered, and evaporated under vacuum to give the corresponding crude compound. The crude product was used in the next step without further purification. A solution of that 1,3-dichloro-2-propyl ester (1 mmol) and sodium iodide (4 mmol) in dried butanone was heated at 115 °C for 48 h in a capped reaction vial. After cooling, *t*-butyl methyl ether was added, and the mixture was filtered and then washed with a saturated solution of sodium thiosulfate and water. The upper layer was recovered and dried over anhydrous magnesium sulfate. The solvent was evaporated under vacuum to give the corresponding crude compound. The crude compound, in the case of allyl decanoate, allyl dodecanoate, allyl tetradecanoate, allyl hexadecanoate, and allyl octadecanoate, was purified by silica column chromatography (45 μm particle size) and eluted with *n*-hexane to produce the corresponding allyl ester after solvent evaporation. Allyl butanoate, allyl hexanoate, and allyl octanoate, were purified by distillation under vacuum, with a Büchi Kugelrohr apparatus (Massó Analítica S.A., Barcelona, Spain).

Allyl butanoate (4a). [CAS Registry No. 2051-78-7] was prepared following the general procedure from butanoic acid **2a** (1.76 g, 20 mmol), glycerol (5.52 g, 60 mmol), and CTMS (25 mL, 200 mmol) to give 1,3-dichloro-2-propyl butanoate **3a** (2.59 g, yield 67%). Compound **3a** (0.52 g, 2.6 mmol) and sodium iodide (11.55 g; 77 mmol) in dried butanone (7.6 mL) gave allyl butanoate **4a** (288 mg, yield 86%) (distillation at 50−71 °C, 20 mbar).

Allyl hexanoate (4b). [CAS Registry No. 123-68-2] was prepared following the general procedure from hexanoic acid **2b** (2.32 g, 20 mmol), glycerol (5.50 g, 60 mmol), and CTMS (25 mL, 200 mmol) to give 1,3-dichloro-2-propyl hexanoate **3b** (4.35 g, yield 96%). Compound **3b** (0.51 g, 2.2 mmol) and sodium iodide (1.33 g; 9 mmol) in dried butanone (6.6 mL) gave allyl hexanoate **4b** (189 mg, yield 54%) (distillation at 75−98 °C, 20 mbar).

Allyl octanoate (4c). [CAS Registry No. 4230-97-1] was prepared following the general procedure from octanoic acid **2c** (2.88 g, 20 mmol), glycerol (5.61 g, 60 mmol), and CTMS (25 mL, 200 mmol) to give 1,3-dichloro-2-propyl octanoate **3c** (4.26 g, yield 84%). Compound **3c** (380 mg, 1.5 mmol) and sodium iodide (0.6 g; 4 mmol) in dried butanone (3 mL) gave allyl octanoate **4c** (257 mg, yield 94%) (distillation at 90−105 °C, 7 mbar).

Allyl decanoate (4d). [CAS Registry No. 57856-81-2] was prepared following the general procedure from decanoic acid **2d** (1.72 g, 10 mmol), glycerol (1.85 g, 20 mmol), and CTMS (6.35 mL, 50 mmol) to give 1,3-dichloro-2-propyl decanoate **3d** (2.75 g yield 97%). The crude compound (0.28 g, 1 mmol) and sodium iodide (0.6 g; 4 mmol) in dried butanone (3 mL) gave allyl decanoate **4d** (177 mg, 84%).

Allyl dodecanoate (4e). [CAS Registry No. 7003-75-0] was prepared following the general procedure from dodecanoic acid **20** (4.1 g, 20 mmol), glycerol (5.53 g, 60 mmol), and CTMS (25 mL, 200 mmol) to give 1,3-dichloro-2-propyl dodecanoate **3e** (6.19 g, yield 96%). The crude compound (6.2 g, 20 mmol) and sodium iodide (11.9 g; 80 mmol) in dried butanone (30 mL) gave allyl dodecanoate **4e** (4.08 g, 89%).

Allyl tetradecanoate (4f). [CAS Registry No. 45236-96-2] was prepared following the general procedure from tetradecanoic acid **2f** (4.58 g, 20 mmol), glycerol (5.69 g, 62 mmol), and CTMS (25 mL, 200 mmol) to give 1,3-dichloro-2-propyl tetradecanoate **3f** (6.79 g, yield 98%). The crude compound (6.62 g, 20 mmol) and sodium iodide (11.64 g; 78 mmol) in dried butanone (30 mL) gave allyl tetradecanoate **4f** (5.01 g, 99%).

Allyl hexadecanoate (4g). [CAS Registry No. 43211-62-7] was prepared following the general procedure from hexadecanoic acid **2g** (3.04 g, 12 mmol), glycerol (2.86 mg, 31 mmol), and CTMS (7.5 mL, 60 mmol) to give 1,3-dichloro-2-propyl hexadecanoate **3g** (3.43 g, yield 77%). The crude compound (0.37 g, 1 mmol) and sodium iodide (0.6 g; 4 mmol) in dried butanone (3 mL) gave allyl hexadecanoate **4g** (287 mg, 100%).

Allyl octadecanoate (4h). [CAS Registry No. 6289-31-2] was prepared following the general procedure from octadecanoic acid **2h** (5.65 g, 20 mmol), glycerol (5.57 g, 60 mmol), and CTMS (25 mL, 200 mmol) to give 1,3-dichloro-2-propyl octadecanoate **3h** (7.85 g, yield 97%). The crude compound (7.85 g, 20 mmol) and sodium iodide (11.8 g; 79 mmol) in dried butanone (30 mL) gave allyl octadecanoate **4h** (6.11 mg, 99%).

Activity on *C. pomonella* Eggs. The *C. pomonella* population was collected from an unsprayed apple tree orchard in 1993 at Lleida (northeastern Spain), and it has been reared since then on an agar-based semisynthetic diet at room temperature under long-day conditions (*19*). The adults were kept in cylindrical rearing cages, where the substrate for egg laying was wax paper (Reynolds Cut-Rite wax paper). Because codling moth adult females have a crepuscular activity, the wax paper was changed in the evening, and the eggs were collected the following morning. This procedure provided eggs that were < 24 h old. The eggs were individually and topically treated with a 0.1 μL drop of the compound to be tested dissolved in pure acetone to the appropriate concentration, using a Harvard Apparatus Pump 11 Injector (Harvard Apparatus, Inc., Holliston, MA). Preliminary experiments showed that a bigger size of the drop caused > 20% mortality in the acetone-treated controls, because of the small size of codling moth eggs. Three replicates of 30 eggs each were carried out per chemical compound and concentration tested. The syringe was washed 10 times with pure acetone between two different compounds. After evaporation of the solvent, the eggs of each replicate were confined in a plastic Petri dish (9 cm diameter) lined on its bottom with slightly wetted filter paper and sealed with parafilm. Petri dishes were kept in a climatic chamber at 22 ± 2 °C, 60 ± 10% relative humidity, and

16:8 h light/darkness photoperiod. The eggs were checked daily for larval emergence, until no more larvae emerged on three consecutive days. Because codling moth larval emergence takes place mostly between 10:00 a.m. and 12:00 p.m. in the morning, the emergence was checked always at the same time of the day: between 12:00 and 2:00 p.m.. Untreated eggs and eggs treated with 0.1 μL of pure acetone were used as controls every time a set of treatments was carried out. The tested concentrations were 10, 7.5, 5, 2.5, 1.75, 1, 0.5, and 0.1 mg/mL.

The following variables were recorded: egg mortality (%), duration of the development (days), and egg developmental stage at death (white egg, red ring, and black head) (*20*).

Statistical Analyses. The mortality of the treated eggs was corrected with the mortality of the pure acetone-treated eggs (*21*). The mortality of the untreated eggs was only used as a check on the validity of the replicate. The whole replicate was discarded when the mortality of the untreated eggs was >20%. The corrected mortality was analyzed using the routine ANOVA of the statistical package SAS, followed by Duncan's multiple-range test ($P < 0.05$).

For each compound, a probit analysis of the mortality versus the concentration was carried out with the program Polo Plus (*22*). Only the concentrations that produced mortality between 5 and 95% were used. Tests of equality and parallelism of the lines were carried out. Comparison of the LC_{50} (concentration that kills 50% of the treated individuals) and LC_{90} (concentration that kills 90% of the treated individuals) of the different compounds was carried out using the overlapping of the confidence intervals as the criterion.

RESULTS AND DISCUSSION

The chemical reaction used to prepare the bioactive compounds is shown in **Figure 1**. The synthetic method is very simple. The first step consisted of heating at 80 °C for 48 h a 2:1:5 mmol mixture of glycerol, a fatty acid, and chlorotrimethylsilane in a solvent-free medium. The formation of the 1,3-dichloro-2-propyl ester was confirmed by GC-MS and the following ^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$ signals at δ: 5.2 (quin, 1, J = 5.2 Hz, O—C<u>H</u>), 3.7 (m, 4, C<u>H$_2$</u>—Cl), 2.3 (t, 2, J = 7.5 Hz, C<u>H$_2$</u>—C=O); 173 (<u>C</u>O—O), 71 (O—<u>C</u>H), 42 (<u>C</u>H$_2$—Cl), 34 (<u>C</u>H$_2$—C=O). The crude compound was then dissolved in butanone and heated at 115 °C in the presence of NaI, producing the corresponding allyl ester. Formation of allyl esters is easy to monitor by NMR. Characteristic signals appear at δ: 2.3 (t, 2, J = 7.5 Hz, −C<u>H$_2$</u>—COO), 4.6 (dt, 2, J = 5.7, 1.5 Hz, −O—C<u>H$_2$</u>—CH−), 5.2 (ddt, 1, J = 10.5, 1.6, 1.6 Hz, C<u>H$_2$</u>=CH−), 5.3 (ddt, 1, J = 17.2, 1.6, 1.6 Hz, C<u>H$_2$</u>=CH−), 5.9 (ddt, 1, J = 17.2, 10.5, 5.7 Hz, CH$_2$=C<u>H</u>−) in ^{1}H NMR (400 MHz, $CDCl_3$); 34 (−<u>C</u>H$_2$—CO−), 65 (−O—<u>C</u>H$_2$−), 118 (<u>C</u>H$_2$=CH−), 132 (CH$_2$=<u>C</u>H−), 173 (<u>C</u>O—O−) in ^{13}C NMR (100 MHz, $CDCl_3$). This description is in accordance with data found in the literature.

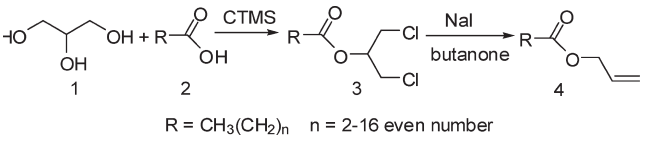

Figure 1. General scheme of the reaction process.

Table 1. Fatty Acids Used and Yields[a] of Crude 1,3-Dichloropropen-2-yl Carboxylate (**3**) and Purified Allyl Carboxylate (**4**)

entry	R (**Figure 1**)	crude **3** (%)	**4** (%)
a	$CH_3(CH_2)_2$	67	86
b	$CH_3(CH_2)_4$	96	54
c	$CH_3(CH_2)_6$	84	94
d	$CH_3(CH_2)_8$	97	84
e	$CH_3(CH_2)_{10}$	96	89
f	$CH_3(CH_2)_{12}$	98	99
g	$CH_3(CH_2)_{14}$	77	100
h	$CH_3(CH_2)_{16}$	97	99

[a] Yield values are rounded to integer figures.

Furthermore, the MS spectrum shows a fragment ion of m/z 100, formed by a McLafferty rearrangement, which is a key fragment for allyl esters of straight-chain acids with a chain length greater than three carbon atoms.

The two steps, synthesis of 1,3-dichloropropyl ester and synthesis of allyl esters, run, in general, with very high yields. All of the allyl esters used in the assays were prepared according to the general procedure. Purification of the reaction crude product yielded pure allyl esters (**Table 1**).

The mean mortality of the controls (untreated and acetone-treated) was always <20% (data not shown), which validates all of the replicates and permits the use of the Abbot formula to calculate the corrected mortality. The corrected mortality ranged from 0 to 100 in the range of concentrations tested. All of the compounds showed a concentration−mortality response and caused 100% mortality at the highest concentration tested, 10 mg/mL (**Table 2**). However, no compound was as effective as fenoxycarb proved to be in previous experiments carried out using the same codling moth population and the same methodology. Fenoxycarb caused 100% mortality when eggs were treated with 0.1 μL at a concentration of 0.5 mg/mL (unpublished data), in contrast to a maximum of 30% achieved with the tested compounds (**Table 2**).

A probit regression line could be adjusted for all of the compounds [values of the heterogeneity index sufficiently low (*22*); **Table 3**]. The regression lines were not equal (chi-square, 408; degrees of freedom, 14; tail probability, 0.000) or parallel (chi-square, 29.23; degrees of freedom, 7; tail probability, 0.000). **Table 4** shows the values and the confidence intervals of the LC_{50} and LC_{90}. There was an inverse relationship between the alkyl chain length and the lethal concentrations. The two compounds bearing the longest chains (**4g** and **4h**) were the least effective, as

Table 2. Corrected Mortality (Percent) of <24-h-Old *C. pomonella* Eggs Treated with 0.1 μL of Allyl Esters Solution at Different Concentrations[a]

	concentration							
compd	10 mg/mL	7.5 mg/mL	5 mg/mL	2.5 mg/mL	1.75 mg/mL	1 mg/mL	0.5 mg/mL	0.1 mg/mL
4a	100 ± 0	100 ± 0 a	98.7 ± 0.6 a	83.3 ± 2.6 d	72.0 ± 3.0 bc	42.7 ± 2.0 c	20.5 ± 1.3 b	6.0 ± 2.0 bc
4b	100 ± 0	100 ± 0 a	98.7 ± 0.6 a	95.8 ± 0.8 b	83.8 ± 2.1 a	51.2 ± 1.7 b	22.4 ± 1.6 b	8.4 ± 1.0 ab
4c	100 ± 0	98.8 ± 0.4 b	97.7 ± 0.5 b	95.9 ± 0.9 b	83.8 ± 1.3 a	59.2 ± 0.8 a	29.9 ± 2.0 a	9.7 ± 0.6 a
4d	100 ± 0	100 ± 0 a	98.7 ± 0.5 a	97.2 ± 0.6 a	76.3 ± 1.3 b	30.5 ± 1.3 e	12.4 ± 1.4 c	7.4 ± 0.03 bc
4e	100 ± 0	98.8 ± 0.4 b	96.5 ± 0.7 c	95.9 ± 0.6 b	71.7 ± 1.6 c	36.4 ± 0.7 d	10.0 ± 0.4 d	0 ± 1.3 e
4f	100 ± 0	97.7 ± 0.5 b	97.2 ± 0.6 bc	87.5 ± 1.8 c	49.5 ± 4.0 d	19.8 ± 1.6 f	7.5 ± 1.4 e	4.6 ± 0.2 d
4g	100 ± 0	87.2 ± 0.4 c	72.2 ± 3.2 e	66.6 ± 1.8 e	32.6 ± 3.3 e	6.0 ± 1.03 g	0 ± 0.5 f	0 ± 0.1 e
4h	100 ± 0	87.2 ± 0.5 c	82.2 ± 3.4 d	41.6 ± 3.7 f	32.1 ± 4.4 e	17.3 ± 1.0 f	11.9 ± 2.0 cd	0 ± 1.4 e

[a] Mean and standard error of three replicates of 30 eggs each. Values followed by the same letter in the same column are not significantly different (Duncan's multiple-range test, $P < 0.05$). See **Table 1** for compound identification.

Table 3. Results of the Probit Regression Analysis for < 24-h-Old *C. pomonella* Eggs Topically Treated with 0.1 μL of Allyl Ester Solution[a]

compd	*n*	slope ± SD	intercept	*t* ratio	chi-square	heterogeneity
4a	270 (29)	2.66 ± 0.29	4.93	4.23	15.53	0.97
4b	270 (28)	3.36 ± 0.40	5.18	1.82	13.50	1.03
4c	300 (29)	2.64 ± 0.43	5.39	−0.63	16.82	1.01
4d	270 (29)	6.14 ± 1.03	4.10	−3.60	28.59	1.78
4e	270 (31)	4.11 ± 0.53	4.76	−1.78	5.51	0.42
4f	300 (29)	3.53 ± 0.39	4.47	−3.83	22.85	1.42
4g	300 (29)	2.51 ± 0.22	4.01	−7.93	40.38	2.12
4h	300 (29)	2.94 ± 0.32	3.73	−6.93	40.23	1.82

[a] *n* = total number of eggs in the acetone-treated control (number of dead eggs in the acetone-treated control). Regression lines not equal (chi-square, 408; df, 14; $P < 0.001$) or parallel (chi-square, 29.23; df, 7; $P < 0.001$). See **Table 1** for compound identification.

Table 4. Values and Confidence Intervals (CI) of the LC_{50} and LC_{90} of <24-h-Old *C. pomonella* Eggs Topically Treated with 0.1 μL of Solution of Allyl Esters[a]

		LC_{50} (mg/mL)		LC_{90} (mg/mL)	
compd	*n* (control)	value	CI	value	CI
4a	270 (29)	1.06 bc	0.86−1.25	3.20 a	2.62−4.29
4b	270 (28)	0.88 ab	0.73−1.02	2.13 a	1.79−2.75
4c	300 (29)	0.71 a	0.53−0.85	2.18 a	1.78−3.06
4d	270 (29)	1.40 c	1.13−1.56	2.26 a	1.98−3.09
4e	270 (31)	1.14 bc	0.98−1.28	2.34 a	2.04−2.86
4f	300 (29)	1.41 c	1.16−1.64	3.24 a	2.69−4.33
4g	300 (29)	2.46 d	1.96−3.03	7.97 b	5.93−12.77
4h	300 (29)	2.69 d	2.19−3.16	7.33 b	5.80−10.88

[a] *n* = total number of eggs in the acetone-treated control (number of dead eggs in the acetone-treated control). Values followed by the same letter in the same column are not significantly different because of the overlapping of the confidence intervals ($P < 0.05$). See **Table 1** for compound identification.

both their LC_{50} and LC_{90} values were significantly higher than the LC_{50} and LC_{90} values of the rest of the compounds. The separation of the LC_{50} is clearer than the separation of the LC_{90} because of the higher values of the confidence intervals of the LC_{90}. Probably, the greater length of the alkyl chain hampers the penetration of the compound through the egg chorion.

The vast majority of the eggs from the untreated control and from the acetone control died at the last egg developmental stage (black head), when the larva is fully developed inside the egg (data for the highest concentration shown in **Table 5**; rest of the data not shown). This fact confirms that the observed mortality at the white egg stage was not due to a lack of egg fertilization. The stage of development at which the eggs treated with 10 mg/mL died depended on the compound; the eggs treated with the longest chain compounds (**4g** and **4h**) died at the black head stage, whereas the eggs treated with the rest of the compounds mostly died at the white egg stage (**Table 5**). Therefore, the less active materials (**4g** and **4h**) also took longer to kill the eggs.

In general, the duration of the development of the eggs treated with any compound was higher than the duration of the development of the acetone-treated eggs (data not shown because the increase was always < 1 day, which has no consequence in the field populations).

Some of the most active allyl esters studied are present in many foods and have been used as flavoring compounds for a long time (*23*). Consequently, they are putative candidates to be considered generally recognized as safe (GRAS) substances. This and also the fact that they can be easily synthesized from a renewable resource obtained in large scale as a byproduct of biodiesel production makes those active esters interesting candidates to be used to control codling moth. Furthermore, these compounds add a new class of products that will help to diversify alternatives for pest management.

Table 5. Distribution (Percent) by Developmental Stages of the Mortality of < 24-h-Old *C. pomonella* Eggs Treated with 0.1 μL of 10 mg/mL Solution of Allyl Esters[a]

	egg developmental stage at death		
compd	white head	red ring	black head
untreated control	0.00 ± 0.00	0.00 ± 0.00	100 ± 0.00
acetone control	1.1 ± 0.44	4.4 ± 0.22	94.4 ± 0.1
4a	75.6 ± 2.96	14.4 ± 1.48	10.0 ± 2.2
4b	67.8 ± 5.19	13.3 ± 2.22	18.9 ± 7.4
4c	80.0 ± 2.22	13.3 ± 2.22	6.7 ± 0.0
4d	68.9 ± 5.19	16.7 ± 0.00	14.4 ± 5.2
4e	68.9 ± 1.48	12.2 ± 3.70	18.9 ± 3.0
4f	54.4 ± 3.70	17.8 ± 5.93	27.8 ± 3.0
4g	28.9 ± 3.70	24.4 ± 5.93	46.7 ± 2.2
4h	43.3 ± 2.22	13.3 ± 2.22	43.3 ± 4.4

[a] Mean and SE of three replicates of initially 30 eggs each. See **Table 1** for compound identification.

In conclusion, a set of allyl alkylcarboxylic esters has been obtained from glycerol, a byproduct of the biodiesel industry. These compounds show ovicidal activity on codling moth eggs. This activity is related to the length of the alkyl chain.

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