Synthesis of Methyl *dl*-Jasmonate

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Reaction of pyrrolidine enamine (**2**) of methyl 2-oxocyclopentane-1-acetate (**1**) with 3-bromo-2-pentanone (**5**) in dioxane afforded methyl (±)-2-oxo-3-(1′-ethyl-2′-oxopropyl)cyclopentane-1-acetate (**3**) along with a small quantity of methyl (±)-2-oxo-3-(2′-oxopentyl)cyclopentane-1-acetate (**4**). When, however, toluene was used as the solvent instead of dioxane, the major product was **4** and the minor one was **3**. Intramolecular aldol condensation of **3** gave (±)-2-ethyl-6-methoxycarbonylmethylbicyclo[3.3.0]oct-1-en-3-one (**7**). Epoxydation of **7** followed by treatment with *p*-toluenesulfonylhydrazine gave methyl (±)-dehydrojasmonate (**10**). Restricted hydrogenation of **10** gave methyl *dl*-jasmonate (**11**).

Jasmone,[1] methyl jasmonate,[2] and jasmine ketolactone[3] constitute indispensable ingredients as the perfume of jasmine flower, known as the Queen of Aroma. These compounds structurally resemble each other and are considered to be produced biogenetically through a related route.[4,5]

Syntheses of jasmone have been reported by many authors[6] and have been the subject of more recent publications.[7,8] Methyl *dl*-jasmonate was synthesized by Demole and Stoll[4] starting from methyl *dl*-3-oxocyclopentane-1-acetate, but their route involved isomer separation *via* the semicarbazones.

An investigation was carried out to synthesize methyl *dl*-jasmonate by another route, starting from the readily available methyl 2-oxocyclopentane-1-acetate (**1**),[9,10] in order to avoid the difficult separation problem.

The pyrrolidine enamine of **1** was prepared according to Stork, *et al.*[11] The structure of the enamines of 2-substituted cyclanones has been examined by various authors,[12] including Stork, *et al.*[11] According to them the pyrrolidine enamine of 2-alkylcyclohexanone exists predominantly as the isomer with the less substituted double bond rather than that with the more substituted one. The nmr spectrum of the present enamine showed a vinyl proton at τ 5.86 with *ca.* one-third the integration of the ester methyl group, and the mass spectrum demonstrated *m/e* 209 (M), 208 (M − 1) with a base peak 136 ($M-CH_2COOCH_3$).[13] The gas chromatogram of the enamine showed a single peak. These observations indicated that the predominant product of the enamine from **1** was methyl 2-pyrrolidinyl-2-cyclopentene-1-acetate (**2**) possibly containing a small (~5%) amount of the corresponding 1-cyclopentene derivative (**2′**).

In accord with the reported reaction[11,14] of an alicyclic pyrrolidine enamine with a primary α-halo ketone to produce a 1,4-dicarbonyl compound, the reaction of **2** with 3-bromopentan-2-one[15] (**5**) in dioxane, followed by hydrolysis, afforded keto esters which were separated into major (87%) and minor (13%) products. On gas chromatography the major component showed two peaks not clearly separated which indicated an existence of a mixture of stereoisomers. The mass spectrum of the component showed peaks *m/e* 240 and 197 corresponding to the molecular ion and the fragment ion of $M-COCH_3$, respectively. In the nmr spectrum absorption of a methyl ketone methyl group were shown at τ 7.78 and 7.88. Thus the major component was considered to be a *trans–cis* isomer mixture of methyl (±)-2-oxo-3-(1′-ethyl-2′-oxopropyl)cyclopentane-1-acetate (**3**) with presumably *trans* isomer predominating.[16]

The minor component, which showed a similar infrared spectrum to that of the major one, exhibited a mass spectrum with different fragmentation patterns. The absence of *m/e* 197 indicated that the compound was not a methyl ketone. In the nmr spectrum, there was no absorption corresponding to the methyl group of a methyl ketone. When the reaction of **2** with 1-bromopentan-2-one[15] (**6**) was carried out in dioxane or in toluene, there was obtained methyl (±)-2-oxo-3-(2′-oxopentyl)-cyclopentane-1-acetate (**4**) as a major product (95%) with a minor component (5%) which seemed to be methyl (±)-2-oxo-1-(2′-oxopentyl)cyclopentane-1-acetate (**4′**). The compound **4** coincided with the above-mentioned minor component in ir, mass spectra and vpc. The ratio of 95:5 seemed to indicate the ratio of the pyrrolidine enamine of **2** and the double-bond isomer **2′**, respectively. The absence of the isomer methyl (±)-2-oxo-1-(1′-ethyl-2-oxopropyl)cyclopentane-1-acetate (**3′**) in the reaction of **2** with **5** might be due to the steric hindrance between the secondary halide and the enamine **2′**.

When the reaction of **2** with **5** was carried out in toluene instead of dioxane, keto esters **3** and **4** were obtained in a ratio of 16:81 with a small amount (3%) of a compound presumed to be methyl (±)-2-oxo-1-(2′-oxopentyl)cyclopentane-1-acetate (**4′**) (Scheme I). The reac-

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(3) E. Demole, B. Willhalm, and M. Stoll, *ibid.*, **47**, 1152 (1964).

(4) E. Demole and M. Stoll, *ibid.*, **45**, 692 (1962).

(5) E. Sundt, B. Willhalm, and M. Stoll, *ibid.*, **47**, 408 (1964).

(6) (a) W. Treff and H. Werner, *Ber.*, **68**, 640 (1935); (b) H. Hunsdiecker, *ibid.*, **75**, 460 (1942); (c) L. Crombie and S. H. Harper, *J. Chem. Soc.*, 869 (1952); (d) S. H. Harper and J. D. Smith, *ibid.*, 1512 (1955).

(7) (a) K. Sisido, S. Torii, and M. Kawanisi, *J. Org. Chem.*, **29**, 2290 (1964); (b) K. Sisido, Y. Kawasima, and T. Isida, *Perfum Essent. Oil Rec.*, **57**, 364 (1966).

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(10) S. Hauptmann and K. Hirschberg, *J. Prakt. Chem.*, **34**, 272 (1966).

(11) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

(12) (a) W. D. Gurowitz and M. A. Joseph, *Tetrahedron Lett.*, 4433 (1965); (b) S. K. Malhorta and F. Johnson, *ibid.*, 4027 (1965); (c) S. Karady, M. Lenfent, and R. E. Wolff, *Bull. Soc. Chim. Fr.*, 2472 (1965); (d) R. Jacquier, C. Petrus, and F. Petrus, *ibid.*, 2845 (1966).

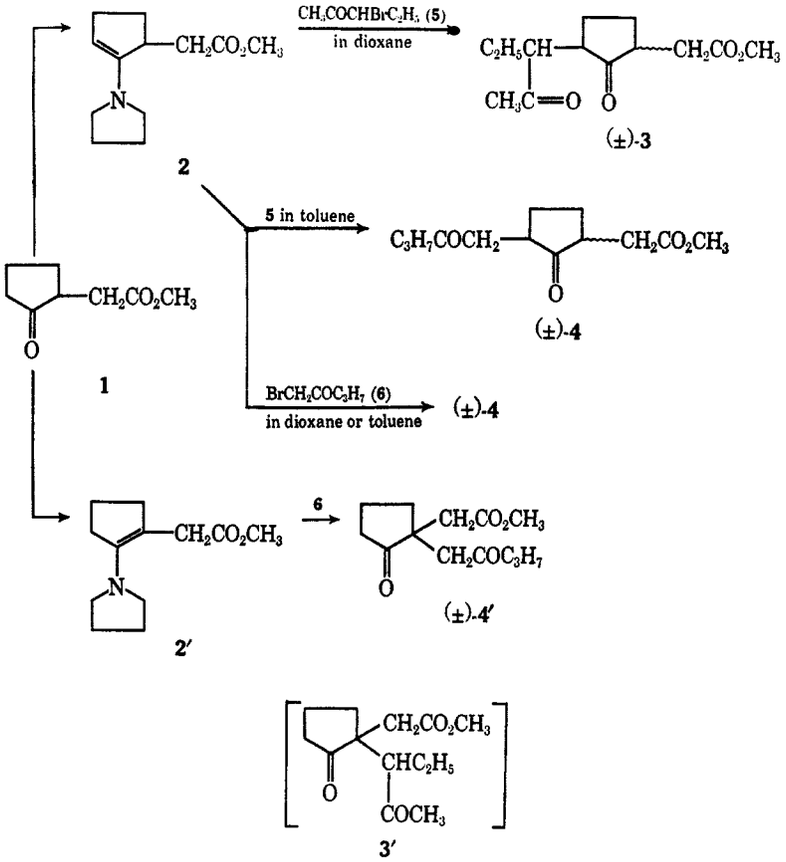
(13) H. J. Jakobsen, S. O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc., B*, 940 (1966).

(14) (a) J. Szmuszkovicz in *Advan. Org. Chem.*, **4**, 1 (1963); (b) H. E. Baumgarten, P. I. Creger, and C. E. Villars, *J. Amer. Chem. Soc.*, **80**, 6609 (1958).

(15) J. R. Catch, D. H. Hey, E. R. H. Jones, and W. Wilson, *J. Chem. Soc.*, 276 (1948).

(16) K. Sisido, S. Kurozumi, K. Utimoto, and T. Isida, *J. Org. Chem.*, **31**, 2795 (1966).

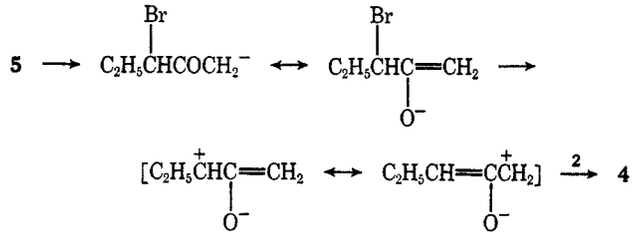
SCHEME I



tion of ethyl 2-oxo-3-ethoxycarbonylcyclopentane-1-acetate with **5** in toluene using potassium followed by saponification, decarboxylation, and esterification gave **3** and **4** in the same ratio of 15:85.

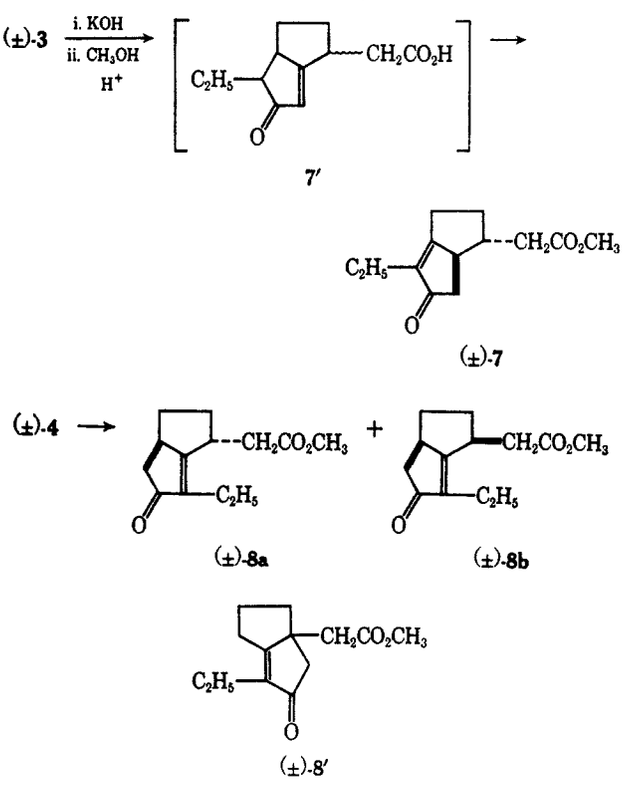
As to the production of **4**, the possibility that the formation of **6** from **5** involved bromine transfer[17] *via* carbanions[18,19] was considered. However, the halo ketone recovered from the reaction contained no 1-bromopentan-2-one (**6**). An alternative and more convincing possibility could involve the formation of the zwitterion[20] suggested as the intermediate in some Favorskii rearrangements (Scheme II). This may be followed by an attack of **2** to afford **4**.

SCHEME II



Intramolecular aldol condensation of **3** (contaminated with 13% **4**) with aqueous potassium hydroxide followed by esterification afforded two products (in a ratio of 7:93), both of which appeared, from their ir and uv spectra, to be esters containing an α,β-disubstituted cyclopentenone moieties (Scheme III). The mass spectra of these compounds showed, however, different

SCHEME III



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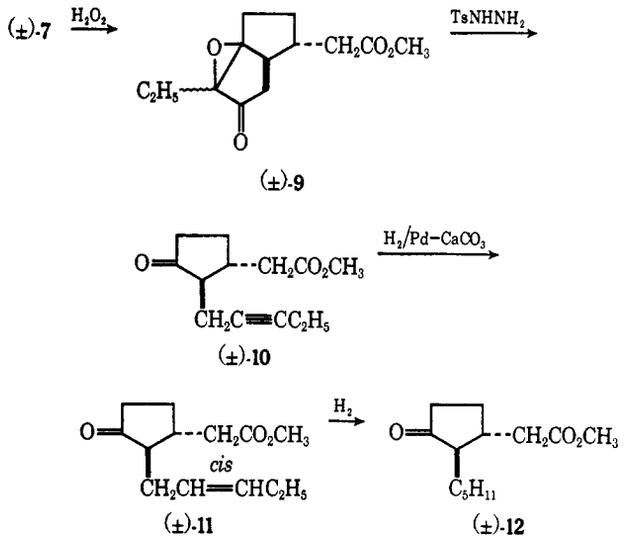
fragmentation patterns. In view of the absence of an olefinic proton in the nmr spectra of both compounds, the major one was considered to be (±)-2-ethyl-6-methoxycarbonylmethylbicyclo[3.3.0]oct-1-en-3-one (**7**) derived from **3**, while the minor one, (±)-2-ethyl-8-methoxycarbonylmethylbicyclo[3.3.0]oct-1-en-3-one (**8**) derived from **4**. The compound **7** was presumed to be derived *via* 2-ethyl-6-carboxymethylbicyclo[3.3.0]oct-4-en-3-one (**7'**) by a double-bond migration to the more substituted enone under the conditions of an alkaline aldol condensation. Treatment of **4** (contaminated with 5% **4'**) with potassium hydroxide afforded **8** (96%) with a small amount (4%) of the compound which was considered to be (±)-2-ethyl-5-methoxycarbonylmethylbicyclo[3.3.0]oct-1-en-3-one (**8'**) derived from **4'**. More precise gas chromatography of **8** showed two peaks (86:14), the mass spectra of which showed the same fragmentation patterns except for differences in relative peak intensities. Thus the two components were stereoisomers, the major one of which was considered to be *trans* isomer **8a** and the minor one *cis* isomer **8b**.[16] The stereochemistry of **7** is assumed to be *trans* since in the process of the double-bond migration the configuration of the bicyclic compound would become the thermodynamically more stable one.

Upon epoxydation of the compound **7** (contaminated with 7% **8**) with hydrogen peroxide in aqueous alkaline solution,[21] the epoxide **9** was obtained in 61% yield as a mixture of two stereoisomers contaminated with unchanged **8**. The ir spectrum of the product showed a very weak absorption corresponding to the conjugated carbonyl group of **8**. Owing presumably to a steric factor, **8** was not readily epoxydized. The separation of **8** and **9** was not feasible by gas chromatography. The crude epoxide **9** was converted into the *p*-toluenesulfonylhydrazone derivative with an equivalent amount of *p*-toluenesulfonylhydrazine,[22] and the product was chromatographed on silica gel. There was obtained in 51% yield methyl (±)-2-(2'-pentynyl)-3-oxocyclopentane-1-acetate (methyl dehydrojasmonate)[4] (**10**) whose analyses and mass spectrum were consistent with the postulated structure.

Hydrogenation of **10** over Lindlar catalyst[23] gave methyl (±)-jasmonate (**11**) whose ir spectrum coincided with that of Demole and Stoll (Scheme IV).[4] The mass spectrum showed a molecular ion peak (*m/e* 224). In the nmr spectrum of the product, the two olefinic protons showed an AB coupling pattern with a *cis* coupling constant of 6 Hz.

When **10** was hydrogenated over palladium–charcoal, methyl (±)-dihydrojasmonate (**12**) was obtained whose mass and ir spectra coincided with those of an authentic sample.[24] The stereochemistry of the substituents on the cyclopentanone ring would be predominantly *trans* for the reason mentioned in the case of compound **7** as well as those described by Varech, *et al.*[25]

SCHEME IV



Experimental Section

Gas chromatography was carried out on Shimadzu GC-2C, with 3 m × 3 mm steel columns packed with 30% PEG-6000 and 30% HVSG on Chromosorb W (80–100 mesh). Infrared spectra were recorded as liquid films on Shimadzu IR-27. Ultraviolet spectra were obtained in ethanol on Hitachi EPS-2 spectrometer. Nmr spectra were measured at 60 MHz with Varian Associates A-60 and Japan Electron Optics C-60-H in 5% solution. Mass spectra were obtained on Hitachi RMS-4 spectrometer. Microanalyses were carried out by Mrs. Huzimoto of this laboratory using Yanagimoto automatic analyzer CHN Corder MT-1. Temperatures are uncorrected.

Pyrrolidine Enamine (2) of Methyl 2-Oxocyclopentane-1-acetate (1).—According to the procedure of Stork, *et al.*,[11] from 16 g (0.10 mol) of methyl 2-oxycyclopentane-1-acetate (**1**)[9,10] and 9.2 g (0.13 mol) of pyrrolidine, 18 g (86%) of pyrrolidine enamine (**2**) was obtained: bp 110–115° (1 mm); ir (liquid film) 3030 (HC=), 1745 (ester C=O), 1625 cm^{-1} (NC=C); nmr ($CDCl_3$) τ 8.40–7.60 (15), 6.34 (s, 3, CO_2CH_3), 5.86 (equivocal t, 1, HC=); mass spectrum (70 eV) *m/e* (relative intensity) 209 (M^+, 91), 208 (87), 194 (7), 178 (20), 150 (70), 136 (100), 135 (99), 122 (27), 108 (17), 94 (12), 79 (20), 70 (47). Gas chromatography (PEG-20M) showed a single peak. Owing to the lability of the substance, an analysis was not performed.

Methyl (±)-2-Oxo-3-(1'-ethyl-2'-oxopropyl)cyclopentane-1-acetate (3).—To a crude pyrrolidine enamine **2**, prepared from 70 g (0.45 mol) of **1**, in 200 ml of dioxane, was added 78 g (0.47 mol) of 3-bromopentan-2-one (**5**)[15] in 50 ml of dioxane. After refluxing for 4 hr, 180 ml of water and 20 ml of concentrated hydrochloric acid were added and refluxing was continued for 30 min. The reaction mixture was poured into saturated sodium chloride solution and extracted with ether. The ether extract, when distilled, gave 26 g (31%) of keto esters, bp 140–150° (2 mm), and 13 g (18%) of the starting material **1**. Gas chromatography (HVSG) of the product showed two main peaks corresponding to **3** and **4** in a ratio of 87:13 with an uncharacterized small peak. The keto ester **3** was purified by preparative gas chromatography: ir (liquid film) 1745, 1740 (ester C=O, cyclic C=O) and 1715 cm^{-1} (C=O); nmr ($CDCl_3$) τ 9.10 9.01 (two triplets, 3, J = 7 Hz, CH_3CH_2–), 8.83–7.90 (m, 5), 7.88, 7.78 (two singlets, 3, CH_3CO–), 7.66–6.80 (6), 6.31 (s, 3, CO_2CH_3).

As expected from the nmr spectrum, **3** showed two close peaks on gas chromatography (HVSG and PEG-20M). The separation of these peaks was unsuccessful: mass spectrum (70 eV) *m/e* 240 (M^+). *Anal.* Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 64.85; H, 8.20.

Methyl (±)-2-Oxo-3-(2'-oxopentyl)cyclopentane-1-acetate (4).—To the crude enamine **2** prepared from 16 g (0.10 mol) of **1** dissolved in 50 ml of toluene was added 17 g (0.10 mol) of **5** in 20 ml of toluene. The reaction was carried out under reflux for 8 hr. After the addition of 26 ml of water and additional re-

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(22) (a) J. Schreiber, D. Felix, A. Eschenmoser, M. Winter, F. Gautschi, K. H. Schulte-Elte, E. Sundt, G. Ohloff, J. Kalvoda, H. Kaufmann, P. Wieland, and G. Anner, *Helv. Chim. Acta*, **50**, 2101 (1967); (b) P. Wieland, H. Kaufmann, and A. Eschenmoser, *ibid.*, **50**, 2108 (1967); (c) A. Eschenmoser, D. Felix, and G. Ohloff, *ibid.*, **50**, 708 (1967); (d) M. Tanabe, D. F. Crowe, R. L. Dehn, and G. Detre, *Tetrahedron Lett.*, 3739 (1967); (e) M. Tanabe, D. F. Crowe, and R. L. Dehn, *ibid.*, 3943 (1967).

(23) H. Lindlar, *Helv. Chim. Acta*, **35**, 446 (1952).

(24) E. Demole, E. Lederer, and D. Mercier, *ibid.*, **45**, 685 (1962).

(25) D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. Chim. Fr.*, 1662 (1965).

fluxing for 2 hr the mixture was treated as above. There was obtained 8.0 g (34%) of keto esters (**3** and **4** in a ratio of 16:81), bp 155–160° (2–3 mm), and 4.7 g (30%) of starting material **1**. Gas chromatography (HVSG) of the product showed two main peaks (**3** and **4**) with a small peak (3%) which was considered to be methyl (±)-2-oxo-1-(2′-oxopentyl)cyclopentane-1-acetate (**4′**) (see below). The major component **4** was separated by preparative gas chromatography: ir (liquid film) 1745, 1740 (ester C=O, cyclic C=O), and 1715 (C=O) cm^{-1}; nmr ($CDCl_3$) τ 9.06 (t, 3, J = 7 Hz, CH_3CH_2), 8.40 (heptet, 2, J = 7 Hz, $CH_3CH_2CH_2$–), 8.10–7.10 (12), 6.30 (s, 3, CO_2CH_3); mass spectrum (70 eV) m/e (relative intensity) 240 (M^+, 4), 222 (7), 208 (33), 181 (13), 169 (23), 164 (17), 152 (31), 149 (28), 137 (77), 123 (28), 109 (16), 105 (7), 81 (20), 71 (100), 55 (24), 43 (95); *Anal.* Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39. Found: C, 65.26; H, 8.11.

Reaction of Ethyl 2-Oxo-3-ethoxycarbonylcyclopentane-1-acetate.—When 16 g (66 mmol) of ethyl 2-oxo-3-ethoxycarbonylcyclopentane-1-acetate[26] was added to 2.5 g (65 mg-atoms) of potassium dispersed in 70 ml of toluene and treated with 16 g (97 mmol) of **5** for 20 hr under reflux, there was obtained 12 g (57%) of keto esters, bp 150–190° (2 mm). On gas chromatography the product showed two peaks in a ratio of 4:6 whose mass spectra demonstrated the similar fragmentation patterns (M^+, m/e 326).

These components were considered to be a pair of stereoisomers of ethyl 2-oxo-3-ethoxycarbonyl-3-(2′-oxopentyl)cyclopentane-1-acetate contaminated with ethyl 2-oxo-3-ethoxycarbonyl-3-(1′-ethyl-2′-oxopropyl)cyclopentane-1-acetate.

Hydrolysis of 11 g (34 mmol) of the keto ester with hydrochloric acid followed by reesterification with methanol in methylene chloride gave 2.1 g (26%) of a mixture of **3** and **4** in a ratio of 15:85, bp 160–163° (4 mm).

Methyl (±)-2-Oxo-3-(2′-oxopentyl)cyclopentane-1-acetate (4).—A mixture of the crude enamine **2** prepared from 16 g (0.10 mol) of **1** and 17 g (0.10 mol) of **6**[15] was stirred and refluxed in 180 ml of toluene for 6 hr and treated as described above. There was obtained, beside 4.5 g (28%) of the starting material **1**, 10 g (42%) of **4**, bp 140–145° (1 mm). Gas chromatography of the product demonstrated two peaks in a ratio of 5:95. The minor component was considered to be methyl 2-oxo-1-(2′-oxopentyl)cyclopentane-1-acetate (**4′**).

When the reaction was carried out in dioxane instead of toluene, the same result was obtained.

(±)-2-Ethyl-6-methoxycarbonylmethylbicyclo[3.3.0]oct-1-en-3-one (7).—A mixture of 5.0 g (21 mmol) of **3** contaminated with 13% of **4**, 2.5 g (45 mmol) of potassium hydroxide, and 75 ml of water was refluxed for 15 hr. After extraction with ether, the aqueous layer was acidified with dilute hydrochloric acid and extracted with ether. The latter ethereal solution, on removal of the solvent, afforded 4.0 g of (±)-2-ethyl-6-carboxymethylbicyclo[3.3.0]oct-1-en-3-one, which, on esterification with 6.0 g of methanol and 5 drops of concentrated sulfuric acid in 30 ml of methylene chloride, gave 2.6 g (56%) of (±) **7**, bp 130–135° (1 mm). The product was shown to be contaminated with 7% of **8** by gas chromatography. Purification of **7** was performed by preparative gas chromatography: uv max (95% ethanol) 238 mμ (ε 10,060); ir (liquid film) 1745 (ester C=O), 1705 (conjugated C=O), 1660 cm^{-1} (conjugated C=C); nmr ($CDCl_3$) τ 8.97 (t, 3, J = 7 Hz, CH_3CH_2–), 8.50–7.10 (12), 6.32 (s, 3, $COOCH_3$); mass spectrum (70 eV) m/e (relative intensity) 222 (M^+, 24), 194 (4), 191 (8), 163 (7), 149 (100), 133 (12), 120 (20), 105 (30), 91 (20), 79 (24), 55 (10), 41 (19). *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.44; H, 8.20.

2,4-Dinitrophenylhydrazone of 7 had mp 139–142°. *Anal.* Calcd for $C_{19}H_{22}O_6N_4$: C, 56.71; H, 5.51; N, 13.92. Found: C, 56.46; H, 5.47; N, 13.66.

(±)-2-Ethyl-8-methoxycarbonylmethylbicyclo[3.3.0]oct-1-en-3-one (8).—A mixture of 6.1 g (25 mmol) of **4** contaminated with 17% **3** (but no detectable amount of **4′**), 3.1 g (55 mmol) of potassium hydroxide, and 70 ml of water was treated as above and there was obtained 2.8 g (50%) of a product. Gas chromatography of the product showed three components corresponding to 74% **8**, 24% **7**, and 2% **8′**. The major compound **8** was purified by preparative gas chromatography (HVSG): uv max (95% ethanol) 238 mμ (ε 7060); ir (liquid film) 1745 (ester C=O), 1705 (conjugated C=O), 1660 cm^{-1} (conjugated C=C); the fingerprint region of **8** was different from that of **7**; nmr ($CDCl_3$) τ 8.96 (t, 3, J = 7 Hz, CH_3CH_2–), 8.50–6.70 (12), 6.28 (s, 3, $COOCH_3$). *Anal.* Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.38; H, 8.15.

2,4-Dinitrophenylhydrazone of 8 had mp 180.5–181°. *Anal.* Calcd for $C_{19}H_{22}O_6N_4$: C, 56.71; H, 5.51; N, 13.92. Found: C, 56.65; H, 5.46; N, 13.66.

Gas chromatographic analyses (PEG-20M) of **8** showed two peaks in a ratio of 86:14, the major one of which was considered to be *trans* isomer **8a** and the minor one, *cis* isomer **8b**.

The mass spectrum [70 eV, m/e (relative intensity)] of **8a** showed 222 (M^+, 46), 194 (32), 178 (4), 163 (23), 149 (32), 135 (20), 134 (19), 133 (16), 120 (100), 105 (60), 91 (44), 79 (41), 65 (12), 55 (16), 41 (29); **8b**, 222 (M^+, 84), 194 (32), 178 (4), 163 (87), 149 (89), 135 (21), 134 (20), 133 (28), 120 (100), 105 (76), 91 (78), 79 (75), 65 (20), 55 (33), 41 (44).

Similar treatment of **4** (contaminated with 5% **4′**) gave a product consisting 79% **8a**, 17% **8b**, and 4% **8′**.

(±)-1,2-Epoxy-2-ethyl-6-methoxycarbonylmethylbicyclo[3.3.0]-octan-3-one (9).—To a solution of 8.2 g (37 mmol) of **7** (contaminated with 7% **8**) in 40 ml of methanol, 11.5 ml of 30% aqueous hydrogen peroxide solution, and 6.6 ml (20 mmol) of 3 *N* sodium hydroxide solution were added at 15–25°. After standing overnight the reaction mixture was poured into saturated sodium chloride solution and extracted with ether and the solvent was removed. There was obtained 5.4 g (61%) of **9**, bp 135–145° (1 mm), whose ir showed the presence of a very small amount of unchanged **8**. Gas chromatography (HVSG) of the product showed two main peaks (stereoisomers) with three small, uncharacterized peaks. The separation of **9** and **8** on gas chromatography was unsuccessful: mass spectrum (70 eV) m/e 238 (M^+). *Anal.* Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.95; H, 7.64.

Methyl (±)-Dehydrojasmonate (10).—A mixture of 2.0 g (8.4 mmol) of crude **9** and 1.6 g (8.4 mmol) of *p*-toluenesulfonylhydrazine in 80 ml of ethanol was warmed at 40–50° for 1.5 hr. Removal of the solvent gave crude tosylhydrazone which was chromatographed over 15 g of silica gel (Mallinckrodt, 100 mesh) using benzene and ethyl acetate (3:1). When the elute was concentrated and distilled, there was obtained 0.95 g (51%) of methyl (±)-dehydrojasmonate (**10**): bp 140–150° (2 mm) [lit.[4] bp 88° (0.001 mm)]; ir (neat) showed similar absorptions of that of methyl jasmonate[4] except slight differences in the fingerprint region; ir (liquid film) 1745, 1465, 1435, 1370, 1340, 1320, 1290, 1265, 1230, 1195, 1165, 1090, 1070, 1015, 995 cm^{-1}; mass spectrum (70 eV) m/e (relative intensity) 222 (M^+, 2), 207 (3), 193 (33), 191 (5), 163 (2), 149 (10), 133 (13), 122 (100), 107 (38), 91 (18), 79 (18), 67 (7), 55 (15), 41 (15). Analyses gave correct values.

Methyl (±)-Jasmonate (11).—Restricted hydrogenation of 0.21 g (0.96 mmol) of **10** over 0.50 g of Lindlar catalyst[23] in 5 ml of methanol gave 0.13 g (60%) of **11**: bp 130–140° (2 mm) [lit.[4] bp 81–84° (0.001 mm)]; ir spectrum was consistent with that of an authentic sample;[4] nmr ($CDCl_3$) τ 9.04 (t, 3, J = 7 Hz, CH_3CH_2–), 8.80–7.10 (12), 6.30 (s, 3, $COOCH_3$), 4.72 (d, 1, J = 6 Hz, HC=), 4.53 (d, 1, J = 6 Hz, HC=); mass spectrum (70 eV) m/e (relative intensity) 224 (M^+, 28), 206 (4), 193 (9), 177 (3), 167 (4), 165 (4), 156 (25), 151 (50), 133 (16), 121 (11), 109 (25), 95 (31), 83 (100), 67 (27), 55 (33), 41 (58). Analyses afforded correct values.

Methyl (±)-Dihydrojasmonate (12).—Hydrogenation of 40 mg (0.18 mmol) of **10** over 0.25 g of 5% palladium–charcoal in 5 ml of methanol gave 35 mg (87%) of methyl (±)-dihydrojasmonate (**12**): ir of the product coincided with that of an authentic sample;[24] mass spectrum (70 eV) m/e (relative intensity) 226 (M^+, 4), 195 (4), 169 (3), 156 (36), 153 (24), 137 (3), 124 (14), 109 (4), 95 (7), 83 (100), 74 (7), 67 (8), 55 (20), 41 (20).

Registry No.—**2**, 20073-04-5; **3**, 20073-05-6; **4**, 20073-06-7; **7**, 20073-07-8; **7** 2,4-dinitrophenylhydrazone, 20126-08-3; **8a**, 20073-08-9; **8a**, 2,4-dinitrophenylhydrazone, 20073-09-0; **8b**, 20073-10-3; **8b**, 2,4-dinitrophenylhydrazone, 20073-11-4; **9**, 20073-12-5; **11**, 20073-13-6.

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