Experimental Section

Ether Cleavage General Procedure. (a) Homogeneous Conditions. To 12.0 mmol of sodium was added to 1.10 mL (12.0 mmol) of dry hexamethylphosphoramide (HMPA) under argon or nitrogen. After this mixture was stirred at room temperature for 40 min, 5.62 mmol of aromatic ether in 10 mL of solvent (THF or diisopropyl ether) was added. The resulting mixture was maintained at room temperature for 6–24 h and then quenched with methanol or deuterium oxide. After all the unused sodium had reacted, the mixture was poured into 8% hydrochloric acid solution and extracted three times (25 mL each) with ether. The combined ether extract was washed (twice each) with 8% hydrochloric acid, water, and brine and then dried over magnesium sulfate. Analysis of the product mixture was performed by GLC with either a Drexil 300 or Tenax column with the temperature programmed from 80 to 250 °C.

(b) Heterogeneous Conditions. The reactions were run as above except that the HMPA was eliminated; the solvent was refluxed for the times shown in Table I.

Trimethylisopropoxysilane. Trimethylchlorosilane (10.86 g, 0.1 mol) was added dropwise to a solution of 2-propanol (6.0 g, 0.1 mol) in 100 mL of tributylamine. The reaction mixture was refluxed under nitrogen. Distillation gave 9.2 g (0.069 mol) of trimethylisopropoxysilane: bp 87 °C (745 mm); NMR ($CDCl_3$) δ 00.00 (s, 9 H), 1.05 (d, J = 6 Hz, 6 H), 3.86 (heptet, J = 6 Hz, 1 H).

Preparation and Quenching of Phenylsodium. To 0.6–0.8 g of sodium (rinsed with hexane) and 30–50 mL of petroleum ether (bp 38–42 °C, distilled twice from $LiAlH_4$) in a flame-dried flask at room temperature was added 1.5–1.7 g of chlorobenzene (freshly distilled). The flask was immersed in an ultrasonic bath and irradiated at 30–35 °C for up to 10 h. The reaction was either (a) quenched at this time with 10 mL of D_2O, (b) treated with 10 mL of diisopropyl ether, or (c) treated with 10 mL of diisopropyl ether and 2 mL of HMPA. After the latter mixtures (b and c) were stirred for 4–5 h, they were quenched with H_2O (b) or D_2O (c), separated, dried, and analyzed by GC. In all reactions the chlorobenzene had completely reacted. Benzene-*d* analyses determined in duplicate by mass spectroscopy were as follows (a) 16.6 (d_0), 82.1 (d_1), 1.4 (d_2); (b) 21.7 (d_0), 78.2 (d_1), 0.4 (d_2); (c) 91.6 (d_0), 5.5 (d_1), 0.1 (d_2).

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Registry No. PhOPh, 101-84-8; CH_3OPh, 100-66-3; $PhCH_2OPh$, 946-80-5; $PhCH_2OCH_2Ph$, 103-50-4.

An Efficient Synthesis[1] of Methyl *dl-cis*-Jasmonate

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An efficient synthesis of methyl *dl-cis*-jasmonate is described, starting from the previously described 2-(methoxycarbonyl)-3-[(methoxycarbonyl)methyl]cyclopentanone (**3**), itself easily prepared from succinyl chloride and methyl potassium malonate. Alkylation of **3** with 1-bromo-2-pentyne followed by selective removal of the 2-carbomethoxy group gave dehydrojasmonic acid. On esterification and reduction (H_2/Pd/C/pyridine) of the triple bond to the cis olefin, dehydrojasmonic acid afforded methyl *dl-cis*-jasmonate in 40% overall yield from succinyl chloride.

The *l* isomer of methyl *cis*-jasmonate (**1**) is one of the essential components[2] of jasmine oil, is a constituent of the flavor aroma of black tea,[3] and has been identified[4] recently as the senescence-promoting agent of wormwood. Although the synthesis of the racemic form by diverse routes has already been reported,[5] we herein present an approach that is efficient and uncomplicated and that easily allows variations in the α-side chain. Additionally, it is adaptable to large-scale synthesis.

Our route to this compound begins with the cyclopentenone diester[6] **2**, whose synthesis from succinyl chloride and methyl hydrogen malonate via a two-step procedure (68% yield overall) we have reported[7] recently. Catalytic hydrogenation[7,8] of **2** using a palladium-on-charcoal catalyst then gave **3** in quantitative yield. Alkylation of the latter compound with 1-bromo-2-pentyne using phase-transfer catalysis[9] afforded the desired product **4**, but the yield was only 75%, and much better results (90%) were obtained when the alkylation was carried out on the anion of **3** pregenerated by means of sodium hydride in benzene–dimethylformamide. The material from the latter reaction crystallized completely on standing and proved to be a single isomer requiring no further purification. Inspection of a molecular model shows that the

(1) Johnson, F.; Favara, D.; Paul, K. G. German Patent 2 508 295.
(2) Demole, E.; Lederer, E.; Mercier, D. *Helv. Chim. Acta* **1962**, *45*, 675, 685.
(3) Yamanishi, T.; Kawatsu, M.; Yokoyama, T.; Nakatani, Y. *Agric. Biol. Chem.* **1973**, *37*, 1075.
(4) Ueda, J.; Kato, J. *Plant Physiol.* **1980**, *66*, 246.
(5) For a review of the synthesis of jasminoid substances, see Ho, Tse-Lok *Synth. Commun.* **1974**, *4*, 265. For more recent work, see the following: Tanaka, H.; Torri, S. *J. Org. Chem.* **1975**, *40*, 462. Torii, S.; Tanaka, H.; Mandai, T. *Ibid.* **1975**, *40*, 2221. Greene, A. E.; Crabbe, P. *Tetrahedron Lett.* **1976**, 4867. Torii, S.; Tanaka, H.; Kobayashi, Y. *J. Org. Chem.* **1977**, *42*, 3473. Dubs, P.; Stuessi, R. *Helv. Chim. Acta* **1978**, *61*, 990, 998. Kondo, K.; Takahatake, Y.; Sugimoto, K.; Tunemoto, D. *Tetrahedron Lett.* **1978**, 907. Gerlach, H.; Kuenzler, P. *Helv. Chim. Acta* **1978**, *61*, 2503. Naf, F.; Decorzant, R. *Helv. Chim. Acta* **1978**, *61*, 2524. Matsui, M.; Kitahara, T.; Takagi, K. *Jpn. Kokai Tokkyo Koho 79*, 117 423; Matsuda, I.; Murata, S.; Isumi, Y. *J. Org. Chem.* **1980**, *45*, 237. Naoshima, Y.; Nishimoto, K.; Wakabayashi, S.; Hayashi, S. *Agric. Biol. Chem.* **1980**, *44*, 637. *Jpn. Kokai Tokkyo Koho 80*, 124 738.
(6) This compound was first synthesized by R. Wilstätter and A. Pfannenstiehl (*Justus Liebigs Ann. Chem.* **1920**, *422*, 1) by electrolysis of ethyl potassium acetone-1,3-dicarboxylate followed by base-catalyzed cyclization of the resulting diethyl 3,6-dioxosuberate. However, the electrolytic coupling proceeds in only 12% yield, making this route to **2** uneconomical.
(7) Johnson, F.; Paul, K. G.; Favara, D.; Ciabatti, R.; Guzzi, U. *J. Am. Chem. Soc.* **1982**, *104*, 2190.
(8) This reduction may also be accomplished with zinc dust in acetic acid, but the yield is only 80%.
(9) Brändstrom, A. *Acta Chem. Scand.* **1969**, *23*, 2204.

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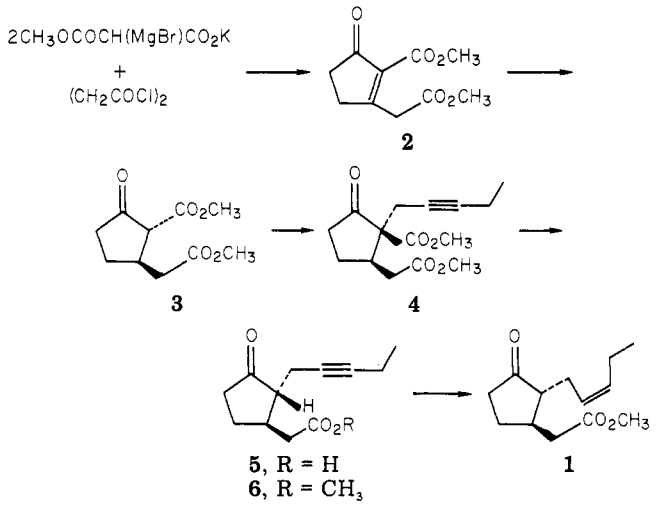

3-substituent of the enolate of **3** would inhibit attack on the β face. Thus it seems likely that in **4** the substituents have the stereorelationships depicted.

Attempts to remove the α-methoxycarbonyl group of **4** under a variety of standard acid conditions did not lead to any of the desired dehydrojasmonic acid (**5**) or its methyl ester **6**, even although the evolution of carbon dioxide was evident. Nevertheless, the desired decarbomethoxylation of **4** could be accomplished[10] cleanly by lithium iodide dihydrate in boiling *s*-collidine, and dehydrojasmonic acid (**5**) was obtained in 71% yield together with a 10% recovery of starting material. The fact that no monodemethylated products could be detected (NMR) in this somewhat incomplete reaction suggests that the initial carboxylate ion that is formed assists in the demethoxylation of the second carboxylic ester group. This likely occurs via a six-membered-ring anhydride.

The remainder of the synthesis proved trivial. Conversion of **5** to its methyl ester **6** was carried out by use of the alkylation method of Alvarez,[11] namely, methyl iodide in *N,N*-dimethylacetamide in the presence of sodium bicarbonate. Finally, hydrogenation of the acetylenic group to the cis olefin was accomplished in the presence of a palladium-on-barium sulfate catalyst in pyridine solution[12] and afforded methyl *dl-cis*-jasmonate (**1**) in almost quantitative yield. The overall yield of **1**, from succinyl chloride and methyl potassium malonate, is 40% and the synthesis constitutes one of the simplest methods yet devised for the preparation of this important perfume constituent.

Experimental Section[13]

2-(Methoxycarbonyl)-3-[(methoxycarbonyl)methyl]-2-(2-pentynyl)cyclopentanone (4). Dry sodium hydride (obtained by washing 0.775 g of a 57% NaH dispersion-in-oil with hexane) was suspended in DMF–benzene (1:1; 20 mL) and the slurry was cooled to −5 °C. A solution of **3** (3.94 g) in the same solvent mixture (4 mL) was then added with stirring. After 5 min, 1-bromo-2-pentyne (2.96 g) was added dropwise and stirring was continued for 3 h. The reaction mixture was poured into water (50 mL) and the whole extracted with ether (2 × 40 mL). The combined extracts were dried ($MgSO_4$) and the solvents removed by evaporation at reduced pressure. The resulting oil was then kept at 100 °C for 1 h in vacuo to remove residual traces of the bromopentyne. The remaining colorless residual oil (4.6 g; 89.8%) solidified on standing (mp 49–50 °C). A sample recrystallized from hexane had the following: mp 50–51 °C; NMR (CCl_4) δ 1.10 (t, 3, CH_3), 2.30 (m, 11), 3.69 (s, 6, CO_2CH_3); IR (Nujol) 1750, 1730 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.26; H, 7.19. Found: C, 64.15; H, 7.15. This compound was previously reported[5b] as an oil.

3-(Carboxymethyl)-2-(2-pentynyl)cyclopentanone (Dehydrojasmonic Acid; 5). To a solution of lithium iodide dihydrate (3.1 g) in dry *s*-collidine (12 mL) under N_2 at 80 °C was added dropwise a solution of the diester **4** (1.70 g) in collidine (3 mL). The mixture was then heated under reflux for 10 h at which point CO_2 evolution became very slow. Both ether and water were added to the cooled reaction mixture, and the organic phase was separated. The aqueous layer was washed 3 times with ether and then acidified (2 N HCl). Extraction with ether (3 × 50 mL) followed by a normal isolation procedure led to **5** as a very viscous oil (0.892 g; 71%): NMR (CCl_4) δ 1.10 (t, 3, CH_3), 1.80–2.80 (m, 12), 10.92 (s, 1, CO_2H); IR (neat) 3500–2600, 1730, 1700 cm^{-1}. Its spectral properties are identical with those previously published.[14] It was characterized as its (2,4-dinitrophenyl)hydrazone, mp 173–174 °C. Anal. Calcd for $C_{18}H_{20}N_4O_6$: C, 55.66; H, 5.19; N, 14.43. Found: C, 55.67; H, 5.39; N, 14.07.

3-[(Methoxycarbonyl)methyl]-2-(2-pentynyl)cyclopentanone (6). The keto carboxylic acid **5** (2.0 g), methyl iodide (2.67 g), and sodium bicarbonate (1.0 g) were added to *N,N*-dimethylacetamide (10 mL), and the mixture was stirred in the dark at 24 °C for 24 h. The solution was diluted with ether (50 mL) and then washed with water (5 × 25 mL). Removal of the ether from the dried ($MgSO_4$) solution then gave the desired racemic methyl dehydrojasmonate (**6**): 1.90 g, 89%; NMR (CCl_4) δ 1.10 (t, 3, CH_3), 1.85–2.80 (m, 12), 3.61 (s, 3, OCH_3); IR (neat) 1730 cm^{-1}. The spectral data for **6** were in agreement with the literature values.[14] Semicarbazone, mp 168–169 °C (lit.[14] mp 167–169 °C).

Racemic Methyl Jasmonate (1). A solution of **6** (0.4 g) in pyridine (10 mL) was hydrogenated at room temperature and pressure over a 5% palladium-on-barium sulfate catalyst. Gas absorption (44 mL; theoretical, 44 mL) ceased completely after 1.5 h. The mixture was filtered and the filtrate was diluted with ether/hexane (1:1; 50 mL) and washed several times with 1 N HCl, saturated sodium bicarbonate solution, and then water. Removal of the solvents from the dried ($MgSO_4$) solution led to racemic methyl *cis*-jasmonate (**1**; 0.392 g, 98%) whose spectral data were identical in all respects with those published. **1**: NMR (CCl_4) δ 0.93 (t, 3, CH_3), 1.60–2.40 (m, 12), 3.61 (s, 3, CO_2CH_3), 5.10 (m, 2, olefinic H); IR (neat) 1740, 1690, 705 cm^{-1}. GLC (QF-1 at 210 °C) showed one major peak (29.5 min) together with minor impurities (28.5 and 30.8 min) that together amount to less than 5%.

Registry No. **1**, 20073-13-6; **2**, 58096-40-5; **3**, 67718-97-2; **4**, 82352-20-3; **5**, 29119-46-8; **5** DNP, 58096-41-6; **6**, 29119-47-9; **6** semicarbazone, 29119-48-0; methyl hydrogen malonate, 16695-14-0; succinyl chloride, 543-20-4.

(10) Elsinger, F. *Org. Synth.* **1965**, *45*, 7.
(11) Alvarez, F. S. *J. Org. Chem.* **1968**, *33*, 2143.
(12) The use of this combination for the reduction of acetylenes to cis olefins is superior to the use of the Lindlar catalyst in all cases that we have examined. There is no danger of overreduction provided neat pyridine is used. The method is ascribed to W. P. Schneider (Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol 1, p 566.
(13) Melting points were determined on a Büchi capillary melting-point apparatus and are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Model 421 spectrophotometer. ^1H NMR spectra were obtained with a Varian Model A56/60 with $(CH_3)_4Si$ as the internal standard. GLC data were obtained with a Hewlett-Packard Model 5750 instrument: gas flow rate, 100 mL/min; column size, 6 ft × 0.25 in. with 15% loading of the liquid phase.
(14) Büchi, G.; Egger, B. *J. Org. Chem.* **1971**, *36*, 2021.