Stereochemical Control over Three Contiguous Stereogenic Centers in the Intramolecular Ene Reaction of Activated 1,6-Dienes. Application to the Synthesis of (±)-Methyl Cucurbate and (±)-Methyl Epijasmonate

Tarun K. Sarkar,*,† Binay K. Ghorai,† Sandip K. Nandy,† Bireswar Mukherjee,† and Asoke Banerji‡

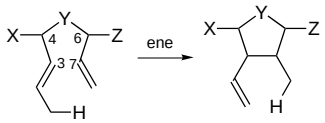
Department of Chemistry, Indian Institute of Technology, Kharagpur 721 302, India, and Bio-organic Division, Modular Laboratory, BARC, Bombay 400 085, India

Received September 10, 1996 (Revised Manuscript Received May 5, 1997⊗)

The influence of a protected alcohol group adjacent to the ene or enophile component on diastereoselectivity in both thermal and Lewis acid-catalyzed 5-(3,4) ene reactions of a series of 1,6-dienes **1**−**7** has been studied. The results indicate that its effect can be considerable, and in one example, with a *gem*-dimethyl group on the connecting chain and a large silyl protecting group on the hydroxyl, the diastereocontrol was almost perfect, with three stereogenic centers and one double bond geometry set up in one step, *e.g.*, **4** → **10**. This new finding was exploited in a synthesis of epijasmonoid natural products, (±)-methyl cucurbate (**19**) and (±)-methyl epijasmonate (**18**) starting from aldehyde **24**, where the key step was a highly diastereocontrolled 5-(3,4) ene cyclization **23** → **22**.

Introduction

The thermal and Lewis acid-catalyzed intramolecular Alder ene reaction has frequently been used in organic synthesis as a tool for carbo- and heterocyclization.[1] The stereochemistry about the forming C,C bond is usually *cis* for five-membered rings, especially from unactivated or moderately activated 1,6-dienes, but 1,6-dienes containing doubly activated enophiles give *trans*-1,2-disubstituted cyclopentanes almost exclusively.[1,2,3a,b,4] The relationship between the stereochemistries of substituents on the tether and the stereochemistry of C,C bond formation is not, however, as easily predicted.[2] As part of our continuing program to explore the potential of intramolecular ene reactions for organic synthesis,[3] we were interested in studying the topological influence (C4/C6) over developing (C3,C7) stereogenic centers in the ene cyclization step (eq 1).



(1)

Although, a few reports have dealt with this issue (X = CH_3, Y = O/CH_2, Z = H; X = H, Y = RN/CH_2, Z = CH_3; X = Ph, Y = O, Z = H),[1,5] the influence of an oxygen substituent in either the ene or enophilic component (X/Z = OR) has not been systematically investigated. Incidentally, some reports on mechanistically related Diels−Alder reactions indicate that lesser steric bulk of an alkoxy group makes it less effective than an alkyl group for diastereoinduction in these reactions.[6] Prompted by the occurrence of hydroxyl-bearing chiral centers in cyclopentanoid natural products,[7] we undertook a study of this facet of 5-(3,4)[1d] ene cyclizations. Accordingly, a series of hydroxylated 1,6-dienes **1**−**7**, with different substituents in the ene, the tether, and the enophile, were prepared and their thermolytic/Lewis acid-catalyzed ene reactions were investigated. In this work, suitable protection of the hydroxyl group was deemed important since the hydroxyl group is sterically very small when compared to a methyl group which has been used in previous studies of diastereoface selectivity in 5-(3,4) ene cyclizations.[1] For example, the A value for a methyl group is 1.8[8] while that for a hydroxyl group is 0.5[9] in nonaqueous solutions. It was hoped that a bulky silyl protecting group would not only prevent decomposition of ene educts but also enhance the stereoselectivity of the ene cyclizations.

The present study has revealed that three contiguous ring stereogenic centers can be created with a very high level of both diastereoselectivity and diastereofacial selectivity by the influence of an oxygen substituent as a stereodirecting resident group in the ene/enophile component.[10] Furthermore, this work has also culmi-

† Indian Institute of Technology.
‡ BARC.
⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

(1) (a) Oppolzer, W.; Snieckus, V. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 476. (b) Taber, D. F. *Intramolecular Diels-Alder and Alder Ene Reactions*; Springer-Verlag: New York, 1984. (c) Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990; Chapter 5. (d) Mikami, K.; Shimizu, M. *Chem. Rev.* **1992**, *92*, 1021. (e) Snider, B. B. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1992; Vol. 5, p 1.

(2) Thomas, B. E.; Loncharich, R. J.; Houk, K. N. *J. Org. Chem.* **1992**, *57*, 1354.

(3) (a) Ghosh, S. K.; Sarkar, T. K. *Tetrahedron Lett.* **1986**, *27*, 525. (b) Sarkar, T. K.; Subba Rao, P. S. V. *Synth. Commun.* **1989**, *19*, 1281. (c) Sarkar, T. K.; Ghosh, S. K.; Subba Rao, P. S. V.; Satapathi, T. K. *Tetrahedron Lett.* **1990**, *31*, 3461. (d) Sarkar, T. K.; Ghosh, S. K.; Subba Rao, P. S. V.; Mamdapur, V. R. *Ibid.* **1990**, *31*, 3465. (e) Sarkar, T. K.; Ghosh, S. K.; Subba Rao, P. S. V.; Satapathi, T. K.; Mamdapur, V. R. *Tetrahedron* **1992**, *48*, 6897. (f) Sarkar, T. K.; Nandy, S. K.; Ghorai, B. K.; Mukherjee, B. *Synlett* **1996**, *97*. (g) Sarkar, T. K.; Nandy, S. K. *Tetrahedron Lett.* **1996**, *37*, 5195. See also refs 10 and 11.

(4) Tietze, L. F.; Beifuss, U.; Ruther, M.; Ruhlmann, A.; Antel, J.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1186.

(5) Mikami, K.; Matsueda, H.; Nakai, T. *Synlett* **1993**, 235.

(6) (a) Tietze, L. F.; Kiedrowski, G. V. *Tetrahedron Lett.* **1981**, *22*, 219. (b) Franck, R. W.; *et al. J. Am. Chem. Soc.* **1982**, *104*, 1106. (c) See also ref 1b, p 54.

(7) Paquette, L. A.; Doherty, A. M. *Polyquinane Chemistry*; Springer-Verlag: Berlin, 1987.

(8) Allinger, N. L.; Freiberg, L. A. *J. Org. Chem.* **1966**, *31*, 804.

(9) Hirsch, J. A. In *Topics Stereochemistry*; Allinger, N. L., Eliel, E. L., Eds.; Wiley-Interscience: New York, 1967; Vol. 1, p 199.

(10) For a preliminary report, see: Sarkar, T. K.; Ghorai, B. K.; Nandy, S. K; Mukherjee, B. *Tetrahedron Lett.* **1994**, *35*, 6903.

S0022-3263(96)01739-2 CCC: $14.00

Table 1. Stereochemical Control over Three Contiguous Stereogenic Centers

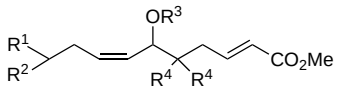
run[a]	educt	temp/time	product/(ratio[b])	combined yield[c] (%)	diastereoselectivity/diastereofacial selectivity
1	**3**	235 °C/40 h	**9**/**12** (79:21)	83	~100% *cis*/79% *trans*
2	**1**	235 °C/40 h	**8**/**11** (88:12)	97	~100% *cis*/88% *trans*
3	**4**	235 °C/18 h	**10**	96	~100% *cis*/100% *trans*
4	**5**	235 °C/40 h	**13**/**14** (88:12)	86	~88% *cis*/100% *trans*
5	**6**	rt/2 h	**15**/**17** (96:4)	90	~96% *trans*/100% *trans*
6	**7**	rt/3 h	**16**	90	~100% *trans*/100% *trans*

[a] In runs 1−4, a 5% solution of the diene in toluene was heated in a sealed Corning tube under argon. In runs 5 and 6, a 0.5 M solution of the diene in CH_2Cl_2 was exposed to $ZnBr_2$ (anhydrous). [b] Capillary GC and GC−MS analyses give the diastereomeric composition of products in these runs which is as follows: run 1 (1.8:77.7:20.5); run 2 (1.09:81.4:5.57:11.9); run 3 (96.4:1.9:0.6:1.1); run 4 (11.9:87.5:0.6); run 5 (95.6:4.4); run 6 (single compound, based on ^{1}H-NMR). Trace diastereomers were not properly characterized and were ignored. [c] Isolated yield after chromatography.

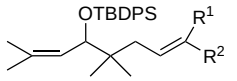
nated in a synthesis of two jasmonoid natural products, e.g., (±)-methyl cucurbate and (±)-methyl epijasmonate.[11]

Results and Discussion

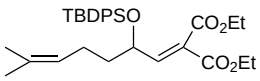
Ene Cyclization of 1−7. The thermolytic cyclizations of **1**−**5** were carried out in toluene (5% solution) in sealed tubes under an atmosphere of argon. Attempts to cyclize the free alcohol **2** under this condition was thwarted as it underwent extensive decomposition. The ene reactions of **6** and **7** were effected at ambient temperature in CH_2Cl_2 in the presence of a Lewis acid ($ZnBr_2$). The product ratios (Table 1) were determined by high-field NMR, capillary GC, and GC−MS analysis.



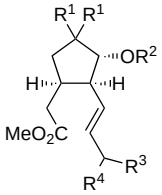
1: $R^1 = R^2 = Me$; $R^3 = TBDPS$; $R^4 = H$
2: $R^1 = R^2 = Me$; $R^3 = R^4 = H$
3: $R^1 = R^2 = Me$; $R^3 = TBDMS$; $R^4 = H$
4: $R^1 = H$; $R^2 = TMS$; $R^3 = TBDPS$; $R^4 = Me$

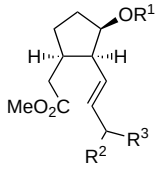


5: $R^1 = H$; $R^2 = CO_2Me$
6: $R^1 = R^2 = CO_2Et$



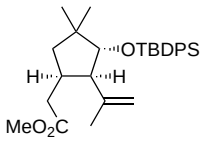
7



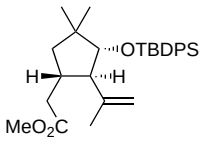


8: $R^1 = H$; $R^2 = TBDPS$; $R^3 = R^4 = Me$
9: $R^1 = H$; $R^2 = TBDMS$; $R^3 = R^4 = Me$
10: $R^1 = Me$; $R^2 = TBDPS$; $R^3 = H$; $R^4 = TMS$

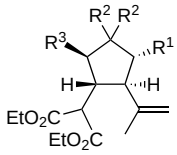
11: $R^1 = TBDPS$; $R^2 = R^3 = Me$
12: $R^1 = TBDMS$; $R^2 = R^3 = Me$



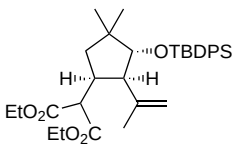
13



14



15: $R^1 = OTBDPS$; $R^2 = Me$; $R^3 = H$
16: $R^1 = R^2 = H$; $R^3 = OTBDPS$



17

Table 1 reveals the following features of the present ene reaction. In runs 1 and 2, diastereoselectivity is uniformly high, but the diastereofacial selectivity increases with increasing steric bulk of the silyl[12] substituent on oxygen. The most striking result is, however, observed in run 3 where the 1,6-diene **4** carrying a strategically located TMS group and a gem-dimethyl group on the tether gives the cyclopentanoid allylsilane **10** in very high yield with nearly 100% diastereoselectivity and 100% diastereofacial selectivity. In runs 4 and 5 while diastereofacial selectivity is very high, diastereoselectivity actually increases in the Lewis acid catalyzed reactions in accordance with previous observations.[3a,b,4] Similarly, in run 6, the doubly activated 1,6-diene yielded **16** as the only product as revealed from ^{1}H-NMR analysis.

In order to rationalize the high stereoselectivities observed in the present ene cyclizations, the Oppolzer model[13] of transition states is invoked as the Houk model[2] is inadequate in the cases of activated enophiles.

In the cases of **1**, **3**, and **4**, only two transition states A and B are possible due to the *Z*-ene geometry (Figure 1). B, with an *endo* OR group, is obviously less preferred. Thus, **8**−**10** are the predominant products. **5** and **6** prefer transition states C,E rather than D,F, where due to the orientation of the OR group, the steric interactions (OR−Me interactions *vs* OR−H interactions) are much more severe compared to those in B. The 100% diastereofacial selectivity in the cases of **5** and **6** can therefore be readily explained. That thermal ene reaction of **5** gives **13** as the major product *via* transition state C, and Lewis acid-catalyzed ene cyclization of **6** gives almost exclusively **15** *via* the transition state E is in accord with previous work from this laboratory.[3a,b,4] The exclusive formation of **16** from **7** can be explained *via* a transition state similar to E.

Synthesis of (±)-Methyl Cucurbate (19) and (±)-Methyl Epijasmonate (18). Having thus developed a highly stereocontrolled route to a functionalized cyclopentane ring system with three contiguous stereogenic centers and a versatile olefinic side chain, we felt well-suited to tackle some natural product total syntheses. The jasmonoid natural products, e.g., (±)-methyl cucurbate (**19**) and (±)-methyl epijasmonate (**18**) were chosen as the initial targets.[14] Incidentally, the rich biological profile displayed by nearly all jasmonoids has contributed to their popularity as targets of intense synthetic interest in recent years.[14]

Our approach to (±)-methyl cucurbate (**19**), a plant growth inhibitor, and thence to (±)-methyl epijasmonate (**18**), the queen of aroma, is summarized by the discon-

(11) For a preliminary report, see: Sarkar, T. K.; Ghorai, B. K.; Banerji, A. *Tetrahedron Lett.* **1994**, *35*, 6907.

(12) Hwu, J. R.; Wang, N. *Chem. Rev.* **1989**, *89*, 1599.
(13) Oppolzer, W.; Robbiani, C. *Helv. Chim. Acta* **1980**, *63*, 2010.

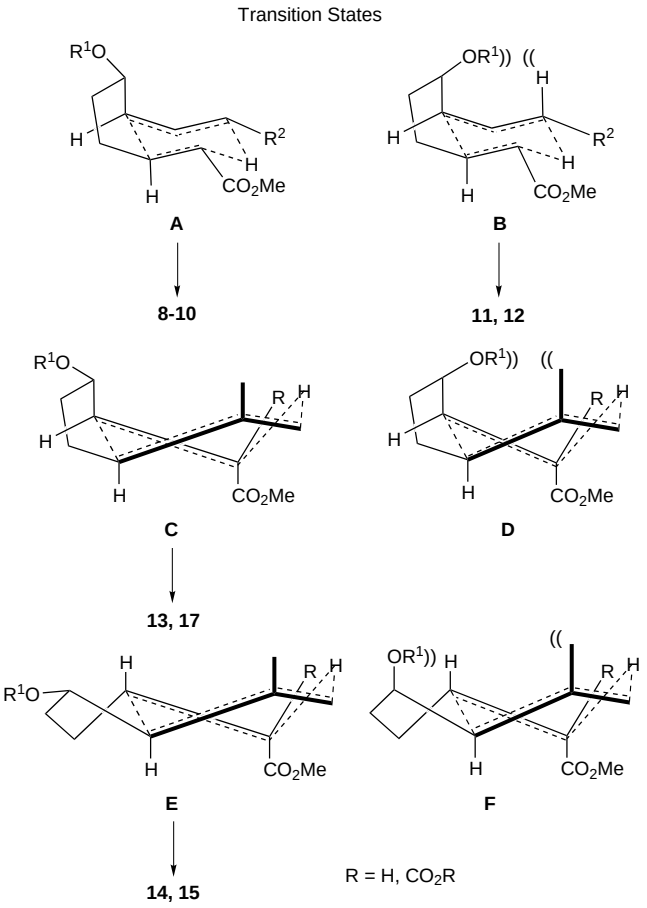
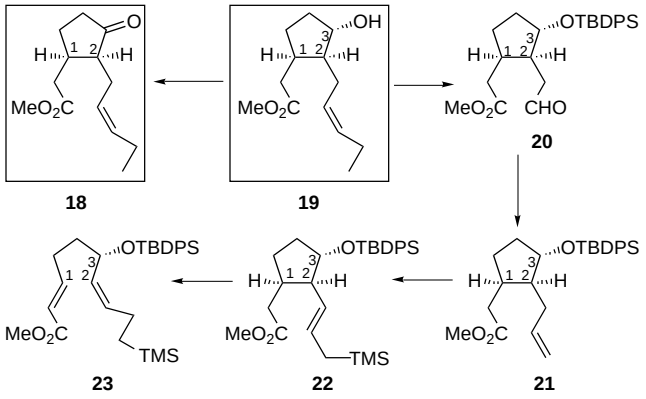


Figure 1.

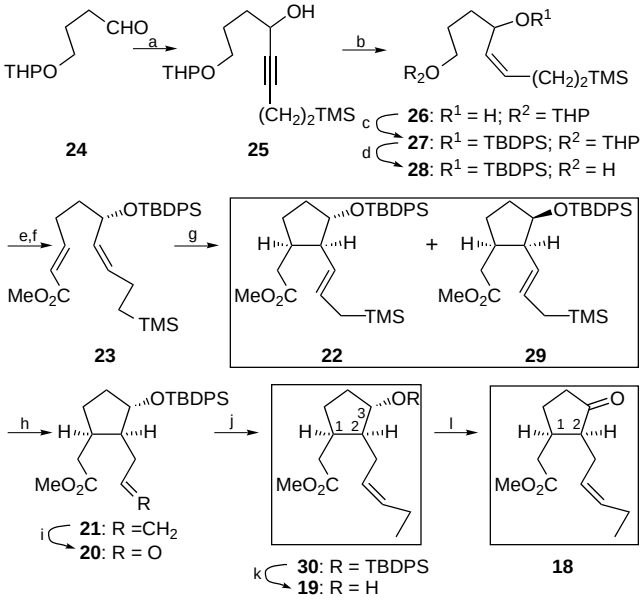
Scheme 1



nective analysis pictured in Scheme 1. Thus, formation of the crucial C2−C1 bond (**23** → **22**) would generate the appropriately functionalized cyclopentane for ready elaboration to **19** and **18**. In light of previous model studies, we expected to achieve excellent induction by the resident center C3 during the ene cyclization step.

Putting this plan into action, the known aldehyde **24**[15] was transformed into the activated 1,6-diene **23** (Scheme 2). Thermolysis of a 5% solution of **23** in toluene under argon in a sealed tube for 18 h gave an inseparable mixture of **22** and **29** in a ratio of ∼9:1. Another trace but unidentified diastereomer (0.5%) was also formed as indicated from capillary GC and GC−MS analyses of the crude product. Syntheses of **19** and **18** were next pursued with the inseparable mixture **22**/**29**. Protodesilylation of **22** → **21** (only one diastereomer is shown henceforth for convenience) was initially fraught with difficulties as most of the recommended reagents including BF_3·2AcOH[16] or concd HCl were ineffective. Fortunately, exposure of **22** to two-phase HI−benzene, water mixture[17] gave the desired terminal olefin **21** in 79% yield. **21** is contaminated with ∼10% of its C3−*β* isomer, C*H*OR signal of which resonates at *δ* 4.2 (^{1}H-NMR) in analogy with C3-*β* isomer of methyl cucurbate where the same signal appears at *δ* 4.2.[18] As expected, the C*H*OR signal of the major diastereomer **21** resonates at *δ* 4.0 (^{1}H-NMR) in analogy with methyl cucurbate where C3-H also appears at *δ* 4.0.[14b] Oxidative cleavage of **21** (with ozone) gave the jasmonoid building block **20** in 88% yield which was next subjected to "salt-free" Wittig olefination using *n*-propyltriphenylphosphorane, generated from the corresponding phosphonium salt with $NaN(TMS)_2$, under the condition described by Bestmann *et al.*[19] to provide **30** (50% yield). Desilylation (with *n*-Bu_4NF) at room temperature gave (±)-methyl cucurbate (**19**) in 89% yield. During this step, the minor C3-*β* isomer (∼10%) carried over from **22**/**29** was eliminated presumably *via* lactone formation as inferred from the appearance of a broad singlet at *δ* 4.6 in the ^{1}H-NMR spectrum of the trace byproduct.[14a] The spectral properties of **19** are in agreement with those reported by Kitahara *et al.*[14b] Also, **19**

Scheme 2[a]



[a] (a) LiC≡C$(CH_2)_2$TMS/THF/HMPA, −78 °C, 80%; (b) *i*-BuMgBr/Cp_2TiCl_2(cat.), 65%; (c) TBDPSCl/Im/DMF, 85%; (d) PPTS/EtOH, 97%; (e) $(COCl)_2$/DMSO, 90%; (f) $(MeO)_2P(O)CH(Li)CO_2Me$, 80%; (g) 235 °C, 18 h, 95%; (h) HI/bz, 79%; (i) O_3, 88%; (j) $Ph_3(Pr)PBr$/$NaN(TMS)_2$, 50%; (k) *n*-Bu_4NF, 89%; (l) H_2CrO_4/ether, 70%.

(14) Cucurbic, acid; for synthesis, see: (a) Seto, H.; Yoshioka, H. *Chem. Lett.* **1990**, 1797. (b) Kitahara, T.; Miura, M.; Warita, Y.; Takagi, Y.; Mori, K. *Agric. Biol. Chem.* **1987**, *51*, 1129. (c) Borm, C.; Winterfeldt, E. *Liebig Ann.* **1996**, 1209. (d) Stadmuller, H.; Knochel, P. *Synlett* **1995**, 463. Methyl epijasmonate; for synthesis, see: (e) Helmchen, G.; Goeke, A.; Laner, G.; Urmann, M.; Fried, J. *Angew. chem., Int. Ed. Engl.* **1990**, *29*, 1024. (f) Kitahara, T.; Nishi, T.; Mori, K. *Tetrahedron* **1991**, *47*, 6999 and references cited therein. (g) Crombie, L.; Mistry, M. K. *J. Chem. Soc., Chem. Commun.* **1988**, 539. (h) See also refs 14a, 14b, and 14d.

(15) Bestmann, H. J.; Gunawardena, N. E. *Synthesis* **1992**, 1239.

(16) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446.

(17) Saloman, R. G.; Coughlin, D. J. *J. Org. Chem.* **1979**, *44*, 3784.

(18) Montforts, F. P.; Gesing-Zibulak, I.; Grammenos, W.; Schneider, M.; Lanman, K. *Helv. Chim. Acta* **1989**, *72*, 1852.

(19) (a) Bestmann, H. J.; Stransky, W.; Vostrowsky, O. *Chem. Ber.* **1976**, *109*, 1694. (b) *Ibid.* **1976**, *109*, 3375.

is free from any *E*-isomer as confirmed from capillary GC as well as ^{13}C-NMR analysis. This is the first synthesis of methyl cucurbate (**19**) wherein three chiral centers on the cyclopentane ring have been created in proper stereochemical relationship in a single operation. The previous syntheses were either nonstereoselective[14b] or required an inversion[14a] of hydroxyl stereochemistry. Finally, two-phase oxidation of (±)-methyl cucurbate (**19**) with chromic acid under Brown's condition[20] gave (±)-methyl epijasmonate (**18**) in 70% isolated yield. The synthetic (±)-methyl epijasmonate (**18**) has a very intense, typical "jasmonate fragrance". The ^{1}H- and ^{13}C-NMR of our synthetic (±)-**18** agreed nicely with those supplied by Prof. G. Helmchen.[14e] However, close examination of the ^{13}C-NMR spectrum of our synthetic (±)-methyl epijasmonate (**18**) shows the presence of traces (∼7−10%) of the C2 epimer, popularly known as methyl jasmonate (from the appearance of signals at δ 134.06(d), 53.99(d), 38.79(t), 38.01(d), 37.71(t)). This was further confirmed by actual epimerization of synthetic (±)-**18** under acidic conditions to give the C2 epimer (methyl jasmonate) containing 5% of (±)-**18**. Note that the C2 proton in (±)-methyl jasmonate (C2 epimer of (±)-**18**) appears as a one-proton multiplet at δ 2.6−2.8 whereas the C2 proton in (±)-**18** appears as one-proton multiplet at δ 2.72−2.97. In addition, in the ^{13}C-NMR spectrum of (±)-methyl jasmonate (C2 epimer of (±)-**18**), C2 (δ 53.91) and C1 (δ 37.94) carbons of the cyclopentane ring lie downward relative to those in (±)-methyl epijasmonate (**18**) by δ ∼1.24 and 2.4, respectively, due to γ-gauche upfield shift.[21]

Finally, the jasmonoid building block **20** should prove valuable for the synthesis of other jasmonoid natural products, namely, methyl tuberonate and congeners.[22] In addition, while **10** should serve as a key intermediate for coriolin[23] and also chloriolin A,[24] **9**/**12** may be tailored into oreodaphnenol[25] *via* intramolecular keto−carbeniod addition across the π-bond, and work in these directions is currently underway in this laboratory.

Experimental Section

General Details. All reactions were carried out under a dry nitrogen or argon atmosphere in flame-dried flasks. Solvents were dried by distillation from drying agents as follows: diethyl ether, THF, DME, toluene, and benzene (sodium benzophenone ketyl), dichloromethane (P_2O_5), DMSO, HMPA, Et_3N, and pyridine (CaH_2). Column chromatography and TLC were carried out on silica gel. ^{1}H-NMR spectra of $CDCl_3$ solutions were recorded at 200, 300, and 400 MHz and that of CCl_4 solutions at 90 MHz.

Methyl (1*RS*,2*SR*,3*SR*)-2-[2-[(*E*)-3-Methyl-1-butenyl]-3-[(*tert*-butyldiphenylsilyl)oxy]cyclopentyl]acetate (8) and Methyl (1*RS*,2*SR*,3*RS*)-2-[2-[(*E*)-3-Methyl-1-butenyl]-3-[(*tert*-butyldiphenylsilyl)oxy]cyclopentyl]acetate (11). A solution of **1** (1.5 g, 3.23 mmol) in dry toluene (30 mL) was taken in seven corning tubes (30 cm long, 2 cm diameter), purged with argon, and sealed. These sample tubes were heated at 235 °C (±2 °C) for 40 h in a constant temperature oven. After the samples were to room temperature, the solvent was removed *in vacuo* and the residue passed through a plug of silica gel and eluted with ethyl acetate−petroleum ether (60−80 °C) (2.5:97.5) to give **8** and **11** (1.40 g, 97%) as a colorless thick oil: IR 3422, 3050, 2945, 1732, 1444 cm^{-1}; ^{1}H-NMR for major isomer **8** ($CDCl_3$) δ 0.86 (d, 3H, J = 6.7 Hz), 0.87 (d, 3H, J = 6.7 Hz), 1.04 (s, 9H), 1.58−1.66 (m, 1H), 1.79−1.84 (m, 1H), 1.93−1.98 (m, 1H), 2.1 (dd, 1H, J = 15.7, 8.8 Hz), 2.26 (dd, 1H, J = 15.6, 6.8 Hz), 2.49−2.59 (m, 1H), 2.69−2.74 (m, 1H), 3.63 (s, 3H), 3.97−4.0 (m, 1H), 4.85 (dd, 1H, J = 15.2, 10.1 Hz), 5.15 (dd, 1H, J = 15.2, 6.7 Hz), 7.32−7.42 (m, 6H), 7.61−7.65 (m, 4H); ^{1}H-NMR for other minor diastereomer **11** (partial) δ 0.99 (d, 6H, J = 6.76 Hz), 1.03 (s, 9H), 4.18−4.22 (m, 1H), 5.36 (dd, 1H, J = 15.2, 9.8 Hz), 5.48 (dd, 1H, J = 15.2, 6.6 Hz); ^{13}C-NMR for major isomer **8** ($CDCl_3$) δ 173.402 (s), 140.556 (d), 135.934 (d), 135.805 (d), 134.632 (s), 134.377 (s), 129.465 (d), 127.504 (d), 124.174 (d), 79.971 (d), 54.996 (d), 51.152 (q), 37.062 (d), 36.348 (t), 33.697 (t), 31.205 (d), 28.811 (t), 27.099 (q), 22.683 (q), 22.510 (q), 19.190 (s); ^{13}C-NMR for minor diastereomer **11** (partial) δ 140.960 (d), 123.394 (d), 77.198 (d), 51.646 (d), 37.379 (d), 37.235 (t), 32.851 (t), 31.454 (d), 28.161 (t), 22.876 (q), 19.302 (s); GC-MS (COL SGE-BP-5, 0.32 mm/25 m, isothermal 260 °C); one major peak **8** t_R = 16.36 min (81.44%); *m*/*z* (relative intensity) no M$^+$, 433 (45), 407 (M − Me_3C, 100), 333 (18), 213 (20), 199 (56), 177 (9), 153 (7), 135 (28), 119 (4), 105 (4), 93 (4), 79 (4), 69 (9); for minor diastereomer **11** t_R = 19.01 min (11.9%); *m*/*z* (relative intensity) no M$^+$, 407 (M − Me_3C, 100), 213 (21), 199 (30), 181 (9), 169 (9), 135 (20), 119 (12), 69 (25). Anal. Calcd for $C_{29}H_{40}O_3Si$: C, 74.95; H, 8.67. Found: C, 74.99; H, 8.61.

Methyl (1*RS*,2*SR*,3*SR*)-2-[2-[(*E*)-3-methyl-1-butenyl]-3-[(*tert*-butyldimethylsilyl)oxy]cyclopentyl]acetate (9) and methyl (1*RS*,2*SR*,3*RS*)-2-[2-[(*E*)-3-methyl-1-butenyl]-3-[(*tert*-butyldimethylsilyl)oxy]cyclopentyl]acetate (12): ^{1}H-NMR for major isomer **9** ($CDCl_3$) δ 0.02 (d, 6H, J = 6.6 Hz), 0.86 (s, 9H), 0.96 (d, 6H, J = 6.5 Hz), 1.1−1.4 (m, 1H), 1.45−1.85 (m, 2H), 1.8−2.12 (m, 2H), 2.2−2.4 (m, 2H), 2.34−2.5 (m, 1H), 2.5−2.7 (m, 1H), 3.64 (s, 3H), 3.88−3.93 (m, 1H), 4.85 (dd, 1H, J = 15.2, 10.1 Hz), 5.15 (dd, 1H, J = 15.2, 6.74 Hz), 7.32−7.41 (m, 6H), 7.61−7.65 (m, 4H); ^{1}H-NMR for other minor diastereomer **12** (partial) 3.72 (s, 3H), 4.08−4.18 (m, 1H), 5.6−5.9 (m, 2H); GLC (column 3%, OV-17, 0.25 mm × 50 m, N_2 40 mL/min, 180 °C isothermal), t_R for major diastereomer **9**, 15.9 min (77.7%), for minor diastereomer **12**, 17.3 min (20.5%). Anal. Calcd for $C_{19}H_{36}O_3Si$: C, 67.01; H, 10.65. Found: C, 67.07; H, 10.69.

Methyl (1*RS*,2*SR*,3*RS*)-2-[2-[(*E*)-3-(trimethylsilyl)-1-propenyl]-3-[(*tert*-butyldiphenylsilyl)oxy]-4,4-dimethylcyclopentyl]acetate (10): IR 2954, 2861, 1741, 1661, 1249, 1162, 1110, 847, 700 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ −0.14 (s, 9H), 0.83 (s, 3H), 0.93−1.15 (m, 15H), 1.56−1.63 (m, 1H), 1.87 (dd, 1H, J = 15.1, 9.5 Hz), 2.19 (dd, 1H, J = 15.1, 5.1 Hz), 2.53−2.62 (m, 2H), 3.44 (d, 1H, J = 5.86 Hz), 3.57 (s, 3H), 4.52 (dd, 1H, J = 15.1, 9.5 Hz), 4.85 (ddd, 1H, J = 15.1, 9.4, 6.0 Hz), 7.28−7.42 (m, 6H), 7.61−7.66 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 173.892 (s), 136.240 (d), 134.827 (s), 134.060 (s), 130.208 (d), 129.285 (d), 127.242 (d), 127.112 (d), 87.429 (d), 52.604 (d), 51.245 (q), 45.073 (t), 41.626 (s), 37.275 (t), 34.544 (d), 28.050 (q), 27.169 (q), 22.939 (t), 22.481 (q), 19.547 (s), −1.88 (q); EIMS *m*/*z* (relative intensity) no M$^+$, 479 (M − Me_3C, 28), 459 (2), 405 (3), 375 (8), 345 (3), 329 (8), 297 (7), 249 (12), 213 (16), 199 (39), 159 (24), 135 (52), 73 (100, Me_3Si). Anal. Calcd for $C_{32}H_{48}O_3Si_2$: C, 71.53; H, 9.02. Found: C, 71.59; H, 9.01.

Methyl (1*RS*,2*SR*,3*RS*)-2-[2-isopropenyl-3-[(*tert*-butyldiphenylsilyl)oxy]-4,4-dimethylcyclopentyl]acetate (13) and Methyl (1*SR*,2*SR*,3*RS*)-2-[2-isopropenyl-3-[(*tert*-butyldiphenylsilyl)oxy]-4,4-dimethylcyclopentyl]acetate (14): ^{1}H-NMR ($CDCl_3$) δ 0.87 (s, 3H), 0.99 (s, 9H), 1.1 (s, 3H),

(20) Brown, H. C.; Garg, C. P.; Liu, K. T. *J. Org. Chem.* **1971**, *36*, 387.

(21) (a) Schneider, H.-J.; Nguyen-ba, N.; Thomas, F. *Tetrahedron* **1982**, *38*, 2327. (b) Whitesell, J. K.; Minton, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 225. (c) Rajanbabu, T. V.; Fukunaga, T.; Reddy, G. S. *J. Am. Chem. Soc.* **1989**, *111*, 1759. (d) Yadav *et al. Can. J. Chem.* **1991**, *69*, 779

(22) (a) Koda, Y.; Omer, E. S. A.; Yoshihara, T.; Shibata, H.; Sakamura, S.; Okazawa, Y. *Plant Cell Physiol.* **1988**, *29*, 1047. (b) Yoshihara, T.; Omer, E. S. A.; Koshino, H.; Sakamura, S.; Kikutu, Y.; Koda, Y. *Agric. Biol. Chem.* **1989**, *53*, 2835. (c) Yoshihara, T.; Matsuura, H.; Ichihara, A.; Kikuta, Y.; Koda, Y. In *Progress in Plant Growth Regulation*; Karssen, C. M., Van Loon, L. C.; Vreugdenhil, D., Eds.; Academic Publishers: Netherlands, 1992; p 286. (d) Matsuura, H.; Yoshihara, T.; Ichihara, A.; Kukuta, Y.; Koda, Y. *Biosci. Biotech. Biochem.* **1993**, *57*, 1253.

(23) Oppolzer, W.; Ando, A. *Chemia* **1992**, *46*, 122.

(24) Cheng, X.-C.; Varoglu, M.; Abrell, L.; Crews, P.; Lobkovvsky, E.; Clardy, J. *J. Org. Chem.* **1994**, *59*, 6344.

(25) Weyerstahl, P.; Marschall-Weyerstahl, H.; Wahlburg, H.-C. *Liebigs Ann. Chem.* **1989**, 307.

1.22 (s, 3H), 1.52−1.68 (m, 2H), 1.87 (dd, 1H, J = 15.4, 9.3 Hz), 2.14 (dd, 1H, J = 15.5, 5.8 Hz), 2.63−2.73 (m, 1H), 2.79 (dd, 1H, J = 11.1, 8.0 Hz), 3.56 (s, 3H), 3.72 (dd, 1H, J = 8.3 Hz), 4.18 (s, 1H), 4.50 (singlet with allylic fine spliting, 1H), 7.28−7.40 (m, 6H), 7.60−7.68 (m, 4H); ^{1}H-NMR for minor diastereomer **14** (partial) δ 0.75 (s, 3H), 2.23−2.38 (m, 2H), 3.57 (s, 3H), 4.54−4.56 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 173.919 (s), 142.859 (d), 136.286 (d), 134.240 (s), 134.008 (s), 129.459 (d), 129.254 (d), 128.305 (s), 127.253 (d), 126.987 (d) 114.246 (t), 84.073 (d), 54.257 (d), 51.259 (q), 45.246 (t), 41.291 (s), 37.131 (t), 32.824 (d), 27.085 (q), 23.532 (q), 21.408 (q), 19.519 (s); ^{13}C-NMR for minor diastereomer **14** (partial) δ 115.247 (t), 83.400 (d), 61.778 (d), 44.883 (t), 39.385 (t), 33.735 (d), 28.633 (q), 27.293 (q), 25.314 (q), 17.639 (q); GC [OV-17 (fused silica), 0.25 mm × 50 m 250 °C isothermal]; minor isomer t_R 17.158 min (11.89%); major isomer t_R 18.112 min (87.5%); HRMS for ($C_{33}H_{40}O_3Si$) EI (M − C_4H_9) calcd 407.2042, found 407.2032.

Diethyl (1*SR*,2*SR*,3*RS*)-2-[2-Isopropenyl-3-[(*tert*-butyldiphenylsilyl)oxy]-4,4-dimethylcyclopentyl]propane-1,3-dioate (15). To a stirred suspension of dry $ZnBr_2$ (457 mg, 1.99 mmol) in dry dichloromethane (3 mL) was added **6** (1.045 g, 1.9 mmol) dropwise over a period of 10 min under argon. After 3 h the reaction mixture was quenched with saturated aqueous ammonium chloride and extracted with ether (3 × 10 mL). The ether layer was washed with brine, dried ($MgSO_4$), and concentrated to give a colorless oil, **15** (940 mg, 90%): IR 949, 2868, 1734, 1654, 1248, 1161, 892 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.79 (s, 3H), 1.01 (s, 9H), 1.03 (s, 3H), 1.07 (s, 3H), 1.18 (t, 3H, J = 7.2 Hz), 1.26 (t, 3H, J = 7.2 Hz), 1.36−1.47 (m, 1H), 1.59−1.71 (m, 1H), 2.25−2.43 (m, 1H), 2.57 (dd, 1H, J = 10.6, 8.5 Hz), 3.26 (d, 1H, J = 8.4 Hz), 3.71 (d, 1H, J = 8.5 Hz), 4.05 (q, 2H, J = 7.2 Hz), 4.17 (q, 2H, J = 7.2 Hz), 4.57−4.58 (m, 2H), 7.30−7.44 (m, 6H), 7.65−7.71 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 168.592 (s), 168.504 (s), 142.586 (s), 136.426 (d), 134.260 (s), 134.088 (s), 129.440 (d), 129.327 (d), 127.272 (d), 127.036 (d), 116.027 (t), 83.453 (d), 61.103 (t), 60.893 (t), 59.155 (d), 56.210 (d), 42.129 (t), 40.529 (s), 35.921 (d), 28.351 (q), 27.161 (q), 24.763 (q), 19.625 (s), 17.418 (q), 14.088 (q), 13.823 (q); HRMS for ($C_{33}H_{46}O_5Si$) EI (M − C_4H_9) calcd for 493.2410, found 493.2403. **15** is contaminated with **17** (4%) as confirmed by conversion of the malonate side chain to methyl acetate and comparison of the products with **13**/**14** by ^{1}H-NMR and capillary GC.

Diethyl (1*SR*,2*RS*,5*RS*)-2-[5-isopropenyl-2-[(*tert*-butyldiphenylsilyl)oxy]cyclopentyl]propane-1,3-dioate (16): ^{1}H-NMR ($CDCl_3$) δ 1.05 (s, 9H), 1.17 (t, 3H, J = 7.2 Hz), 1.18 (t, 3H, J = 7.2 Hz), 1.42−1.75 (m, 6H), 1.76 (s, 3H), 2.58−2.64 (m, 2 H), 3.30 (d, 1H), 3.96−4.10 (m, 5H), 4.68−4.71 (m, 2H), 7.26−7.42 (m, 6H), 7.60−7.69 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 168.65 (s), 168.38 (s), 146.95 (s), 135.92 (d), 135.80 (d), 134.67 (s), 133.96 (s), 129.55 (d), 129.49 (d), 127.53 (d), 127.46 (d), 111.01 (t), 78.13 (d), 60.93 (t), 60.86 (t), 52.84 (d), 50.94 (d), 48.31 (d), 34.18 (t), 29.37 (t), 26.97 (q), 19.17 (s), 18.80 (q), 13.91 (q); HRMS for ($C_{31}H_{42}O_5Si$) EI (M − C_4H_9) calcd for 465.2096, found 465.2097.

Methyl (1*RS*,2*SR*,3*SR*)-2-[2-[(*E*)-3-(trimethylsilyl)-1-propenyl]-3-[(*tert*-butyldiphenylsilyl)oxy]cyclopentyl]-acetate (22) and methyl (1*RS*,2*SR*,3*RS*)-2-[2-[(*E*)-3-(trimethylsilyl)-1-propenyl]-3-[(*tert*-butyldiphenylsilyl)-oxy]cyclopentyl]acetate (29): IR 3050, 2942, 1738, 1624, 1440, 1258, 1168, 1092, 842, 704 cm^{-1}; ^{1}H-NMR for major isomer **22** ($CDCl_3$) δ −0.10 (s, 9H), 1.04 (s, 9H), 1.17−1.25 (m, 1H), 1.29 (d, 2H, J = 8.0 Hz), 1.59−1.66 (m, 1H), 1.78−1.86 (m, 1H), 1.93−2.0 (m, 1H), 2.15 (dd, 1H, J = 15.5 and 8.7 Hz), 2.30 (dd, 1H, J = 15.5 and 6.7 Hz), 2.52 (t, 1H, J = 8 Hz), 2.69−2.80 (m, 1H), 3.636 (s, 3H), 3.98−4.00 (m, 1H), 4.73 (dd, 1H, J = 15 and 10 Hz), 5.13 (dt, 1H, J = 15 and 8 Hz), 7.32−7.41 (m, 6H), 7.60−7.65 (m, 4H). Irradiation at δ 2.75 results in collapse of two four-line signals at δ 2.14 and 2.3 (due to CH_2CO$_2$Me) into a two two-line signals: ^{1}H-NMR for other minor diastereomer **29** (partial) δ 0.01 (s, 9H), 1.03 (s, 9H), 2.35−2.48 (m, 2H), 3.61 (s, 3H), 4.15−4.21 (m, 1H), 5.34−5.36 (m, 2H); ^{13}C-NMR for major isomer **22** δ 173.923 (s), 135.889 (d), 135.799 (d), 134.729 (s), 134.526 (s), 129.414 (d), 129.228 (d), 127.464 (d), 125.504 (d), 80.376 (d), 55.520 (d), 51.262 (q), 37.032 (d), 36.400 (t), 33.347 (t), 28.481 (t), 27.024 (q), 23.103 (t), 19.146 (s), −1.958 (q); ^{13}C-NMR ($CDCl_3$) for other minor diastereomer **29** δ 124.863 (d), 77.210 (d), 51.954, 37.459, 37.251, 32.485 (t), 29.696, 27.861, −1.812 (q); GC−MS (COL SGE-BP-5, 0.32 mm/25 m, isothermal 260 °C) one major peak **22** t_R = 23.22 min (89.5%); m/z (relative intensity) no M$^+$, 493 (M − Me, 41), 486 (4), 477 (54), 451 (M − Me_3C, 100) 419 (1.5), 377 (4), 347 (3), 335 (3), 303 (4), 273 (3), 271 (26), 221 (4), 213 (23), 199 (44), 181 (5), 153 (5), 135 (21), 119 (5), 105 (12), 91 (4), 79 (5), 73 (38); trace diastereomer t_R = 23.40 min (0.8%); m/z (relative intensity) no M$^+$, 451 (M − Me_3C, 100), 441 (4), 417 (5), 395 (4), 380 (8), 349 (7), 319 (6), 281 (36), 269 (36), 257 (12), 252 (13), 243 (28), 231 (12), 219 (40), 199 (68), 181 (20), 155 (14), 135 (18), 119 (75), 107 (14), 92 (12), 73 (24), 69 (84); minor diastereomer **29** t_R = 25.55 min (9.7%); m/z (relative intensity) no M$^+$, 451 (M − Me_3C, 100), 431 (2), 419 (3), 393 (9), 348 (9), 335 (17), 301 (7), 281 (5), 271 (20), 263 (5), 225 (14), 213 (25), 199 (40), 183 (10), 166 (5), 135 (28), 105 (12), 73 (68). Anal. Calcd for $C_{30}H_{44}O_3Si_2$: C, 70.71; H, 8.74. Found: C, 70.82; H, 8.71.

Methyl 2-[2-(2-Propenyl)-3-[(*tert*-butyldiphenylsilyl)-oxy]cyclopentyl]acetate (21). To a stirred solution of **22**/**29** (450 mg, 0.89 mmol) in dry benzene (12 mL) was added 57% aqueous hydrogen iodide (0.113 mL), and the mixture was stirred for 12 h at room temperature. The organic layer was washed with water (2 × 15 mL) and brine, dried (Na_2SO_4), and concentrated. Preparative layer chromatography [silica gel 2% ethyl acetate−petroleum ether (60−80 °C) as developing solvent] of the residue gave **21** (305 mg, 79%) as a colorless thick oil: IR 3056, 2942, 1736, 1642, 1444, 1362, 1268, 1174, 1090, 914, 826, 706 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.07 (s, 9H), 1.14−1.33 (m, 1H), 1.55−2.1 (m, 6H), 2.17 (dd, 1H, J = 15.09 and 9.4 Hz), 2.39 (dd, 1H, J = 15.09 and 6.4 Hz), 2.7−2.92 (m, 1H), 3.67 (s, 3H), 3.98−4.08 (m, 1H), 4.75−4.90 (m, 2H), 5.27−5.52 (m, 1H), 7.32−7.48 (m, 6H), 7.62−7.75 (m, 4H); ^{1}H-NMR for other minor diastereomer δ 2.52−2.62 (m, 1H), 4.18−4.28 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 173.787 (s), 137.083 (d), 135.855 (d), 134.622 (s), 134.380 (s), 129.455 (d), 127.476 (d), 115.484 (t), 78.186 (d), 51.421 (q), 50.056 (d), 36.158 (d), 35.422 (t), 32.513 (t), 31.470 (t), 28.182 (t), 27.019 (q), 19.131 (s); EIMS m/z (relative intensity) 435 (M − 1, 0.7), 405 (2), 379 (M − Me_3C, 64), 347 (5), 305 (18), 259 (18), 213 (25), 199 (100), 181 (20), 149 (14), 135 (22), 107 (25), 79 (23). Anal. Calcd for $C_{27}H_{36}O_3Si$: C, 73.98; H, 8.32. Found: C, 74.27; H, 8.30.

Methyl 2-[2-(2-Oxoethyl)-3-[(*tert*-butyldiphenylsilyl)-oxy]cyclopentyl]acetate (20). Ozone was bubbled through a solution of **21** (265 mg, 0.61 mmol) in methanol (25 mL) at −78 °C till the blue color persisted for more than 10 min. The excess ozone was removed by allowing nitrogen gas to bubble through the solution at −78 °C. Dimethyl sulfide (3.2 mL) was added dropwise at the same temperature. The mixture was allowed to attain room temperature and stirred for 2 h. Excess dimethyl sulfide was removed by bubbling nitrogen gas through the solution, and solvent was removed *in vacuo*. Preparative layer chromatography [silica gel 5% ethyl acetate−petroleum ether (60−80 °C) as developing solvent] of the residue gave **20** (237 mg, 88%): IR 2932, 2720 (w), 1728, 1444, 1268, 1178, 1098, 824, 708 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.06 (s, 9H), 1.12−1.27 (m, 1H), 1.55−2.58 (m, 9H), 2.72−2.95 (m, 1H), 3.65 (s, 3H), 3.88−3.98 (m, 1H), 7.33−7.48 (m, 6H), 7.6−7.7 (m, 4H), 9.28 (unresolved triplet 1H); ^{1}H-NMR (partial) for other minor diastereomer δ 4.25−4.42 (m, 1H).

Methyl 2-[2-[(*Z*)-2-Pentenyl]-3-[(*tert*-butyldiphenylsilyl)oxy]cyclopentyl]acetate (30). To a mixture of triphenylpropylphosphonium bromide (810 mg, 2.1 mmol) and $NaN(TMS)_2$ (365 mg, 2.0 mmol) was added tetrahydrofuran under argon atmosphere. The mixture was stirred for 1 h at room temperature. During this period the mixture developed a bright orange color, indicating the formation of the ylide. To a solution of **20** (220 mg, 0.5 mmol) in tetrahydrofuran (8 mL) was added the solution of the ylide at −78 °C during 30 min. The mixture was stirred for 1.5 h at −78 °C, 1 h at −50 °C, 1 h at −30 °C, and 1.5 h at 0 °C and then the mixture allowed to attain room temperature and stirred overnight whereby the orange color disappeared and a whitish suspension formed. This was diluted with petroleum ether (60−80 °C) and the precipitated triphenylphosphine oxide separated

by filtration. The filtrate was concentrated and the residue passed through a bed of silica gel. The crude oil thereby obtained was chromatographed over silica gel and eluted with ethyl acetate−petroleum ether (60−80 °C) (3:97) to give **30** as a colorless thick oil (116 mg, 50% yield): IR 2924, 2856, 1744, 1611, 1248, 1158, 1098, 1053, 841, 698, 611 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.85 (t, 3H, J = 7.5 Hz), 1.05 (s, 9H), 1.15−1.38 (m, 1H), 1.55−2.1 (m, 8H), 2.17 (dd, 1H, J = 15 and 9.4 Hz), 2.38 (dd, 1H, J = 15 and 6.4 Hz), 2.70−2.91 (m, 1H), 3.67 (s, 3H), 3.96−4.05 (m, 1H), 4.85−5.0 (m, 1H), 5.12−5.35 (m, 1H), 7.3−7.48 (m, 6H), 7.58−7.7 (m, 4H); ^{1}H-NMR for other minor diastereomer (partial) δ 0.955 (t, 3H, J = 7.5 Hz), 2.45−2.6 (m, 1H), 4.15−4.25 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 173.768 (s), 135.776 (d), 134.456 (s), 134.325 (s), 132.268 (d), 129.358 (d), 127.394 (d), 127.010 (d), 78.296 (d), 51.332 (q), 50.772 (d), 36.196 (d), 35.423 (t), 32.570 (t), 28.113 (t), 26.949 (q), 24.390 (t), 20.402 (t), 19.056 (s), 14.010 (q); ^{13}C-NMR for other minor diastereomer (partial) δ 128.219 (d), 48.459, 33.149, 28.741, 22.880. Anal. Calcd for $C_{29}H_{40}O_3Si$: C, 74.78; H, 8.70; Found: C, 74.96; H, 8.67.

Methyl (1*RS*,2*SR*,3*SR*)-2-[2-[(*Z*)-2-Pentenyl]-3-hydroxycyclopentyl]acetate (Methyl Cucurbate, 19). To a solution of **30** (145 mg, 0.312 mmol) in tetrahydrofuran (5 mL) was added tetrabutylammonium fluoride trihydrate (198 mg, 0.63 mmol) under an argon atmosphere. After being stirred for 24 h at room temperature, the mixture was partitioned between ether and saturated aqueous sodium chloride, and the aqueous layer was extracted with ether (3 × 15 mL). The combined ether extracts were dried ($MgSO_4$) and concentrated *in vacuo*. Preparative layer chromatography [silica gel 15% ethyl acetate−petroleum ether (60−80 °C) as developing solvent] of the residue afforded a first fraction (∼3 mg) [^{1}H NMR δ 0.97 (t), 4.6 (bs), 5.35−5.45 (m)] and a second fraction, **19** (63 mg, 89%), as a colorless oil: IR 3420, 2924, 2857, 1730, 1631, 1454, 1250, 1162, 1054, 689, 615 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.94 (t, 3H, J = 7.5 Hz), 1.19−1.36 (m, 1H), 1.42−1.64 (m, 2H), 1.78−2.11 (m, 7H), 2.17 (dd, 1H, J = 15.1 and 9.3 Hz), 2.39 (dd, 1H, J = 15.1 and 6.3 Hz), 2.53−2.75 (m, 1H), 3.64 (s, 3H), 3.83−4.06 (m, 1H), 5.22−5.50 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 173.699 (s), 133.014 (d), 127.079 (d), 77.412 (d), 51.474 (q), 50.559 (d), 36.661 (d), 35.264 (t), 32.472 (t), 28.289 (t), 25.249 (t), 20.607 (t), 14.115 (q); GLC (column 3% OV-17, N_2 40 mL/min, 210 °C isothermal) t_R = 9.77 min; EIMS m/z (relative intensity) 226 (M^+, 0.6), 208 (M − 18, 5), 195 (2), 165 (7), 153 (85), 134 (37), 119 (17), 109 (20), 97 (35), 83 (100), 79 (64), 67 (45), 55 (49), 41 (74), 29 (30).

Methyl (1*RS*,2*SR*)-2-[2-[(*Z*)-2-Pentenyl]-3-oxocyclopentyl]acetate (Methyl Epijasmonate, 18). A chromic acid solution was prepared from sodium dichromate (5.0 g, 16.8 mmol) and 95% sulfuric acid (6.93 g, 54.2 mmol) and diluted with water to make up 25 mL of total volume. To a solution of **19** (33 mg, 0.146 mmol) in ether (2.5 mL) was added chromic acid solution (0.29 mL of the stock solution) with ice cooling. The mixture was stirred for 20 min, and to this were added excess 2-propanol and then sodium bicarbonate. The mixture was filtered and extracted with ether. The combined ether extracts were washed with water and brine, dried (Na_2SO_4), and concentrated *in vacuo*. The residue was chromatographed over silica gel and eluted with ethyl acetate−petroleum ether (60−80 °C) (1:9) to give **18** (23 mg, 70%): IR 2960, 1737, 1642, 1442, 1311, 1259, 1168, 1021, 807, 696, 616 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.91 (t, 3H, J = 7.5 Hz), 1.62−2.44 (m, 11H), 2.72−2.97 (m, 1H), 3.64 (s, 3H), 5.2−5.5 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 218.768 (s), 172.855 (s), 133.479 (d), 125.460 (d), 52.672 (d), 51.671 (q), 35.590 (d), 35.247 (t), 33.739 (t), 25.668 (t), 22.949 (t), 20.626 (t), 14.016 (q); ^{13}C-NMR of the trace (7−10%) C2 epimer of (±)-**18** (partial) δ 134.069, 53.999, 38.795, 38.015, 37.712.

Methyl (1*RS*,2*RS*)-2-[2-[(*Z*)-2-Pentenyl]-3-oxocyclopentyl]acetate (Methyl Jasmonate, C2 Epimer of (±)-18). A drop of 1.5 N HCl was added to a solution of **18** (12 mg) in benzene. The solution was stirred for 1.5 h. The crude product was passed through a short silica gel column, and elution with 10% ethyl acetate−petroleum ether (60−80 °C) and concentration of the solvent gave the C2 epimer of (±)-**18** (10 mg) as an oil: IR 2925, 1860, 1739, 1447, 1245, 1162 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 0.93 (t, 3H, J = 7.5 Hz), 1.4−1.6 (m, 1H), 1.72−1.92 (m, 1H), 1.94−2.45 (m, 10H), 2.6−2.8 (m, 1H), 3.67 (s, 3H), 5.18−5.37 (m, 1H), 5.38−5.05 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 219.0 (s), 172.43 (s), 134.0 (d), 124.87 (d), 53.91 (d), 51.51 (q), 38.72 (t), 37.94 (d), 37.64 (t), 27.13 (t), 25.42 (t), 20.52 (t), 14.0 (q); ^{13}C-NMR of the minor epimer **18** (partial) δ 125.37, 52.6, 35.52, 35.18, 33.65, 22.87; GC [OV-17 (fused silica) 10.25 mm × 50 m, 80−220 °C, 4 °C min] t_R = 25.16 min (95%) and t_R = 25.97 min (5%).

Acknowledgment. We thank CSIR [2(323)/91-EMR-II] and DST (SP/SI/G76/90), Government of India, for funding of this work. The CSIR, New Delhi, is also thanked for the award of Senior Research Fellowship to B.K.G., S.K.N., and B.M. We are thankful to Prof. G. Helmchen and Prof. T. Kitahara for providing comparison spectra of authentic methyl epijasmonate. Dr. C. Fehr (Firmenich, Geveva), Mr. P. Pradhan (BARC, Bombay), and Dr. S. K. Ghosh (BARC, Bombay) are thanked for their help.

Supporting Information Available: Complete experimental procedure for **1**−**7** and **23** and spectroscopic/chemical characterization of **8**−**17** and **22** (20 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

JO961739N