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Stereoselective Synthesis of Octadecapolyenoic Esters as an Insecticide

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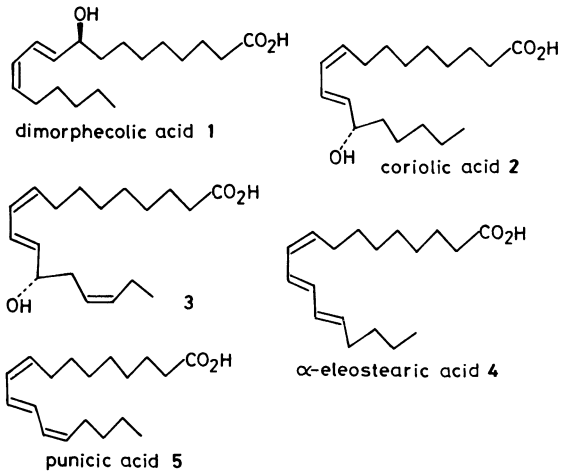
Octadecapolyenoic acid derivatives such as (±)-*t*-butyl coriolate, α-eleostearic acid, *t*-butyl punicate, and *t*-butyl (9*Z*,11*E*)-13-hydroxy-9,11-octadecadien-15-ynoate were synthesized starting from oleic acid with high stereoselectivity and their insecticidal activity was examined.

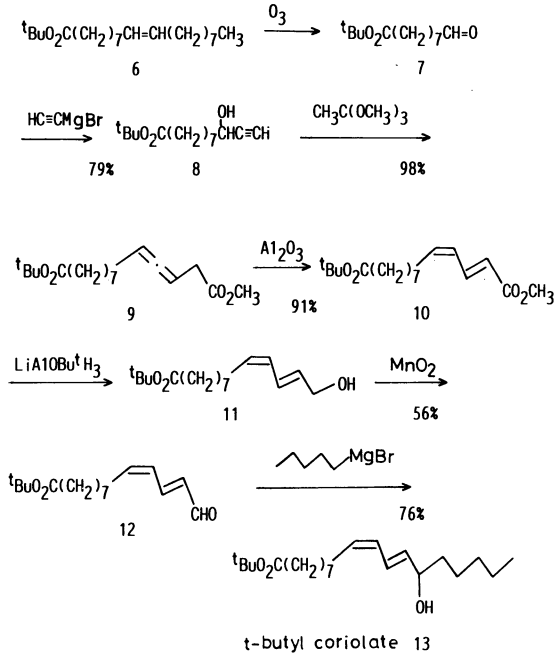
Hydroxyoctadecapolyenoic acids such as dimorphecolic acid (**1**), coriolic acid (**2**), and (13*S*,9*Z*,11*E*,15*Z*)-13-hydroxy-9,11,15-octadecatrienoic acid (**3**) are self defensive substances in rice plant against rice blast disease, which were isolated by Kato et al.[1] α-Eleostearic acid [(9*Z*,11*E*,13*E*)-9,11,13-octadecatrienoic acid] (**4**) and punicic acid [(9*Z*,11*E*,13*Z*)-9,11,13-octadecatrienoic acid] (**5**) are components in some seed oils,[2] and methyl α-eleostearate is a feeding deterrent for the boll weevil on cotton.[3] Kawazu[4] found that esters of octadecapolyenoic acids such as linoleic acid and linolenic acid possess insecticide activity by preliminary experiments. Recently, we reported the



synthesis of **1** and its analogs.[5] As an extention of the previous work,[5] here we report the synthesis of (±)-*t*-butyl coriolate, *t*-butyl punicate, **4**, and an analog of **3**. Furthermore, insecticidal activity of these products was examined.

Coriolic acid (**2**) is a component of plant seed oils[6] and also a self defensive substance in rice plant against rice blast disease.[1] Syntheses of **2** have been reported by some groups.[7] Our synthetic sequence is shown in Scheme 1. Readily available oleic acid was used as a starting material. Ozonolysis of *t*-butyl oleate (**6**) at −20—−30 °C gave *t*-butyl 9-oxononanoate (**7**) in a fair yield. Ethynylation of **7** with ethynylmagnesium bromide yielded *t*-butyl 9-hydroxy-10-undecynoate (**8**) in 79% yield. Ortho-Claisen rearrangement of **8** with an excess of trimethyl orthoacetate gave β-allenic ester **9** quantitatively. Conversion of **9** to 1-methyl 13-*t*-butyl (2*E*,4*Z*)-2,4-tridecadiene-1,13-dioate (**10**) was established by the economical and convenient method which was developed by two of us.[8] Treatment of **9** with alumina at the reflux temperature of benzene gave (2*E*,4*Z*)-dienoic diester **10** in 91% yield with high stereoselectivity. Both proton and carbon-13 NMR analyses showed no presence of stereoisomers.

Regioselective reduction of **10** with various reducing agent was attempted and the results were summarized in Table 1. Reduction of **10** with diisobutylaluminum hydride (DIBAL) gave diol **14** as a major product. Reduction with lithium aluminum hydride (LAH) yielded a mixture of the desired product **11** and diol **14**. Prolonged reaction with LAH



Scheme 1.

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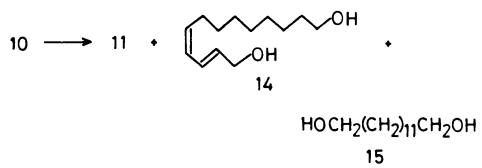
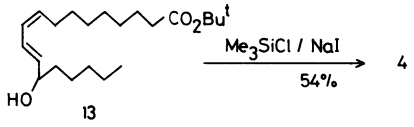
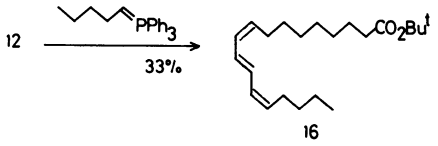


gave a hydrogenated product, 1,13-tridecanediol (**15**) in addition to the reduced products, **11** and **14**. Reduction of **10** with lithium di- or tri-*t*-butoxyaluminum hydride resulted in the formation of *t*-butyl (9*Z*)-13-hydroxy-9-tridecenoate or in the recovery of the starting material. The best result was obtained by the reduction of **10** with lithium *t*-butoxyaluminum hydride at −50 °C to give **11** in 60% yield. Oxidation of the alcohol **11** with active manganese dioxide at room temperature gave *t*-butyl (9*Z*,11*E*)-13-oxo-9,11-tridecadienoate (**12**) in an excellent yield, which is pure by ^{1}H NMR analysis. Reaction of **12** with pentylmagnesium bromide at −15 °C proceeded regioselectively to give (±)-*t*-butyl coriolate **13** in 84% yield as a sole product. The ^{1}H NMR spectrum was identical with that of methyl coriolate[9] except the signal of the ester group. Any 1,4- or 1,6-addition products could not be detected.

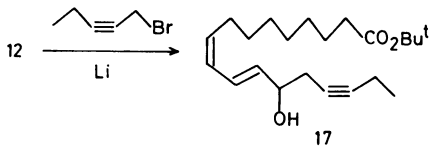
Conversion of (±)-*t*-butyl coriolate **13** to naturally occuring carboxylic acid **2** was attempted. However, the hydrolysis of **13** with chlorotrimethylsilane-sodium iodide[10a] at 25 °C afforded α-eleostearic acid (**4**)[11] in 54% yield with simultaneous dehydration. Synthesis of 1,3-diene from cyclic allylic alcohols and from allylic vicinal diols with Me_3SiCl–NaI is known.[10b] However, to our knowledge this type of dehydration for acyclic allylic alcohols has never reported before, and the general applicability is now under an investigation. On the other hand, acid-catalyzed hydrolyses resulted in the formation of polymerized products.



Punicic acid (**5**) is a component of plant seed oils.[2] Conacher and Gunstone[12] reported the synthesis of **5** from linoleic acid. We prepared *t*-butyl ester **16** of **5** by the Wittig reaction of **12** with pentylidenetriphenylphosphorane.



Shimura et al.[13,14] have reported the isolation and structural elucidation of anti-conidial germination substance, (9*Z*,11*E*,15*Z*)-13-hydroxy-9,11,15-octadecatrienoic acid (**3**). The absolute configuration of **3** was determined to be S-configuration by Kato et al.[1] We attempted the synthesis of (±)-**3**. Although it is reported that lithiation of 1-bromo-2-pentyne and the following reaction with a carbonyl compound gave acetylenic alcohol as a major product,[15,16] our attempts on the reaction of 2-pentynyllithium with aldehyde **12** afforded *t*-butyl (9*Z*,11*E*)-13-hydroxy-9,11-octadecadien-15-ynoate (**17**) in low yield along with an allenic compound. Conversion of **17** to *t*-butyl ester of (±)-**3** with stereoselective hydrogenation resulted in the formation of polymerized products.



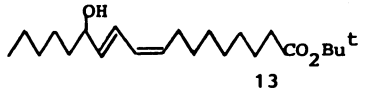
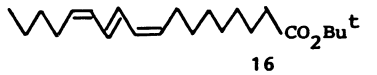
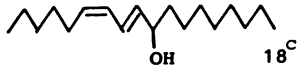
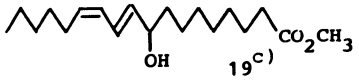
Insecticidal activity of polyenoic esters prepared in the present synthesis and also in the previous paper was examined and the results were shown in Table 2. All of compounds showed fair insecticidal activity (LD_{50}=ca. 25—50 μg/fly) against adults of the fruitfly, *Drosophila melanogaster*. No notable relationship between the molecular structure and the activity was observed.

Table 1. Reduction of **10** with Various Reducing Agents

10 R	Reducing Agent (mol ratio to **10**)	Reaction condition		Yield/% of product[a]		
		Temp/°C	h	**11**	**14**	**15**
Et	DIBAL (2.20)	−15	0.5	2	52	14
Me	$LiAlH_4$ (1.10)	−40——35	2.5	41	37	
Et	$LiAlH_4$ (1.26)	−50——40	5.0	39	35	23
Et	$LiAl(OBu^t)_3H$ (3.0)	15	42	b)		
Et	$LiAl(OBu^t)_2H_2$ (2.0)	−20	5.0	c)		
Et	$LiAl(OBu^t)H_3$ (1.3)	−40	3.0	49	21	
		−20	4.0			
Me	$LiAl(OBu^t)H_3$ (1.0)	−50	3.0	60	8	

a) Isolated yield. b) The desired product was not detected. The structure of the product was supposed to be *t*-butyl (9*Z*)-13-hydroxy-9-tridecenoate. c) The starting material **10** was recovered in 91% yield.

Table 2. Insecticidal Activity of Polyenoic Esters against of Drosophilamelanogaster[a)]

Compds	Number of survivors[b)]					
	Dose 0	0.125	0.25	0.50	1.0	2.0 mg
 13	10 (8)	8 (0)	7 (0)	4 (0)	2 (0)	2 (0)
 16	9	9	7	6	8	1
 17	10	7	6	7	6	0
 18[c)]	10	8	4	3	0	0
 19[c)]	10	7	9	2	0	0

a) Dry film method. b) The number after 24 h. The number in parenthesis is after 48 h. c) The synthesis is reported in the previous paper. See Ref. 5.

Experimental

The melting and boiling points are uncorrected. Infrared (IR) spectra were obtained with a JASCO Model A-102 infrared spectrophotometer. ^{1}H NMR spectra (60 MHz) were recorded with a JEOL JNM-FX100 apparatus, with $CDCl_3$ as a solvent. All chemical shifts are reported in δ units downfield from internal Me_4Si, and J values are given in hertz. Column chromatography was accomplished with 100—200 mesh Wakogel C-200.

Petroleum ether was distilled (bp 40—60 °C) and dried over sodium wire. Tetrahydrofuran (THF) and diethyl ether were dried over sodium benzophenone ketyl and distilled under an atmosphere of nitrogen prior to use. Activated manganese dioxide was prepared according to the procedures in the literature.[17)]

t-Butyl oleate (**6**) was prepared by the reaction of oleoyl chloride with *t*-butyl alcohol in the presence of 2 equivalents of pyridine at 60—80 °C for 3 h: 88% yield.

t-Butyl 9-oxononanoate (**7**) was obtained by the ozonolysis of *t*-butyl oleate according to the procedure of the literature;[18)] bp 85—90 °C/0.08 mmHg (1 mmHg=133.322 Pa); 52.1% yield.

t-Butyl 9-hydroxy-10-undecynoate (**8**) was prepared by following the method described in the preparation of the methyl ester:[19)] 79% yield; IR (neat) 3500, 3300, 2100, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (m, 10H, $(CH_2)_5$), 1.43 (s, 9H, $C(CH_3)_3$), 2.22 (m, 4H, CH_2CO, $>CHCH_2$), 2.40 (d, 1H, J=2 Hz, HC≡C), 4.35 (m, 1H, >CHOH).

13-*t*-Butyl 1-Methyl 3,4-Tridecadiene-1,13-dioate (9). A mixture of **8** (6.33 g, 0.0249 mol), trimethyl orthoacetate (20.9 g, 0.174 mol), and propionic acid (0.1 g) was heated to the reflux temperature for 24 h with removal of methanol produced by distillation. Removal of volatile materials under reduced pressure gave 7.58 g (98%) of **9**: IR (neat) 1960 (C=C=C), 1730 cm^{-1} (ester C=O); ^{1}H NMR ($CDCl_3$) δ=1.30 (m, 10H, $(CH_2)_5$), 1.45 (s, 9H, $C(CH_3)_3$), 2.12 (m, 4H, $=CHCH_2(CH_2)_5$, $CH_2CO_2Bu^t$), 3.02 (m, 2H, $CH_2CO_2CH_3$), 3.64 (s, 3H, CO_2CH_3), 5.14 (m, 2H, CH=C=CH). Analytical sample was purified by column chromatography (SiO_2, hexane/ethyl acetate (10:1)). Found: C, 69.47; H, 9.50%. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%.

1-Methyl 13-*t*-Butyl (2*E*,4*Z*)-2,4-Tridecadiene-1,13-dioate (10). A mixture of **9** (7.53 g, 0.0243 mol), alumina[8)] (12.4 g), and dry benzene (40 ml) was heated at the reflux temperature for 11 h. After filtration, removal of the solvent gave 6.85 g (91%) of **10** as a clean oil: IR (neat) 1720 (C=O), 1640, 1610 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.32 (m, 10H, $(CH_2)_5$), 1.41 (s, 9H, $C(CH_3)_3$), 2.17 (m, 4H, $=CHCH_2$, $CH_2CO_2Bu^t$), 3.66 (s, 3H, CO_2CH_3), 5.50—6.33 (m, 3H, CH=CHCH=CHCO), 7.45 (dd, 1H, J=10 and 15.0 Hz, CH=CHCO). ^{13}C NMR ($CDCl_3$) δ=25.1 (t), 28.1 (s), 29.0 (t), 29.3 (t), 29.5 (t), 29.7 (t), 35.5 (t), 51.4 (q), 79.8 (s), 118.3 (d), 126.5 (d), 139.7 (d), 141.6 (d), 167.6 (s), 173.1 (s). Analytical sample was purified by column chromatography (SiO_2, hexane/ethyl acetate (10:1)). Found: C, 69.41; H, 9.51%. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%.

***t*-Butyl (9*Z*,11*E*)-13-Hydroxy-9,11-tridecadienoate (11).** Lithium aluminum hydride (250 mg, 6.59 mmol) and 10 ml of THF was charged in 60 ml two-necked, round-bottomed flask under an atmosphere of nitrogen. To a stirred mixture was added 0.62 ml (49 mg, 6.58 mmol) of *t*-butyl alcohol at 0 °C. After 10 min, a solution of 2.04 g (6.57 mmol) of **10** in 10 ml of THF was added dropwise at −50 °C. The mixture was stirred for 3 h and then quenched with 1 ml of ethyl acetate and 2.5 ml of 10% HCl. After the mixture was poured into cold water, the organic layer was extracted with

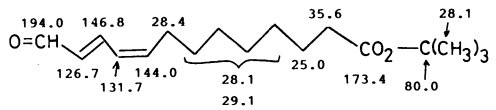
ether. The combined extracts were washed with water and dried over $MgSO_4$. Removal of the solvent gave 1.90 g of a crude product which was purified by column chromatography (SiO_2, hexane/ethyl acetate (9:1—1:1)) to give 1.13 g (60%) of **11** as a clean oil: IR (neat) 3425 (OH), 1735 (ester C=O), 1455, 1365, 1255 cm^{-1}; ^1H NMR δ=1.15—1.75 (m, 10H, $(CH_2)_5$), 1.40 (s, 9H, $C(CH_3)_3$), 1.75—2.40 (m, 4H, CH_2CH=CH, $CH_2CO_2Bu^t$), 3.96 (br d, 2H, J=5.6 Hz, CH_2OH), 5.05—6.63 (m, 4H, CH=CHCH=CH). Found: C, 72.32; H, 10.70%. Calcd for $C_{17}H_{30}O_3$: C, 72.30; H, 10.71%. The last fraction gave 110 mg (8%) of **14**: ^1H NMR ($CDCl_3$) δ=1.32 (m, 12H, J=6 Hz, CH_2OH), 4.19 (d, 2H, J=5.5 Hz, $HOCH_2CH$=), 5.17—6.33 (m, 3H, CH=CHCH=CH), 6.54 (dd, 1H, J=10 and 15.5 Hz, $HOCH_2CH$=CH). Found: C, 73.67; H, 11.52%. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39%.

Reduction of 10 with LiAl(OBu^t)$_3$H. To a stirred mixture of $LiAlH_4$ (120 mg, 3.16 mmol) and THF (3 ml) was added t-butyl alcohol (0.89 ml, 9.44 mmol) at 0 °C. After 10 min a solution of **10** (162 mg, 0.499 mmol) in 5 ml of THF was added dropwise at 15 °C, and the mixture was stirred for 42 h. The work up as described above gave a clean oil (148 mg) or t-butyl (9Z)-13-hydroxy-9-tridecenoate (supposed structure): ^1H NMR (CCl_4) δ=1.03—1.81 (m, 12H), 1.40 (s, 9H), 1.9—2.36 (m, 6H), 2.51 (br s, 1H), 3.50 (t, 2H, J=6 Hz), 5.11—5.52 (m, 2H).

Reduction of 10 with Diisobutylaluminum Hydride (DIBAL). Compound **10** (325 mg, 1 mmol) was reduced in 2 ml of ether with DIBAL (1.0 M in hexane) under the conditions described in Table 1 and worked up as above, giving 63.9 mg of **10**, 30.3 mg (14%) of 1,13-tridecanediol (**15**)[20]: ^1H NMR (CCl_4) δ=1.28 (s, 22H), 1.65 (br s, 2H), 3.40 (t, 4H), 5.9 mg (2%) of **11**, and 110 mg (52%) of **14**.

***t*-Butyl (9*Z*,11*E*)-13-Oxo-9,11-tridecadienoate (12).** (a) To a mixture of 11.0 g of activated manganese dioxide[17] and 100 ml of petroleum ether was added a solution of 1.13 g (4.01 mmol) of **11** in 20 ml of petroleum ether at 5 °C with stirring. The mixture was stirred for 3 h at 25 °C and then filtered off. Concentration of the filtrate gave 0.887 g of an oil which was chromatographed on 10 g of silica gel eluting with hexane/ethyl acetate (10:1) to give 0.624 g (56%) of **12** as a clean oil: IR (neat) 2950, 1725 (ester C=O), 1680 (aldehyde C=O), 1630 (C=C), 1365, 1155, 850 cm^{-1}: ^1H NMR (CCl_4) δ=1.05—1.91 (m, 10H, $(CH_2)_5$), 1.95—2.55 (m, 4H, $CH_2CO_2Bu^t$, CH_2CH=CH), 5.69—6.45 (m, 3H, CH=CHCH=CHCHO), 7.29 (dd, 1H, J=11 and 15 Hz, CH=CHCHO), 9.50 (d, 1H, J=7 Hz, CHO). Found:C, 72.72; H, 10.30%. Calcd for $C_{17}H_{28}O_3$: C, 72.82; H, 10.06%.

^{13}C NMR ($CDCl_3$, δ)

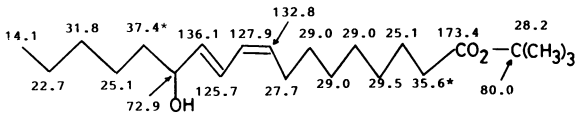


The last fraction eluted with ethyl acetate gave 100 mg of polymerized products.[21]

(b) To a mixture of 0.130 g (1.5 mmol) of activated manganese dioxide and 2 ml of petroleum ether was added a solution of 27 mg (0.096 mmol) of **11** in 0.5 ml of petroleum ether at 25 °C with stirring. The mixture was stirred for 2 h and then filtered off. Concentration of the filtrate gave 25 mg (93%) of **12** as a clean oil. TLC analysis (SiO_2, hexane/ethyl acetate (2:1)) showed one spot at R_f 0.75. IR and ^1H NMR data were identical with those of the authentic sample.

(±)-*t*-Butyl (9*Z*,11*E*)-13-Hydroxy-9,11-octadecadienoate ((±)-*t*-Butyl Coriolate) (13). To a mixture of 18.9 mg (0.778 mmol) of magnesium and 0.3 ml of THF was added dropwise 122 mg (0.808 mmol) of pentyl bromide with stirring. After 2 h, a solution of 96.8 mg (0.345 mmol) of **12** in 3 ml of THF was added dropwise at −15 °C, and then the mixture was stirred for 2 h. The mixture was poured into ice water, and the organic layer was extracted with ether. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated. The resulting residue was chromatographed on 8 g of silica gel eluting with hexane/ethyl acetate (10:1) to give 63.3 mg (76%) of **13**: IR (neat) 3350 (OH), 1730 (C=O); ^1H NMR (CCl_4) δ=0.85 (t, 3H, CH_3), 1.30 (m, 18H, $(CH_2)_5$, $(CH_2)_4$), 1.38 (s, 9H, $C(CH_3)_3$), 2.10 (m, 4H, CH_2CO, $=CHCH_2$), 4.00 (m, 1H, >CHOH), 5.03—6.53 (m, 4H, $(CH=CH)_2$). Found: C, 74.62; H, 11.20%. Calcd for $C_{22}H_{40}O_3$: C, 74.95; H, 11.44%.

^{13}C NMR ($CDCl_3$, δ)



* May be interchangeable.

(9*Z*,11*E*,13*E*)-9,11,13-Octadecatrienoic Acid (α-Eleostearic Acid) (4). To a mixture of 66.3 mg (0.442 mmol) of sodium iodide and 0.5 ml of acetonitrile was added a solution of 82.1 mg (0.233 mmol) of **13** in 1 ml of acetonitrile under an atmosphere of nitrogen. Chlorotrimethylsilane (0.056 ml, 0.44 mmol) was added at 0 °C with stirring and the mixture was stirred for 3 h at 25 °C, and then poured into ice water. The organic layer was extracted with ether, washed with water, dried over $MgSO_4$. After removal of the solvent, the residual oil was chromatographed on silica gel eluting with hexane/ethyl acetate (20:1) to give 35 mg (54%) of **4**. Spectral data were identical with those of the authentic sample.[11]

***t*-Butyl (9*Z*,11*E*,13*Z*)-9,11,13-Octadecatrienoate (*t*-Butyl Punicate) (16).** To a stirred mixture of 143 mg (0.346 mmol) of pentyltriphenylphosphonium bromide and 2 ml of dry THF was added 0.23 ml (0.346 mmol) of 1.65 M butyllithium (1 M=1 mol dm^{-3}) in hexane at −20 °C. After 20 min, a solution of 47 mg (0.168 mmol) of **12** in 1 ml of dry THF was added dropwise. The mixture was stirred for 15 min at −78 °C, then poured into ice water, and neutralized with dilute HCl. The organic materials were extracted with ether, washed with water, and dried over $MgSO_4$. Removal of the solvent gave 71.8 mg of an oil, which was chromatographed (SiO_2, 2.8 g; eluent: hexane/ethyl acetate, 30:1—10:1) to afford 18.6 mg (33%) of **16** as an oil: TLC (hexane/ethyl acetate (1:1)), R_f 0.87. Spectral data were identical with those of the authentic sample[22] except signals due to the ester group. IR (neat) 2950, 1730 (C=O), 1460, 1365, 1255, 1150, 995 cm^{-1}; ^1H NMR (CCl_4) δ=0.90 (br t, 3H, J=6 Hz, CH_3), 1.30 (m, 14H, $7CH_2$), 1.38 (s, 9H, $C(CH_3)_3$), 2.11 (m, 6H, $2CH_2CH$=), 5.00—6.45 (m, 6H, 3CH=CH). ^{13}C NMR ($CDCl_3$) δ=13.9 (q), 22.3 (t), 25.1 (t), 27.8 (t), 28.1 (q), 29.1 (t), 31.8 (t), 35.6 (t), 79.9 (q), 127.9 (d), 128.8 (d), 130.0 (d), 132.7 (d), 173.3 (s). Found: C, 78.83; H,

11.67%. Calcd for $C_{22}H_{38}O_2$: C, 78.99; H, 11.45%.

***t*-Butyl (9*Z*,11*E*)-13-Hydroxy-9,11-octadecadien-15-ynoate (17).** To a stirred mixture of 10 mg (1.44 mmol) of lithium and 1.0 ml of THF was added a solution of 73.5 mg (0.542 mmol) of 1-bromo-2-pentyne and 160 mg (0.571 mmol) of **12** in 1 ml of THF at −40 °C over 1.5 h. Additionally, 73.5 mg (0.542 mmol) of 1-bromo-2-pentyne was added. After being stirred for 4 h at −40 °C, the mixture was poured into ice water. The organic layer was extracted with ether. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated. The residue (178 mg) was purified by column chromatography (SiO_2, hexane/ethyl acetate/methanol (80:9:1), developed twice) to give 47 mg (24%) of **17**: TLC (SiO_2, hexane/ethyl acetate (4:1)), R_f 0.76—0.63; IR (neat) 3450, 2940, 2100 (C≡C), 1730: ^{1}H NMR (CCl_4) δ=0.85—1.86 (m, 13H, $(CH_2)_5$, CH_3), 1.91—2.61 (m, 8H, $CH_2C{\equiv}CCH_2$, $CH_2CH{=}CH$, CH_2CO), 4.20 (br d, 1H, J=5 Hz, CHOH), 5.03—6.89 (m, 4H, olefinic protons); ^{13}C NMR ($CDCl_3$) δ=12.3 (t), 14.0 (q), 24.9 (t), 27.5 (t), 27.9 (t), 27.9 (q), 28.8 (t), 29.3 (t), 35.4 (t), 70.6 (d), 75.0 (s), 79.7 (s), 84.6 (s), 126.3 (d), 217.4 (d), 133.1 (d), 133.4 (d), 173.2 (s). Found: C, 75.55; H, 10.38%. Calcd for $C_{22}H_{36}O_3$: C, 75.82; H, 10.41%. The second fraction gave 35 mg of unidentified compound as an oil. IR (neat) 3450 (OH), 2950, 1950 (C=C=C), 1734 (C=O); ^{1}H NMR (CCl_4) δ=1.0 (t, J=6 Hz), 1.1—1.75 (m), 1.75—2.55 (m), 4.16 (q, 1H, J=6 Hz), 4.80 (t, J=4 Hz), 5.1—6.17 (m), 6.45 (q, J=10 and 15 Hz). The last fraction gave 62 mg of polymerized compounds.

Insecticidal Test (dry film method). The fruitfly, *Drosophila melanogaster*, was reared in the medium described in the literature.[23] An ethyl acetate solution of the test compounds was added to a Petri-dish (ϕ 3 cm). After spontaneous evaporation of the solvent, ten adults of the fruitfly were introduced to the dish and kept at 25 °C for 48 hours. The survivors after 24 or 48 hours were counted and the numbers were shown in Table 2.

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