A New Synthetic Method for Methyl Dihydrojasmonate from a Butadiene Telomer

Jiro Tsuji,* Kazuyuki Kasuga, and Takashi Takahashi
Tokyo Institute of Technology, Meguro, Tokyo 152
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Ethyl 2-acetyl-4, 9-decadienoate, easily obtained by the palladium catalyzed telomerization of butadiene with ethyl acetoacetate, was selectively hydrogenated to ethyl 2-acetyl-9-decenoate using $RuCl_2(PPh_3)_3$ as a catalyst. Deacetylation, followed by hydrolysis produced 4-decenoic acid, which was converted into acid chloride. The $AlCl_3$-promoted cyclization gave 2-pentyl-2-cyclopentenone, from which methyl dihydrojasmonate was prepared.

Methyl dihydrojasmonate (**7**) is an important fragrant compound. A number of synthetic approaches for this ester have been reported.[1,2] We now wish to report a simple synthetic method for methyl dihydrojasmonate starting from an easily available butadiene telomer, which has functionality suitable for the synthesis of jasmonate. Palladium catalyzed telomerization of butadiene with various nucleophiles affords a variety of interesting telomers,[3] which can be used for syntheses of various natural products. We have already reported the syntheses of queen substance,[4] royal jelly acids,[5,6] civetone,[7] Matsutake alcohol,[8,9] pellitorine,[10] Recifeiolide,[11] and diplodialide[12] from various telomers. Butadiene and ethyl acetoacetate react readily using a palladium catalyst to give ethyl 2-acetyl-4,9-decadienoate (**1**) in a high yield.[13] This compound has the right carbon numbers and suitable functionality for a facile synthesis of 2-pentyl-2-cyclopentenone, an important precursor of dihydrojasmonate. Thus the compound **1** is a good starting compound for dihydrojasmonate.

Results and Discussion

The synthesis of methyl dihydrojasmonate using the butadiene telomer **1** was carried out by the following sequence of reactions.

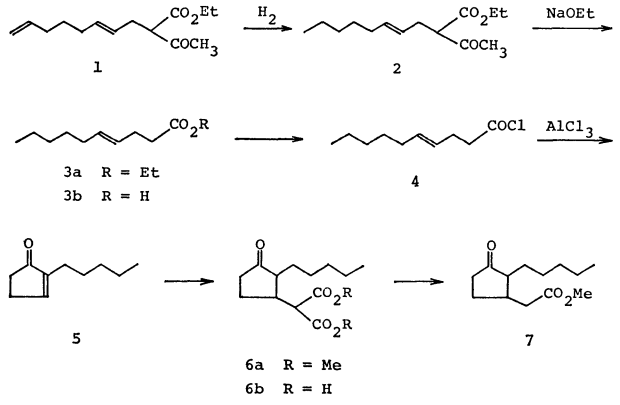

Fig. 1.

Regioselective hydrogenation of the terminal double bond of ethyl 2-acetyl-4,9-decadienoate (**1**) without attacking the internal double bond was achieved easily by homogeneous hydrogenation using $RuCl_2(PPh_3)_3$ as a catalyst under mild conditions.[14] The acetyl group of **2** was removed by the treatment with sodium ethoxide in ethanol to give ethyl 4-decenoate (**3a**) in 83% yield. Then the ester **3a** was hydrolyzed with a base to give 4-decenoic acid (**3b**) in 89% yield. The acid has a double bond at the position suitable for an acid catalyzed intramolecular cyclization to form a cyclopentenone ring. At first, the direct cyclization of the acid **3b** was attempted by using polyphosphoric acid, but the yield of the cyclopentenone was only 20%. In order to carry out the more efficient cyclization, the acid **3b** was converted to the more reactive acid chloride **4**. Then the intramolecular acylation of the double bond was carried out by using $AlCl_3$ in dichloromethane. By this method, the desired 2-pentyl-2-cyclopentenone (**5**) was obtained in 53% yield. The structure of **5** was confirmed by elemental analysis, and mass and NMR spectra. The conversion of **5** to methyl dihydrojasmonate (**7**) is the known reaction.[15] The Michael addition of dimethyl malonate (65.5% yield), followed by hydrolysis produced the diacid **6b**. Decarboxylation and methylation gave methyl dihydrojasmonate (**7**), which was identified by comparing its NMR and IR spectra with those of an authentic sample.

Experimental

NMR spectra were recorded by a Hitachi R-24A spectrometer at 60 MHz. Chemical shifts (δ) are given in ppm relative to an internal standard of TMS. IR spectra were recorded with a JASCO IRA-2 spectrometer. Ethyl 2-acetyl-4,9-decadienoate (**1**) was prepared according to the method of Hata *et al.*[13]

Regioselective Hydrogenation of Ethyl 2-Acetyl-4,9-decadienoate (1). A mixture of **1** (5.55 g, 23.3 mmol) and $RuCl_2(PPh_3)_3$ (87.6 mg, 0.09 mmol) in dry ethanol (15 ml) and dry benzene (15 ml) was pressured to 30 atm with hydrogen in a 100 ml autoclave and stirred at room temperature for 5 h. When the hydrogen pressure decreased to 19 atm, the autoclave was opened and the solvent was evaporated. Distillation of the residue afforded ethyl 2-acetyl-4-decenoate (**2**), bp 105—106 °C/1 Torr; 5.28 g (94% yield): IR (neat) 2920, 1740, 1718 cm^{-1}; NMR (CCl_4) 0.87 (t, J=4.8 Hz, 3H), 1.25 (t, J=7.2 Hz, 3H), 1.04—1.65 (m, 6H), 1.75—2.05 (m, 2H), 2.09 (s, 3H), 2.20—2.55 (m, 2H), 3.27 (t, J=7.2 Hz, 1H), 4.08 (q, J=7.2 Hz, 2H), 5.15—5.45 (m, 2H).

Ethyl 4-Decenoate (3a). Sodium metal (412 mg, 17.9 mmol) was dissolved in dry ethanol (50 ml) to which the ester **2** (8.62 g, 35.9 mmol) was added. The resulting mixture was refluxed for 6 h and neutralized with acetic acid. Ethanol was evaporated, and the residue was extracted

with ether. The extract was washed with brine and dried over sodium sulfate. After removal of ether, distillation of the residue gave **3a**, bp 114 °C/6 Torr; 5.9 g (83% yield): IR (neat) 2920, 1734 cm^{-1}; NMR (CCl_4) 0.87 (t, J=4.8 Hz, 3H) 1.05—1.50 (m, 6H), 1.22 (t, J=7.2 Hz, 3H), 1.55—2.13 (m, 4H), 2.13—2.33 (bs, 2H), 8.02 (q, J=7.2 Hz, 2H), 5.15—5.45 (m, 2H).

*4-Decenoic Acid (**3b**).* An aqueous KOH solution (2.51 g, 44.8 mmol in 20 ml) was added to a solution of **3a** (5.9 g, 29.8 mmol) in methanol (20 ml). The resulting mixture was stirred for 6 h at room temperature. The reaction mixture was washed with hexane and acidified with 6 M HCl. Methanol was evaporated and the aqueous phase was extracted with dichloromethane. The extract was dried over magnesium sulfate. The crude acid **3b** was obtained after evaporation of the solvent (4.1 g, 81% yield): IR (neat) 3000, 2930, 1705 cm^{-1}; NMR (CCl_4) 0.87 (t, J=4.8 Hz, 3H), 1.05—1.53 (m, 6H), 1.53—2.13 (m, 4H), 2.20—2.48 (bs, 2H), 5.24—5.53 (m, 2H), 10.84 (bs, 1H).

*Cyclization of **3b** with Polyphosphoric Acid.* A mixture of the acid **3b** (510 mg, 3 mmol) and polyphosphoric acid (1.6 g) was stirred at 95 °C for 4 h. Crushed ice and water were then added. The mixture was stirred until it became homogeneous and ether extraction was carried out. The extract was washed with saturated $NaHCO_3$ solution and brine, and dried over sodium sulfate. After evaporation of ether, the cyclized product was isolated by column chromatography (silica gel using hexane/ether as an eluent) (95 mg, 21% yield.

*4-Decenoyl Chloride (**4**).* A mixture of acid **3b** (1.5 g, 8.82 mmol) and thionyl chloride (1.26 g, 10.6 mmol) was heated at 60 °C under nitrogen for 5 h. The chloride **4** was obtained by distillation at 62.5 °C/1.5 Torr; (1.52 g, 91% yield): IR (neat) 2940, 1800 cm^{-1}; NMR (CCl_4) 0.88 (t, J=4.8 Hz, 3H), 1.07—1.75 (m, 6H), 1.77—2.65 (m, 4H), 2.74—3.07 (m, 2H), 5.26—5.55 (m, 2H).

*Cyclization of **4** by $AlCl_3$.* A mixture of **4** (600 mg, 3.18 mmol) and $AlCl_3$ (506 mg, 3.81 mmol) in dry dichloromethane (10 ml) was stirred at 0 °C for 2 h. Ice water (20 ml) was added and the aqueous phase was extracted with ether. The extract was washed sequentially with cold saturated $NaHCO_3$ and brine, and dried over sodium sulfate. The pure enone **5** was obtained by column chromatography (silica gel using hexane/ether as an eluent) after removal of ether (255 mg, 53% yield): IR (neat) 2920, 1700, 1630 cm^{-1}; NMR (CCl_4) 0.89 (t, J=4.8 Hz, 3H), 1.08—1.80 (m, 6H), 1.80—2.35 (m, 4H), 2.35—2.70 (m, 2H), 7.04—7.23 (m, 1H). Found: C, 78.56; H, 10.44%. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.59%. MS *m/e* 152 (M^+).

*The Michael Addition of **5**.* Sodium metal (23.5 mg, 1.02 mmol) was dissolved in dry methanol (3 ml) and dimethyl malonate (261 mg, 1.98 mmol) was added under nitrogen at 0 °C. After 15 min, the enone **5** (171 mg, 1.13 mmol) in dry methanol (3 ml) was added dropwise during 15 min at −10 °C. After the addition, the reaction mixture was poured into a cold saturated NH_4Cl and the aqueous phase was extracted with ether. The combined organic layer was washed with brine and dried over magnesium sulfate. The addition product **6a** was isolated by column chromatography (silica gel using hexane/ether as an eluent) (209 mg, 65.5% yield): IR (neat) 2930, 1755, 1735 cm^{-1}; NMR (CCl_4) 0.90 (t, J=4.8 Hz, 3H), 1.05—1.58 (m, 8H), 1.80—2.30 (m, 6H), 3.40 (d, J=7.2 Hz, 1H), 3.71 (s, 6H).

*Methyl Dihydrojasmonate (**7**).* To aqueous NaOH (36.8 mg, 0.92 mmol) in 1 ml was added **6a** (125 mg, 0.44 mmol) in THF (2 ml). The resulting mixture was stirred for 1 h at room temperature. The solution was acidified with sulfuric acid, and refluxed for 3 h. Then, the product was extracted with ether. The extract was dried over sodium sulfate. After evaporation of ether, crude dihydrojasmonic acid was obtained. This crude acid was dissolved in dry methanol (2 ml) and the solution was heated at 40 °C for 3 h in the presence of a catalytic amount of sulfuric acid. Methanol was evaporated and the residue was extracted with ether. The ether extract was washed with cold saturated $NaHCO_3$ and brine, and dried over sodium sulfate. After evaporation of ether, pure methyl dihydrojasmonate **7** was isolated by column chromatography (silica gel using hexane/ether as an eluent) (70 mg, 70% yield): IR (neat) 2940, 1740, 1440, 1170 cm^{-1}; NMR (CCl_4) 0.88 (t, J=4.8 Hz, 3H), 1.07—1.60 (m, 8H), 1.85—2.65 (m, 8H), 3.60 (s, 3H). MS, *m/e* 226 (M^+). The IR and NMR spectra were identical with those of an authentic sample.

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