Electrolytic Decarboxylation Reactions. II. Syntheses of Methyl Dihydrojasmonate and Methyl *dl*-Jasmonate from 3-Methoxycarbonyl-2-carboxynorbornane via Anodic Acetoxylation

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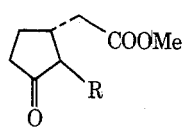
Methyl dihydrojasmonate (**1a**) and methyl *dl*-jasmonate (**1b**) were prepared from 3-methoxycarbonyl-2-carboxynorbornane (**2a**) via anodic acetoxylation. Electrolysis of **2a** in a mixed solvent of AcOH–*t*-BuOH–Et_3N gave a desired key intermediate, *exo*-2-acetoxy-*anti*-7-methoxycarbonylnorbornane (**3**), in 56% yield (GLC peak area) together with several minor products, **4** (12%), **5** (7%), **6** (11%), and **7** (4%). Hydrolysis of **3** followed by oxidation with chromic acid afforded 7-methoxycarbonyl-2-norbornanone (**9**) in good yield. The Baeyer–Villiger oxidation of **9** and subsequent hydrolysis and oxidation gave 2-methoxycarbonyl-3-methoxycarbonylmethylcyclopentanone (**12**) in 54% yield. Alkylation of **12** with pentyl and 2-pentynyl bromide and following cis hydrogenation and demethoxycarbonylation afforded **1a** and **1b**, efficiently.

In the preceding paper we reported the product-selective and chemically controlled electrolytic decarboxylation reaction involving the formation of either radical or carbonium ion intermediate.[1] We have now extended this electrochemical decarboxylation method to a novel acetoxylation reaction for the preparation of *exo*-2-acetoxy-*anti*-7-methoxycarbonylnorbornane (**3**), which is expected to be an intermediate for the methyl *dl*-jasmonate synthesis.[2]

Although electrolysis of *exo*- and *endo*-norbornane-2-carboxylic acid in Et_3N–MeOH has been shown to afford *exo*-2-methoxynorbornane in a sufficient yield via a carbonium intermediate,[3] instead of alkoxides acetoxy derivatives have been generally considered to be more useful intermediates for synthetic purposes. Indeed, one of the precursors for the preparation of methyl *dl*-jasmonate (**1b**) must be the acetoxy compound **3**, which may be derived from 2-methoxycarbonyl-3-carboxynorbornane (**2a**)[4] by electrolytic acetoxylation.

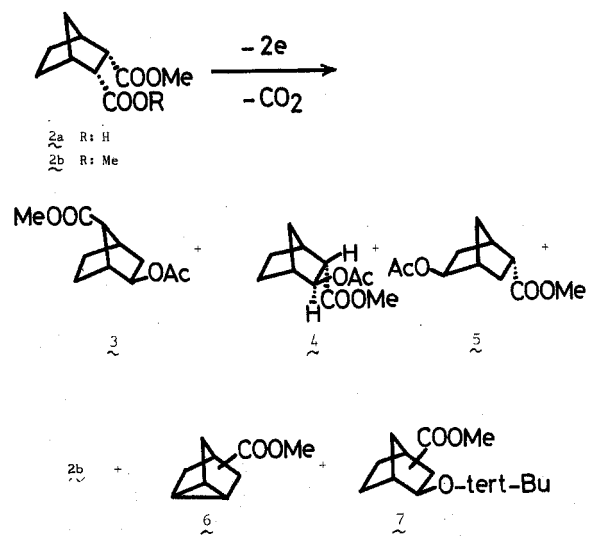


1a, R = *n*-C_5H_{11}
b, R = $CH_2CH{=}CHEt$-*cis*
c, R = $CH_2C{\equiv}CEt$

Results and Discussion

Electrolysis of the half-acid **2a** to the desired acetate **3** was carried out in a mixed solvent of AcOH–*t*-BuOH (2:1) using triethylamine as a supporting electrolyte on carbon rod electrodes (Table I, run 4). As shown in Scheme I, the electrolysis afforded **3** as a major product (56% yield based on GLC peak area) along with several minor products, **4**, **5**, **6**, and **7** (Table II). The structures of the products isolated by preparative GLC were elucidated by NMR, infrared, and mass spectral analyses together with elemental analysis.

Scheme I



The acetates **3**, **4**, and **5** (75% yield based on the neutral portion of the electrolysis product) isolated by column chromatography over silica gel from the reaction mixture were subjected to the ester exchange reaction[5] by stirring in dry methanol in the presence of sodium methoxide. The alcohol **8** (90% yield) isolated by column chromatography was homogeneous on GLC (3 m × 4 mm, SE-30 10% coated

Table I
Electrolytic Conditions and Results

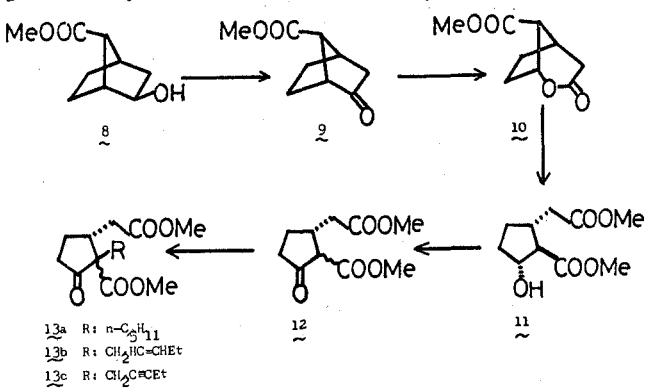
Run	Substrate 2a, g	Solvent (ml)	Supporting electrolyte (g)	Current, A	Applied voltage, V	Temp, °C	Time, hr	Product: Acetates (MeO), mg	Product: Others	Product: Recovered 2a, mg
1	0.5	MeOH (30)	Et_3N (0.7)	0.5	20	30	6	(378)	66.2	10
2	1.0	AcOH (30)	AcONa (1.0)	0.14	50	32	20	286	143	300
3	1.0	AcOH (30)	Et_3N (0.7)	0.27	35	34	20	295	210	230
4	1.0	AcOH–*t*-BuOH (20) (10)	Et_3N (0.7)	0.18	35	30	20	353	117	340

Table II
Electrolytic Products (Table I, Run 4) from 2a

Products	6	7	4	3	5	Unknown	2b
Retention time,[a] min	4.4	9.4	23	26	28	30	31
Peak area, %	11	4	12	56	7	2	8

[a] GLC column, 3 m × 4 mm, 10% polyneopentyl glycol succinate coated on 80–100 mesh Chromosorb W, at 180°, carrier gas H_2, 30 ml/min.

column); however, the GLC analysis of the acetate regenerated from the alcohol still exhibited the presence of the minor peaks due to **4** and **5**. Without further purification the alcohols were oxidized with the Jones reagent[6] to the corresponding ketone in 90% yield. The difficulty was encountered in obtaining pure ketone **9** by simple column chromatography. By the above operation only the keto ester obtained from **4** could be stripped. The preparative route leading to methyl *dl*-jasmonate (**1b**) from **8** is shown in Scheme II. Thus, the ketone **9** contaminated with a small amount of the isomer derived from **5** was treated with monoperphthalic acid for 2 days at 17°. The reaction mixture was worked up in the usual manner and the product exhibited two spots on TLC, and was chromatographed over silica gel to give the pure Baeyer–Villiger product **10** in 71% yield. The ir, NMR, and mass spectral data fully support the structure **10**. Successful hydrolysis of **10** and following esterification with diazomethane afforded alcohol ester **11** in 92% yield. Further, the Jones oxidation of **11** gave the key intermediate **12**[7] in 82.6% yield.



Alkylation of the β-keto ester **12** with 2-pentynyl bromide using potassium *tert*-butoxide in dry dimethyl sulfoxide gave the corresponding C-alkylation product **13c** in 75% yield. In contrast, the reaction of **12** with *n*-pentyl bromide in the same base and solvent gave 39.5% of **13a** along with 17% of O-alkylation product. Cis hydrogenation of **13c** with Lindlar catalyst[8] gave **13b** in quantitative yield.

Recently, Krapcho and Lovey[9] have shown an efficient demethoxycarbonylation method of β-keto esters by heating in wet dimethyl sulfoxide containing sodium chloride. Thus, demethoxycarbonylation of **13b** with the solvent in a sealed tube at 180° for 3–4 hr yielded methyl *dl*-jasmonate (**1b**) in 56% yield. In a similar fashion, demethoxycarbonylation of **13c** and following hydrogenation could also lead to **1b** in 77.4% yield. Methyl dihydrojasmonate (**1a**) could be obtained in 70% yield from **13a**.

Electrolysis of 2a. Linstead[10] explored the electrolytic acetoxylation of diphenylacetic acid in AcOH–AcONa using platinum electrodes, giving the corresponding acetate in ca. 73% yield. On the other hand, electrolytic methoxylation of diphenylacetic acid in Et_3N–MeOH affords diphenylmethoxymethane in 80% yield.[11] These results demonstrate that attack of both nucleophiles to diphenylmethyl

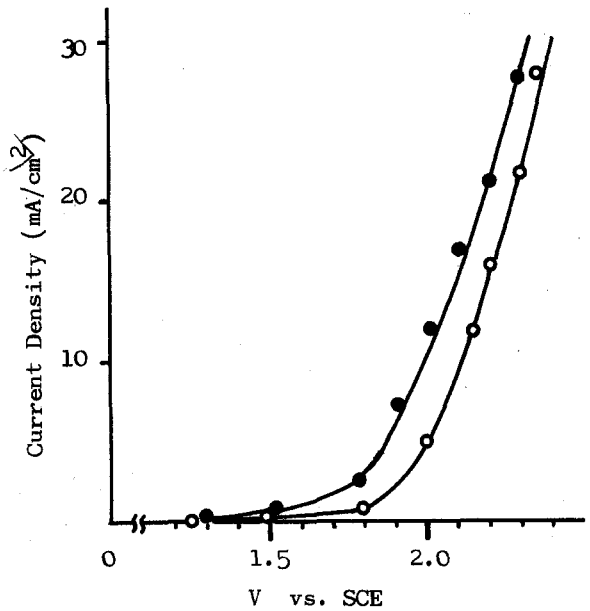


Figure 1. Current–potential curve of 2-carboxy-3-methoxycarbonylnorbornane (**2a**): ○, AcOH–*t*-BuOH–Et_3N (20:10:0.7) system; ●, AcOH–*t*-BuOH–Et_3N (20:10:0.7)–**2a** (0.6 *M*) system.

cation in the electrolytic solutions can proceed smoothly. The nucleophilic substitution of methanol, however, to *N*-acylaminomethyl cations derived from the electrolysis of *N*-acylaminoacetic acids has been shown to occur giving *N*-methoxymethylacylamides in 74–91% yields as compared with the reaction with acetic acid giving the corresponding acetate in ca. 38% yield.[12] These results are remarkable considering the problems involved in the electrolytic acetoxylation of complex carboxylic acids.

As shown in Table I, we examined the anodic acetoxylation of **2a** under several conditions (runs 1–4). Both routine electrolytic conditions (runs 1 and 2) provided the desired products in sufficient yield; however, the formation of acid anhydride[13] from **2a** (run 2) in addition to the low current efficiency prompted us to change the choice of the electrolytic solvent. In run 3, the improvement of the yield could be achieved but we experienced ease in producing the acid anhydride. However, the mixed solvent of AcOH–*t*-BuOH–Et_3N (run 4) afforded the more favorable result considering suppression of the formation of by-products, increase of the current efficiency, and facile isolation of the acetates.

The electrolysis of **2a** in run 4 (Table I) was carried out at the terminal voltage of ca. 35 V (cell voltages 2.2–2.3 V vs. SCE) under a constant current of ca. 0.18 A. The current–potential curve of the electrolysis of **2a** in AcOH–*t*-BuOH–Et_3N using platinum electrodes is shown in Figure 1, indicating that in this condition discharges of both **2a** and acetate anion occur competitively and the condition gives rise to the oxidation of **2a** favorably.

The analytical result of the product obtained in run 4 on GLC (Table II) indicates the presence of 75% of the acetates **3**, **4**, and **5** in the neutral portion. The product ratio of **3**, **4**, and **5** is well in accordance with the results from the solvolytic investigations on various norbornanes,[14] suggesting that the electrolytic reaction of **2a** would also proceed via nonclassical norbornyl cation.

Experimental Section

Melting points and boiling points are uncorrected. NMR spectra were determined with a Hitachi R-24 instrument. Ir spectra were recorded on a Hitachi EPI-S2, with only major absorptions being

cited. Mass spectral analyses were carried out with a Hitachi RMS-4 mass spectrometer at 70 eV, with molecular and major fragment ions being cited. Elemental analyses were performed by Mr. Tsutomu Okamoto of our Laboratory.

Electrolysis Apparatus. The electrolysis cell was a water-jacketed beaker, 3.5 cm in diameter and 10 cm high, fitted a gas-lead pipe, a thermometer, a magnetic stirrer, and two carbon rods (10 mm in diameter and 10 cm long) being placed parallel to each other 3 mm apart. Current was controlled by manually adjusting the applied voltage as required. The direction of current was changed every 30 sec by means of a commutator.

Electrolysis of 2-Carboxy-3-methoxycarbonylnorbornane (2a). The half-acid **2a**[4] (1 g, 5.05 mmol) was dissolved in a mixed solution of AcOH (20 ml), *t*-BuOH (10 ml), and Et_3N (700 mg). The mixture was electrolyzed at a constant current of 0.18 A (applied voltage ca. 35 V) at 30° for 20 hr. The solvent was rotoevaporated and the residue was taken up in benzene–ether (1:1). The organic layer was washed with water and saturated Na_2CO_3 and dried (Na_2SO_4). The starting material **2a** (340 mg) was recovered from the alkaline solution. The organic layer was concentrated to give a neutral oil (470 mg). The result from GLC analysis of the oil is shown in Table II. The components were separated by preparative GLC and the analytical results are as follows. *exo*-2-Acetoxy-*anti*-7-methoxycarbonylnorbornane (**3**): bp 62.0–63.0° (0.005 mm); ir 1739 and 1733 cm^{-1}; NMR ($CDCl_3$) δ 1.04–1.90 (m, 6 H), 2.00 (s, 3 H, CH_3CO), 2.54 (m, 2 H, bridgehead protons), 2.76 (s, 1 H, CHCO), 3.66 (s, 3 H, CH_3O), and 4.59 (double doublet, 1 H, CHO); mass spectrum *m/e* (rel intensity) 181 ($M^+ - CH_3O$, 13), 170 (14), 169 ($M^+ - CH_3CO$, 14), 153 (10), 152 (77), 142 (28), 138 (25), 137 (19), 124 (31), 121 (17), 110 (30), 109 (21), 100 (25), 93 (43), 92 (23), 87 (26), 81 (34), 74 (20), 67 (57), 66 (55), and 43 (100).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.27; H, 7.43.

exo-2-Acetoxy-*endo*-3-methoxycarbonylnorbornane (**4**): bp 62.0–63.0° (0.005 mm); ir (neat) 1738 and 1733 cm^{-1}; NMR ($CDCl_3$) δ 1.00–1.90 (m, 6 H), 2.00 (s, 3 H, CH_3CO), 2.37 (broad s, 1 H), 2.64 (broad s, 2 H), 3.70 (s, 3 H, CH_3O), and 4.88 (m, 1 H, CHO); mass spectrum *m/e* (rel intensity) 170 (24), 169 ($M^+ - CH_3CO$, 50), 153 (7), 152 (41), 143 (9), 142 (99), 138 (12), 137 (29), 124 (33), 121 (48), 110 (29), 109 (18), 103 (22), 100 (21), 93 (43), 87 (45), 82 (18), 81 (31), 79 (21), 77 (16), 74 (22), 68 (19), 67 (73), 66 (81), 65 (20), 59 (24), 55 (23), 53 (24), and 43 (100).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.43; H, 7.80.

exo-2-Acetoxy-*endo*-5-methoxycarbonylnorbornane (**5**): bp 62.0–63.0° (0.005 mm); ir (neat) 1744 and 1730 cm^{-1}; NMR ($CDCl_3$) δ 1.00–1.90 (m, 6 H), 1.92 (s, 3 H, CH_3CO), 2.44 (s, 1 H, CHCO), 2.67 (m, 2 H, bridgehead protons), 3.66 (s, 3 H, CH_3O), and 4.65 (double doublet, 1 H, CHO); mass spectrum *m/e* (rel intensity) 170 (69), 169 ($M^+ - CH_3CO$, 23), 153 (8), 152 (33), 142 (8), 141 (14), 139 (47), 138 (39), 137 (15), 127 (34), 126 (11), 111 (12), 110 (44), 109 (26), 100 (44), 93 (32), 92 (33), 91 (53), 87 (23), 81 (37), 79 (27), 67 (67), 66 (62), 59 (23), and 43 (100).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.06; H, 7.59.

Methoxycarbonyltricyclo[2.2.1.$0^{2,6}$]heptane (**6**): ir (neat) 1735 cm^{-1}; NMR ($CDCl_3$) δ 1.10–1.55 (m, 6 H), 1.60 (m, 1 H), 2.25 (m, 1 H), 2.45 (m, 1 H, CHCO), and 3.65 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 152 (M^+, 5.7), 151 (64), 137 (11), 121 (17), 120 (22), 119 (13), 111 (22), 98 (17), 93 (100), 92 (70), and 91 (94).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 70.92; H, 7.97.

exo-2-*tert*-Butoxymethoxycarbonylnorbornane (**7**): ir (neat) 1734 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (s, 9 H, 3 CH_3), 1.21–1.91 (m, 5 H), 2.37 (m, 3 H), 2.80 (m, 1 H), 3.53 (q, 1 H, CHO), and 3.65 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 226 (M^+, 0.3), 195 (17), 171 (21), 170 (100), 152 (25), 151 (26), 142 (23), 141 (22), 139 (61), 138 (86), 127 (85), 110 (83), 100 (63), 93 (44), 92 (30), 91 (42), 90 (29), 87 (62), 81 (45), 67 (62), 66 (65), and 57 (93).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.93; H, 9.84.

cis-1,2-Dimethoxycarbonylnorbornane (**2b**), bp 153–155° (14.5 mm) [lit.[15] bp 152° (14 mm)], spectral data identical with those of an authentic sample.

The neutral oil (470 mg) obtained by the above work-up was chromatographed over silica gel using hexane–THF (15:1) and two fractions were collected. The first fraction gave an oil (117 mg) containing the compounds **6** and **7**. From the following fraction 353 mg of the acetates **3**, **4**, and **5** were obtained.

Ester Exchange Reaction of the Acetates 3, 4, and 5. Sodium metal (300 mg, 1.3 mg-atoms) was allowed to react with dry MeOH (6 ml) and cooled to 10°. To this solution the second elution (353 mg) obtained by the above chromatography dissolved in dry MeOH (0.5 ml) was added dropwise. The mixture was stirred for 12 hr at room temperature under nitrogen, quenched with ice–water (5–8 ml), extracted with $CHCl_3$, and dried (Na_2SO_4). The solvent was removed and the residue (280 mg) was carefully chromatographed over silica gel. Hexane–THF (10:1) elution gave 254 mg (90%) of the alcohol **8** containing a small amount of isomeric alcohols derived from **4** and **5**: bp 78.0–80.0° (0.01 mm); ir (neat) 3410 (broad, OH) and 1735 cm^{-1}; NMR ($CDCl_3$) δ 0.93–1.93 (m, 6 H), 2.49 (m, 2 H), 2.82 (broad, 1 H), 3.06 (broad, 1 H, OH), 3.62 (s, 3 H, CH_3O), and 3.68 (m, 1 H, HCO); mass spectrum *m/e* (rel intensity) 170 (M^+, 2), 153 (8), 152 (78), 151 (18), 142 (12), 141 (25), 139 (75), 138 (86), 127 (72), 124 (36), 120 (30), 111 (43), 110 (96), 109 (37), 100 (71), 97 (67), 95 (45), 93 (87), 92 (54), 91 (40), 87 (45), 81 (87), 79 (46), 77 (42), 74 (53), 69 (51), 68 (52), 67 (100), 66 (90), and 55 (68).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.31; H, 8.36.

7-Methoxycarbonyl-2-norbornanone (9). The alcohol **8** (120 mg, 0.706 mmol) contaminated with the isomeric alcohols derived from **4** and **5** was dissolved in CH_2Cl_2 (5 ml) and cooled to 0–4° in an ice bath. The Jones reagent (2.1 ml) prepared by dissolving $Na_2Cr_2O_7 \cdot 2H_2O$ (1 g, 3.3 mmol) in water (3 ml) and 97% of H_2SO_4 (1.36 g, 1.34 mmol), was added dropwise with vigorous stirring for 15 min and continued cooling and stirring for an additional 15 min. The ice bath was removed and the mixture was stirred for 3 hr at room temperature. The CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated. The residue was chromatographed over silica gel using hexane–THF (6:1) to give **9** (107 mg, 90%) containing a small amount of isomeric ketones derived from **4** and **5**: bp 52.0–53.0° (0.01 mm); ir (neat) 1752 and 1741 cm^{-1} (ester and ketone carbonyls); NMR ($CDCl_3$) δ 1.23–2.23 (m, 6 H), 2.73 (broad s, 2 H), 2.82 (broad s, 1 H), and 3.66 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 168 (M^+, 19), 152 (4), 140 (50), 137 (28), 136 (16), 121 (17), 108 (80), 81 (96), 80 (60), 79 (61), 74 (76), 67 (100), and 66 (59).

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.57; H, 6.89.

8-Methoxycarbonyl-3-oxo-2-oxabicyclo[3.2.1]octane (10). 7-Carbomethoxy-2-norbornanone (**9**, 168 mg, 1 mmol) contaminated with a small amount of the isomeric ketones was dissolved in ether (3 ml) containing monoperphthalic acid[16] (364 mg, 2 mmol) and the mixture was allowed to stand for 2 days at 17°. The mixture was shaken with cooled saturated $NaHCO_3$ solution and dried (Na_2SO_4). The residue from rotoevaporation of the ether layer was extracted several times with hexane and the extracts were concentrated to give 160 mg of crude products. TLC of the residue on silica gel showed [Merck 60 PF_{254}, benzene–EtOAc (5:1)] showed two spots at R_f 0.45 and 0.37 (ca. 4:1). Repeated chromatography of the residue over silica gel using benzene–EtOAc (7:1) gave **10** (130 mg, 70.6%, R_f 0.45): bp 56.0–57.0° (0.015 mm); ir (neat) 1739 and 1724 cm^{-1}; NMR ($CDCl_3$) δ 1.50–2.47 (m, 4 H), 2.47–2.98 (m, 3 H), 3.06 (s, 1 H, CHCO), 3.65 (s, 3 H, CH_3O), and 4.90 (broad s, 1 H, CHO); mass spectrum *m/e* (rel intensity) 184 (M^+, 1), 156 (20), 153 (18), 140 (13), 126 (27), 124 (15), 113 (16), 111 (24), 102 (21), 96 (36), 83 (100), 82 (69), and 81 (64).

Anal. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57. Found: C, 58.70; H, 6.55.

2-Methoxycarbonyl-3-methoxycarbonylmethylcyclopentanol (11). The δ-lactone ester **10** (184 mg, 1 mmol) was dissolved in a solution of KOH (112 mg, 2 mmol) in MeOH (1 ml) containing 3 drops of water. The mixture was stirred for 12 hr at room temperature and then most of the solvent was rotoevaporated. The residue was neutralized with *l*-tartaric acid (83 mg) in MeOH (1.1 ml) and the white precipitate was deposited. The precipitate was filtered off and washed with ether. The combined organic phases were concentrated and the residue was dried azeotropically with benzene (3 ml). The residual oil was extracted several times with ether. The extracts were rotoevaporated and treated with excess diazomethane. Removal of the solvent and following column chromatography over silica gel [benzene–EtOAc (10:1)] gave the alcohol **11** (197 mg, 92%): bp 85–86° (0.02 mm); ir (neat) 3455 (OH), 1745, and 1732 cm^{-1}; NMR ($CDCl_3$) δ 1.39–2.79 (m, 9 H), 3.66 (s, 3 H, CH_3O), 3.71 (s, 3 H, CH_3O), and 4.38 (m, 1 H, HCO); mass spectrum *m/e* (rel intensity) 188 (7), 168 (4), 167 (48), 166 (8), 160 (7),

159 (18), 156 (81), 140 (31), 139 (48), 128 (53), 127 (90), 125 (48), 115 (65), 111 (57), 107 (27), 99 (66), 97 (24), 96 (32), 95 (44), 83 (100), 82 (61), 79 (57), 74 (44), and 59 (58).

Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.71; H, 7.56.

2-Methoxycarbonyl-3-methoxycarbonylmethylcyclopentanone (12). The cyclopentanol 11 (216 mg, 1 mmol) was dissolved in CH_2Cl_2 (5 ml) and cooled to 0–4° (ice bath). The Jones reagent (2.5 ml) was added dropwise with vigorous stirring for 15 min, then additional Jones reagent (2.5 ml) was added at 0–4° and the mixture was stirred at 15° for 3 hr. After work-up in a usual manner, the crude oil was distilled to give **12** (177 mg, 82.6%): bp 85.0° (0.01 mm); ir (neat) 1756, 1744, 1731, 1661, and 1626 cm^{-1}; NMR ($CDCl_3$) δ 1.00–2.73 (m, 7 H), 2.89 (broad s, 1 H, CH), 3.60 (s, 3 H, CH_3O), and 3.68 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 214 (M^+, 2), 182 (36), 154 (78), 141 (100), 127 (82), 109 (99), 99 (81), 95 (56), 83 (97), 82 (78), and 74 (64).

Anal. Calcd for $C_{10}H_{14}O_5$: C, 56.07; H, 6.59. Found: C, 55.78; H, 6.62.

2-Methoxycarbonyl-2-(2′-pentynyl)-3-methoxycarbonylmethylcyclopentanone (13c). To a stirred solution of **12** (50 mg, 0.234 mmol) and *t*-BuOK (26 mg) in dry dimethyl sulfoxide (2 ml) was added 2-pentynyl bromide (34 mg, 0.233 mmol) at room temperature and the stirring was continued overnight. The mixture was poured into ice-cold brine. Extraction with hexane, washing with cold brine, drying (Na_2SO_4), and solvent removal in vacuo gave 60 mg of a crude oil. Column chromatography over silica gel using benzene–EtOAc (15:1) gave 49 mg (75%) of **13c**: bp 78.0–80.0° (0.02 mm); ir (neat) 1755 and 1740 cm^{-1}; NMR ($CDCl_3$) δ 1.08 (t, 3 H, CH_3), 1.53–2.63 (m, 9 H), 2.73 (m, 2 H), 3.68 (s, 3 H, CH_3O), and 3.70 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 263 (10), 248 (16), 221 (34), 220 (50), 192 (23), 180 (50), 175 (35), 161 (37), 152 (41), 147 (66), 139 (30), 138 (33), 133 (34), 119 (41), 110 (41), 105 (49), 93 (43), 91 (67), 81 (42), 79 (49), 77 (54), 67 (100), 66 (62), 65 (40), 59 (80), and 55 (69).

Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.32; H, 6.99.

Similarly, 2-methoxycarbonyl-2-pentyl-3-methoxycarbonylmethylcyclopentanone (**13a**) was obtained in 39.5% yield together with 17% of O-alkylation product **14**: R_f [silica gel, benzene–EtOAc (40:1)] **13a**:**14** 0.58:0.53. The compound **13a** boiled at 77.0–80.0° (0.02 mm): ir (neat) 1756, 1745, and 1733 cm^{-1}; NMR ($CDCl_3$) δ 0.87 (t, 3 H, CH_3), 0.95–3.02 (m, 15 H), 3.68 (s, 3 H, CH_3O), and 3.70 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 284 (M^+, 0.6), 254 (3), 253 (28), 252 (14), 225 (13), 224 (10), 214 (51), 197 (34), 196 (21), 195 (13), 183 (18), 182 (100), 179 (12), 169 (19), 168 (21), 167 (32), 166 (32), 165 (15), 154 (90), 151 (29), 141 (74), 138 (87), 125 (38), 124 (40), 122 (30), 109 (76), 107 (37), 95 (35), 93 (45), 81 (45), and 79 (79).

Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.35; H, 8.53.

2-(2′-Pentynyl)-3-methoxycarbonylmethylcyclopentanone, Methyl *dl*-Dehydrojasmonate (1c). A solution of **13c** (24 mg, 0.086 mmol) and NaCl (10 mg) in a mixed solution of dimethyl sulfoxide (1.5 ml) and water (20 mg) was heated for 3–4 hr at 180° in a sealed tube. After cooling the mixture was poured into ice-cold brine and extracted with hexane. The extracts were washed with brine, dried (Na_2SO_4), and rotoevaporated. Distillation of the residue gave 16.3 mg (86%) of **1c**: bp 102.0–103.0° (3 mm) [lit.[2b] bp 88° (0.001 mm)]; ir (neat) 2230 (C≡C), 1743 (shoulder), 1741, 1441, 1412, 1380, 1340, 1196, 1169, and 986 cm^{-1}; NMR ($CDCl_3$) δ 1.06 (t, J = 7.2 Hz, 3 H, CH_3), 1.44–3.02 (m, 12 H), and 3.70 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 222 (M^+, 0.2), 205 (1), 194 (9), 193 (67), 162 (5), 161 (3), 149 (27), 148 (14), 147 (17), 133 (28), 123 (21), 122 (100), 119 (15), 107 (76), 105 (34), 91 (52), 79 (51), and 77 (31).

Similarly, demethoxycarbonylation of **13a** afforded methyl dihydrojasmonate (**1a**) in 70% yield: bp 92.0–94.0° (3 mm) [lit.[17] bp 133–135° (1 mm)]; ir (neat) 1742 (broad), 1465, 1442, 1381, 1338, 1261, 1197, 1172, 1098, 1013, and 988 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (t, 3 H, CH_3), 1.05–1.90 (m, 11 H), 2.00–2.80 (m, 5 H), and 3.70 (s, 3 H, CH_3O); mass spectrum *m/e* (rel intensity) 226 (M^+, 2), 196 (2), 156 (33), 153 (32), 149 (5), 109 (4), 97 (8), 96 (11), 95 (7), 84 (8), 83 (100), 82 (36), and 55 (25).

Methyl *dl*-Jasmonate (1b) from 1c. A mixture of Lindlar catalyst (222 mg) and methyl *dl*-dehydrojasmonate (**1c**, 22 mg, 0.1 mmol) in hexane (1 ml) was stirred under 1 atm of hydrogen. After 20 min hydrogen uptake stopped and the mixture was filtered free of catalyst and concentrated to yield 20 mg (90%) of methyl *dl*-jasmonate (**1b**): bp 110.0–112.0° (5 mm) [lit.[2b] bp 81–84° (0.001 mm)]; ir (neat) 1742, 1462, 1440, 1412, 1379, 1339, 1262, 1197, 1164, 1095, 1072, 1018, 982, and 795 cm^{-1}; NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH_3), 1.40–2.90 (m, 12 H, CH_2), 3.68 (s, 3 H, CH_3O), and 5.35 (m, 2 H, HC=C); mass spectrum *m/e* (rel intensity) 224 (M^+, 23), 206 (1), 195 (1), 193 (7), 177 (2), 156 (16), 151 (42), 150 (7), 149 (20), 135 (9), 133 (8), 121 (8), 109 (24), 95 (30), 93 (17), 91 (13), 83 (100), 82 (25), 79 (25), 67 (30), and 55 (30).

Similarly, hydrogenation of **13c** gave 2-methoxycarbonyl-2-(*cis*-2′-pentenyl)-3-methoxycarbonylmethylcyclopentanone (**13b**) in 91.2% yield: bp 84.0–85.0° (0.015 mm); ir 3020, 1752 (shoulder), 1740, 1442, 1227, and 1175 cm^{-1}; NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH_3), 1.65–2.85 (m, 11 H), 3.66 (s, 3 H, CH_3O), and 4.85–5.75 (m, 2 H, HC=C); mass spectrum *m/e* (rel intensity) 282 (M^+, 4), 251 (16), 250 (19), 223 (17), 222 (40), 219 (25), 214 (21), 194 (45), 193 (100), 190 (15), 182 (33), 180 (17), 176 (15), 163 (18), 162 (18), 154 (45), 149 (46), 141 (49), 122 (30), 121 (33), 120 (20), 109 (52), 107 (44), 93 (38), 91 (43), 79 (54), 77 (43), 67 (40), and 55 (63).

Anal. Calcd for $C_{15}H_{22}O_5$: C, 63.81; H, 7.85. Found: C, 63.85; H, 7.84.

Demethoxycarbonylation of **13b** in aqueous dimethyl sulfoxide containing a small amount of NaCl at 180° afforded 56% of methyl *dl*-jasmonate (**1b**), whose spectral data (ir, NMR, and mass spectrum) were identical with those of an authentic sample.

Registry No.—**1a**, 2570-03-8; **1b**, 20073-13-6; **1c**, 29119-47-9; **2a**, 55298-06-1; **2b**, 4098-47-9; **3**, 55254-64-3; **4**, 55254-65-4; **5**, 55254-66-5; **6**, 55254-63-2; **7**, 55254-62-1; **8**, 55254-67-6; **9**, 55254-68-7; **10**, 55254-69-8; **11**, 55254-70-1; **12**, 55254-71-2; **13a**, 55254-72-3; **13b**, 55254-73-4; **13c**, 55254-74-5.

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