An Efficient Synthesis of Methyl Jasmonate and Methyl Dihydrojasmonate

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A simple and an efficient synthesis of methyl jasmonate (**1**) and methyl dihydrojasmonate (**5**) is described. Starting from alkyl acetoacetate or acetonedicarboxylate, **1** and **5** were obtained in only a few steps *via* intramolecular Michael addition.

Methyl jasmonate (**1**) is found in *Jasminum grandiflorum* L¹⁾ and is well known as a key substance for the characteristic odor of jasmine oil. Much attention has been paid to the synthesis of *dl*-methyl jasmonate (**1**) and related compounds, including jasmone (**2**), jasmine keto lactone (**3**), cucurbitic acid²⁾ (**4**) and methyl dihydrojasmonate (**5**), because of their usefulness in the perfume industry and as new members of the plant hormones, and various syntheses of **1** have been reported.³⁾ Here we wish to describe a novel and efficient synthesis of methyl jasmonate (**1**) and methyl dihydrojasmonate (**5**).

devise a better procedure.

SCHEME I.

FIG. 1.

Our first plan to employ the Diels-Alder reaction of cyclopentenone (**6**) with 2-ethoxybutadiene⁴⁾ (**7**) turned out to be insufficient, because partial isomerization of the double bond of the desired adduct (**8**) to the $\Delta^{5,6}$ isomer (**9**) caused a low overall yield of **1**, (less than 5%),⁵⁾ so we continued the study to

Intramolecular Michael route-1

In order to improve the yield, an intramolecular Michael-type reaction was examined, and therefore intermediates **A** and **B** were selected for cyclization to the substituted cyclopentanone (**C**). Alkylation of the dianion⁶⁾ of acetoacetate (**16**) with methyl γ -bromocrotonate (**15**) was tried at first to afford the intermediate **A**. If the alkylation initially takes place, it should give an anion of **A** (**17**) which would spontaneously cyclize to give an anion of a cyclopentanone (**18**) and subsequent alkylation with **RX** would give the desired product (**19**) by a one-pot reaction.

SCHEME II.

SCHEME III.

No.	Base	Catalyst	Solvent	Temperature, reaction time	Yield
1	LiH (0.5 eq.)	—	THF	Reflux/20 hr	Trace
2	NaH (1.0 eq.)	—	DME	Reflux/20 hr	12%
3	NaH (1.0 eq.)	—	Dioxane	Reflux/20 hr	15%
4	NaH (1.0 eq.)	—	DME/DMSO	Reflux/20 hr	Trace
5	(TMS) ₂ NNa (0.1 eq.)	—	Benzene	Reflux/20 hr	Trace
6	<i>t</i> BuOK (0.1 eq.)	—	<i>t</i> BuOH	Reflux/20 hr	Trace
7	<i>t</i> BuOK (0.1 eq.)	—	DME	Reflux/20 hr	Trace
8	Pyrrolidine (4 eq.)	TiCl ₄ (0.2 eq.)	Benzene	Reflux/20 hr	Trace
9	Pyrrolidine (4 eq.)	TiCl ₄ (0.2 eq.)	Toluene	Reflux/20 hr	8
10	Pyrrolidine (4 eq.)	TiCl ₄ (0.2 eq.)	Xylene	Reflux/20 hr	24
11	Pyrrolidine (4 eq.)	TsOH (0.1 eq.)	Xylene	Reflux/20 hr	15
12	Pyrrolidine (4 eq.)	AcOH (0.1 eq.)	Benzene	Reflux/20 hr	6
13	Morpholine (4 eq.)	TiCl ₄ (0.2 eq.)	Xylene	Reflux/20 hr	0

Treatment of the dianion (**16**)⁶ with **15** at room temperature for 15 min, however, afforded a *cis*, *trans* mixture (*ca.* 1 to 3) of cyclopropane derivatives (**21**) in 76% yield. These results mean that not alkylation but the Michael addition of **16** to **15** initially occurred and successive intramolecular alkylation with *more reactive anion* yielded the undesired product (**21**). So the intermediate *B* was alternatively employed for the synthesis. β -Keto esters (**23a, b**) obtainable *via* alkylation of the dianion (**16**) or base-catalyzed methoxycarbonylation of the corresponding methylketones (**22a, b**), were directly alkylated with **15** to give the *B* type intermediates (**24a, b**).

Base treatment or NaCl-DMSO assisted demethoxycarbonylation⁷ of **24a** did not give the desired cyclization product (**5**) but afforded a dihydrofuran derivative (**25**) and therefore **24a, b** were submitted to acid-hydrolysis (6N HCl-MeOH = 1 : 2, reflux). Only the activated ester group in the molecule was hydrolyzed and subsequently decarboxylated *via* this procedure to give ketoesters (**26a, b**), which were submitted to a cyclization reaction by employing various base catalysts. (See Table I.) As shown in Table I, an inorganic base-catalyzed reaction did not give a good result and finally it was found that using pyrrolidine with TiCl₄ afforded the best result. Thus refluxing precursors (**26a, b**) with excess pyrrolidine and TiCl₄ (0.25 eq.) in benzene gave enaminopyrrolidine esters (**27a, b**) which without purification were heated in xylene for 20 hr to give cyclopentanones (**5, 29**), after hydrolytic work-up in 30~40% yield based on the recovery of **26a, b**. Partial hydrogenation of **29** afforded **1** nearly in quantitative yield. Total yield of **1** for the overall 5 steps, however, was not more than 15% in this procedure, because strenuous conditions were required to effect the cyclization.

Intramolecular Michael route-2

In order to activate the methylene group adjacent to the carbonyl function in the precursors, we had to use more expensive dialkyl

SCHEME IV.

acetonedicarboxylate as a starting material instead of acetoacetic ester.

Recently, Naoshima, Ueda *et al.* reported an excellent procedure to afford a monoalkylation product of acetonedicarboxylate by employing Mg(OEt)₂ as a base.⁸ We also studied the modification of this alkylation under various conditions, the results of which are shown in Table II. It is noteworthy that even LiOH and K₂CO₃ were useful bases in the case of 2-pentynyl halide. This modification should be very important, because these are cheaper bases and it did not need to be done under anhydrous conditions, although the yields were slightly lowered (up to 75%). Second alkylation was achieved with bromocrotonate (**15**) under the ordinary procedure (NaH-THF) to give enone-triesters (**32a, b**) in a 80 and 91% yield respectively, based on the recovery of **31a, b**, which were refluxed with NaH in benzene for 20 hr to give cyclopentanones (**33a, b**) in a 73 and 68% yield. Treatment of **33a, b** with 6N HCl-MeOH (1 : 2) afforded selectively hydrolyzed and decarboxylated products (**5, 29**) in a 66 and 70% yield. **1** was obtained in a 38% yield for an overall 5 steps. It was unnecessary to isolate the intermediate (**32**) and thus the alkylation and successive Michael reaction could be done in one pot using excess base. Then, without purification of the crude product (**33**), decarboxylation was effected to give **5** and **29** in a good overall yield. In this manner, methyl jasmonate (**1**) was synthesized in 42% total yield for an overall 4 steps from acetonedicarboxylate (**30**). Thus a short and efficient synthesis of jasmonoid analogues was estab-

TABLE II.

No.	Substrate	R'	Base	Solvent	Temperature reaction time	Yield (31)
1	30b	$n\text{C}_5\text{H}_{11}$	$\text{Mg}(\text{OMe})_2$	MeOH	Ref/10 hr	62%
2	30b	$n\text{C}_5\text{H}_{11}$	LiOH	MeOH	Ref/10 hr	Trace
3	30b	$n\text{C}_5\text{H}_{11}$	K_2CO_3	MeOH	Ref/10 hr	Trace
4	30b	$n\text{C}_5\text{H}_{11}$	NaH	THF	t_R /20 hr	26%
5	30a	$n\text{C}_5\text{H}_{11}$	$\text{Mg}(\text{OEt})_2$	EtOH	Ref/10 hr	96%
6	30a	$n\text{C}_5\text{H}_{11}$	LiOH	EtOH	Ref/10 hr	Trace
7	30b	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2$	$\text{Mg}(\text{OMe})_2$	MeOH	Ref/10 hr	68%
8	30b	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2$	LiOH	MeOH	Ref/10 hr	72%
9	30b	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2$	K_2CO_3	MeOH	Ref/10 hr	53%
10	30b	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2$	NaH	THF	t_R /10 hr	29%
11	30a	$\text{C}_1\text{H}_5\text{C}\equiv\text{CCH}_2$	$\text{Mg}(\text{OEt})_2$	EtOH	Ref/10 hr	92%
12	30a	$\text{C}_2\text{H}_5\text{C}\equiv\text{CCH}_2$	LiOH	EtOH	Ref/10 hr	75%

lished. Synthesis of jasmine keto lactone (3) and related jasmonoids is now in progress in our laboratory and will be published in due course.⁹⁾

EXPERIMENTAL

All bps were uncorrected. IR were determined on a Shimadzu IRA-400 and a JASCO IRA-2 spectrometer. NMR spectra were recorded at 60 MHz with TMS as an internal standard on a Varian EM-360 and a Hitachi R-24A spectrometer. MS spectra were obtained on a Hitachi RMU-5M GC-MS spectrometer.

Dimethyl 5-heptanoyl-2(E)-hexene-1,6-dioate (24a).

a) *From methyl acetoacetate (16a).* To the solution of the dianion of 16a (11.6 g) in dry THF, prepared in the same manner as reported,⁶⁾ was added dropwise a solution of *n*-amyl bromide (15.0 g) in dry THF over 10 min at 0°C under N_2 , the mixture being stirred for further 1 hr at room temperature. To this was added dropwise a solution of methyl γ -bromocrotonate (15, 17.9 g) in dry THF (10 ml) over 10 min at 0°C. After stirring for 20 hr at room temperature, the reaction mixture was poured into NH_4Cl aq. and extracted with ether. The extract was washed with brine, dried over MgSO_4 and concentrated. The residue was distilled to give 24a (15.3 g, 54%): bp 145~148°C/0.05

mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1735, 1715, 1650, 980. NMR (CDCl_3) δ : 0.88 (3H, t, $J=7$ Hz), 1.0~1.9 (8H), 2.2~2.9 (4H), 3.63 (1H, t, $J=7$ Hz), 3.71 (3H, s), 3.74 (3H, s), 5.89 (1H, d-t, $J=16$, 1 Hz), 6.90 (1H, d-t, $J=16$, 7 Hz).

b) *From 2-octanone (22a).* To a stirred suspension of NaH (6.0 g of 60% mineral oil dispersion) in dry THF (150 ml) was added dropwise a mixture of 2-octanone (15.5 g) and dimethyl carbonate (13.5 g) in dry THF (20 ml) over 10 min at room temperature, the mixture being stirred for 20 hr. To this was added dropwise a solution of methyl γ -bromocrotonate (21.5 g) in dry THF (20 ml) over 10 min at room temperature. After stirring for a further 20 hr at room temperature, the reaction mixture was quenched with NH_4Cl aq. and worked up in the same manner as described above. Distillation afforded the recovered 22a (5.6 g) and 24a (18.9 g, 86% based on the recovery of 22a).

Dimethyl 5-(4-heptynol)-2(E)-hexene-1,6-dioate (24b). The dianion prepared in the same manner from methyl acetoacetate (11.6 g) was treated with 2-pentynyl bromide (16.0 g) and subsequently with methyl γ -bromocrotonate (17.9 g). After the same work-up, the residue was distilled to give 24b (17.3 g, 62%): bp 164~167°C/0.08 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1735, 1715, 1650, 975. NMR (CDCl_3) δ : 1.10 (3H, t, $J=7$ Hz), 1.8~3.0 (8H), 3.75 (3H, s), 3.77 (1H, t, $J=7$ Hz), 3.79 (3H, s), 5.91 (1H, d-t, $J=16$, 1 Hz), 6.93 (1H, d-t, $J=16$, 7 Hz).

Methyl 6-oxo-2(E)-dodecenoate (26a).

a) *via Acidic cleavage.* A mixture of **24a** (6.1 g) and 6 N HCl aq. (20 ml) in MeOH (40 ml) was refluxed for 20 hr. The reaction mixture was cooled, diluted with water and extracted with ether. The extract was washed with NaHCO₃ aq. and brine, dried over MgSO₄ and concentrated. The residue was distilled to give **26a** (4.0 g, 84%): bp 108~110°C/0.08 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1720, 1710, 1655, 975. NMR (CDCl₃) δ : 0.90 (3H, t, $J=7$ Hz), 1.0~1.9 (8H), 2.2~2.9 (6H), 3.74 (3H, s), 5.86 (1H, d-t, $J=16$, 1 Hz), 7.02 (1H, d-t, $J=16$, 7 Hz). MS m/z 226 (9%), 156 (17), 124 (18), 113 (100), 109 (17), 97 (17), 96 (32), 85 (29), 81 (27), 71 (30), 57 (20), 55 (25), 43 (48), 41 (38).

b) *via DMSO-NaCl Procedure.* A mixture of **24a** (1.0 g), water (0.2 g) and NaCl (0.3 g) in DMSO (3.0 ml) was stirred at 160°C for 6 hr. The reaction mixture was cooled, diluted with water and extracted with ether. The extract was washed with brine, dried over MgSO₄ and concentrated. The residue on SiO₂ chromatography (100 g) eluted with *n*-hexane-EtOAc (85:15) gave **26a** (320 mg, 40%) and 2-hexyl-3-methoxycarbonyl-5-methoxycarbonylmethyl-4,5-dihydrofuran (**25**) (82 mg, 8%).

25: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1730, 1690, 1640, 985. NMR (CDCl₃) δ : 0.89 (3H, t, $J=7$ Hz), 1.05~1.75 (8H), 2.30~3.30 (6H, m), 3.70 (3H, s), 3.72 (3H, s), 4.80~5.20 (1H, m). MS m/z 284 (16%), 253 (21), 211 (100), 195 (30), 183 (17), 179 (20), 141 (25), 140 (30), 139 (21), 113 (25), 109 (23), 81 (30), 74 (32), 59 (40), 55 (53), 43 (70), 41 (51).

Methyl 6-oxo-2(E)-dodecen-9-ynoate (26a). In the same manner, **24b** (6.0 g) was treated with 6 N HCl aq. (20 ml) in MeOH (40 ml) to give **26b** (3.7 g, 78%): bp 106~108°C/0.05 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1720, 1710, 1655, 975. NMR (CDCl₃) δ : 1.08 (3H, t, $J=7$ Hz), 1.8~2.9 (10H), 3.72 (3H, s), 5.84 (1H, d-t, $J=16$, 1 Hz), 6.98 (1H, d-t, $J=16$, 7 Hz). MS m/z 222 (4%), 123 (69), 122 (38), 113 (35), 109 (58), 81 (100), 79 (42), 71 (46), 53 (54), 41 (69).

Methyl dihydrojasmonate (5) from 26a.

a) A solution of **26a** (2.0 g) in dry benzene (200 ml) containing pyrrolidine (2.5 g) and TiCl₄ (0.4 g) was refluxed for 6 hr with continuous azeotropic removal of the water. The reaction mixture was concentrated *in vacuo* and the residue was diluted with dry xylene (200 ml) and the mixture refluxed for 20 hr. To the cooled reaction mixture was added a solution of NaOAc (5.0 g) in 50% AcOH aq. (20 ml). After refluxing for 1 hr, the reaction mixture was cooled, washed with water, NaHCO₃ aq. and brine, dried over MgSO₄ and concentrated. The residue on SiO₂ chromatography (80 g) eluted with *n*-hexane-EtOAc (9:1) gave the recovered **26a** (480 mg) and **5** (605 mg, 40% based on the recovery of **26a**): IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1735. NMR (CDCl₃) δ : 0.90 (3H, t, $J=7$ Hz), 1.1~2.8 (16H), 3.70 (3H, s). MS m/z : 226 (2.5%), 156 (16), 153 (15), 83 (100), 82 (25), 55 (31), 41 (40). These data of synthetic **5** were identical to those of the authentic sample.

b) A mixture of **26a** (200 mg), TiCl₄ (40 mg) and pyrrolidine (250 mg) in dry toluene (20 ml) was refluxed for 20 hr with continuous azeotropic removal of the water. To this was added 2 N HCl aq. (20 ml) and the mixture refluxed for 30 min. The reaction mixture was cooled and the organic layer was separated, washed with water, NaHCO₃ aq. and brine, dried over MgSO₄ and concentrated. The residue on SiO₂ chromatography (10 g) eluted with *n*-hexane-EtOAc (9:1) gave the recovered **26a** (42 mg, 21%) and **5** (16 mg, 8%). The mother liquor was neutralized with NaHCO₃ aq. and extracted with ether. The extract was washed with brine, dried over MgSO₄ and concentrated *in vacuo* to give methyl 6-oxo-3-(1-pyrrolidine) dodecanoate (69 mg, 26%): IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1730, 1710. NMR (CDCl₃) δ : 0.90 (3H, t, $J=7$ Hz), 1.05~2.10 (14H), 2.10~3.00 (10H, m), 3.00~3.20 (1H, m), 3.65 (3H, s).

c) A mixture of **26a** (200 mg) and NaH (40 mg of 60% mineral oil dispersion) in dry dioxane (10 ml) was refluxed for 20 hr under N₂. The reaction mixture was cooled, poured into NH₄Cl aq. and extracted with ether. The extract was washed with brine, dried over MgSO₄ and concentrated. The residue on SiO₂ chromatography (10 g) eluted with *n*-hexane-EtOAc (9:1) gave the recovered **26a** (44 mg, 22%) and **5** (30 mg, 15%).

Methyl dehydrojasmonate (29) from 26b. **26b** (2.0 g) was treated in the same manner as described above (**5** from **26a**, column a) to give the recovered **26b** (590 mg) and **29** (440 mg, 31% based on the recovery of **26b**): IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1735. NMR (CDCl₃) δ : 1.09 (3H, t, $J=7$ Hz), 1.5~2.9 (12H), 3.72 (3H, s). MS m/z : 222 (1%), 193 (27), 133 (16), 122 (100), 107 (52), 91 (30), 79 (30), 41 (31). The physical data of synthetic **29** were identical to those reported.^{3d,h}

Methyl jasmonate (1).

a) A mixture of **29** (100 mg) and Lindlar catalyst (200 mg) in MeOH (2 ml) was stirred at room temperature under 1 atm of H₂. After the H₂-uptake ceased in 2 hr, the mixture was filtered and the filtrate was concentrated. The residue on SiO₂ chromatography (12 g) eluted with *n*-hexane-EtOAc (95:5) gave **1** (93 mg, 93%): IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1735. NMR (CDCl₃) δ : 0.96 (3H, t, $J=7$ Hz), 1.52~2.8 (12H), 3.70 (3H, s), 5.38 (2H, m). MS m/z 224 (20%), 156 (18), 151 (40), 83 (100), 41 (58). These data for synthetic **1** were identical with those of the authentic sample.

b) A mixture of **26b** (7.0 g), quinoline (0.7 g) and Lindlar catalyst (0.7 g) in MeOH (100 ml) was stirred at room temperature under 5 kg/cm² of H₂ in an autoclave. Hydrogen-uptake ceased in about 1 hr and the mixture was filtered, concentrated and diluted with ether. The ethereal solution was washed with dil HCl aq., NaHCO₃ aq. and brine, dried over MgSO₄ and concentrated. The residue was distilled to give **1** (6.7 g, 95%). bp 110~113°C/1 mmHg.

cis- and trans-Methyl 4-(2-methoxycarbonyl-1-cyclo-

propyl)-3-oxobutanoate (**21a, b**). To a solution of the dianion of methyl acetoacetate (1.5 g) in THF, prepared as reported,⁶⁾ was added dropwise a solution of methyl γ -bromocrotonate (2.3 g) in dry THF (20 ml) over 10 min at 0°C under N₂ and the mixture was stirred for further 5 min at 0°C. The reaction mixture was poured into NH₄Cl aq. and extracted with ether. The extract was washed with brine, dried over MgSO₄ and concentrated. The residue on SiO₂ chromatography (100 g) eluted with *n*-hexane–EtOAc (3:1) gave *cis*-isomer (**21b**, 0.52 g, 19%) and *trans*-isomer (**21a**, 1.58 g, 57%).

21b: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 3010, 1740, 1720. NMR (CDCl₃) δ : 0.80~2.00 (4H, m), 2.92 (2H, d, *J*=7 Hz), 3.47 (2H, s), 3.70 (3H, s), 3.75 (3H, s).

21a: IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 3020, 1745, 1720. NMR (CDCl₃) δ : 0.65~1.80 (4H, m), 2.60 (2H, d, *J*=7 Hz), 3.49 (2H, s), 3.70 (3H, s), 3.75 (3H, s).

Dimethyl 2-(2-pentynyl)-3-oxoglutarate (31c). A mixture of dimethyl 3-oxoglutarate (3.8 g), 2-pentynyl bromide (3.5 g) and LiOH (0.8 g) in MeOH (50 ml) was refluxed for 20 hr under N₂. The mixture was cooled, poured into NH₄Cl aq. and extracted with ether. The extract was washed with brine, dried over MgSO₄ and concentrated. The residue was distilled to give **31c** (3.8 g, 72%): bp 127~132°C/1 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1740, 1720. NMR (CDCl₃) δ : 1.05 (3H, t, *J*=7 Hz), 2.11 (2H, t-q, *J*=2, 7 Hz), 2.68 (2H, t-d, *J*=2, 7 Hz), 3.65 (2H, s), 3.74 (6H, s), 3.90 (1H, t, *J*=7 Hz).

4-Ethoxycarbonyl-3-oxo-2-pentyl-6-octenedioic acid 1-ethyl, 8-methyl ester (32a). To a stirred suspension of NaH (4.8 g of 60% mineral oil dispersion) in dry THF (250 ml) was added dropwise a solution of diethyl 3-oxo-2-pentylglutarate (**31a**, 21.8 g) in dry THF (50 ml) over 30 min at 0°C and the mixture stirred for 20 min at room temperature. To this was added dropwise a solution of methyl γ -bromocrotonate (17.2 g) in dry THF (50 ml) over 30 min at 0°C under N₂. After stirring for a further 20 hr at room temperature, the reaction mixture was poured into NH₄Cl aq. and extracted with ether. The extract was washed with brine, dried over MgSO₄ and concentrated. The residue was distilled to give the recovered **31a** (3.4 g) and **32a** (20.1 g, 80% based on the recovery of **31a**): bp 160~166°C/1 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1730, 1660. NMR (CCl₄) δ : 0.88 (3H, t, *J*=7 Hz), 1.25 (6H, t, *J*=7 Hz), 1.2~2.0 (8H), 2.63 (2H, t, *J*=7 Hz), 3.52 (1H, t, *J*=7 Hz), 3.60 (3H, s), 3.71 (1H, t, *J*=7 Hz), 4.10 (4H, q, *J*=7 Hz), 5.73 (1H, t-d, *J*=2, 16 Hz), 6.68 (1H, t-d, *J*=7, 16 Hz).

4-Ethoxycarbonyl-3-oxo-2-(2-pentynyl)-6-octenedioic acid 1-ethyl, 8-methyl ester (32b). In the same manner, diethyl 3-oxo-2-(2-pentynyl) glutarate (**31b**, 26.8 g) was treated with methyl γ -bromocrotonate (21.6 g) in the presence of NaH (6.0 g of 60% mineral oil dispersion) at room temperature for 20 hr. After the same work-up, the residue on SiO₂ chromatography (1 kg) eluted with *n*-hexane–EtOAc (6:1) gave the recovered **31b** (4.2 g) and **32b**

(28.2 g, 91% based on the recovery of **31b**): IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1730, 1660. NMR (CCl₄) δ : 1.08 (3H, t, *J*=7 Hz), 1.26 (6H, t, *J*=7 Hz), 1.8~2.9 (6H), 3.65 (3H, s), 3.73 (1H, t, *J*=7 Hz), 3.94 (1H, t, *J*=7 Hz), 4.16 (4H, q, *J*=7 Hz), 5.79 (1H, t-d, *J*=2, 16 Hz), 6.72 (1H, t-d, *J*=7, 16 Hz).

2,5-Diethoxycarbonyl-3-methoxycarbonylmethyl-2-pentylcyclopentanone (33a).

a) *From 32a*. A mixture of **32a** (14.8 g) and NaH (1.6 g of 60% mineral oil dispersion) in dry benzene (150 ml) was refluxed for 20 hr under N₂. The reaction mixture was cooled, washed with NH₄Cl aq. and brine, dried over MgSO₄ and concentrated. The residue was distilled to give **33a** (10.8 g, 73%): bp 149~154°C/1 mmHg. IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1740. NMR (CCl₄) δ : 0.88 (3H, t, *J*=7 Hz), 1.26 (6H, t, *J*=7 Hz), 1.1~2.7 (13H), 3.60 (3H, s), 3.68 (1H, t, *J*=7 Hz), 4.12 (4H, q, *J*=7 Hz).

b) *One-pot reaction from 31a*. To a stirred suspension of NaH (2.0 g of 60% mineral oil dispersion) in dry benzene (100 ml) was added dropwise a solution of **31a** (5.44 g) in dry benzene (20 ml) over 30 min at 0°C and the mixture was stirred for 30 min at room temperature. To this was added dropwise a solution of methyl γ -bromocrotonate (5.37 g) in dry benzene (20 ml) over 30 min at 0°C under N₂ and stirring was continued for 20 hr at room temperature and then for 20 hr at reflux. The reaction mixture was cooled, washed with NH₄Cl aq. and brine, dried over MgSO₄ and concentrated. The residue was distilled to give **33a** (4.58 g, 62%).

2,5-Diethoxycarbonyl-3-methoxycarbonylmethyl-2-(2-pentynyl) cyclopentanone (33b).

a) *From 32b*. In the same manner as above, **32b** (18.3 g) was treated with NaH (2.0 g) in dry benzene (200 ml) under reflux for 20 hr. After the same work-up, the residue on SiO₂ chromatography (500 g) eluted with *n*-hexane–EtOAc (6:1) gave **33b** (12.4 g, 68%): IR $\nu_{\text{max}}^{\text{film}}$ cm⁻¹: 1740. NMR (CCl₄) δ : 1.07 (3H, t, *J*=7 Hz), 1.24 and 1.28 (6H, t, *J*=7 Hz), 1.8~2.9 (9H), 3.61 and 3.68 (3H, s), 3.70 (1H, t, *J*=7 Hz), 4.07 (3H, q, *J*=7 Hz).

b) *One-pot reaction from 31b*. In the same manner as above, a suspension of **31b** (5.36 g) in dry benzene (150 ml) containing NaH (2.0 g) was treated with methyl γ -bromocrotonate (5.37 g) for 20 hr at room temperature and then for 20 hr at reflux. After the same work-up, the residue on SiO₂ chromatography (300 g) eluted with *n*-hexane–EtOAc (6:1) gave **33b** (4.66 g, 63%).

Methyl dihydrojasmonate (5) from 33a. A mixture of **33a** (9.0 g) and 6 N HCl aq. (30 ml) in MeOH (60 ml) was refluxed for 20 hr. The mixture was cooled, diluted with water and extracted with ether. The extract was washed with NaHCO₃ aq. and brine, dried over MgSO₄ and concentrated. The residue was distilled to give **5** (3.6 g, 66%): bp 106~108°C/1 mmHg.

Methyl dehydrojasmonate (29) from 33b. In the same

manner, **33b** (9.0 g) was treated with 6 N HCl aq. (30 ml) in MeOH (60 ml) under reflux for 20 hr. After the same work-up, the residue was distilled to give **29** (3.8 g, 70%): bp 118~120°C/1 mmHg.

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