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Synthetic Photochemistry. XXIX.[1] A Convenient Preparation of 1,2,3-Substituted Cyclopentenes from the Photoadducts of Methyl 2,4-Dioxopentanoate-Isoprene

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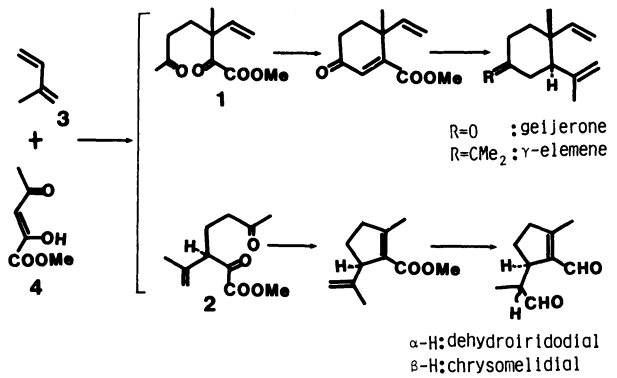
Photoadducts obtained by cycloaddition of isoprene with methyl 2,4-dioxopentanoate were converted to cyclopentene derivatives. The stereochemistry of the intermediate glycols was estabilished by chemical correlations to each other; only the *cis*-glycols were convertible to the cyclopentenes under the conditions employed, suggesting a fore-going acetylation of the hindered glycol functions.

Previously, we have obtained two photocycloadducts (**1** and **2**) from isoprene (**3**) and methyl 2,4-dioxopentanoate (**4**),[2] and have utilized them for mono- and sesquiterpenoid syntheses; *i.e.*, **1** to geijerone and γ-elemene,[2] and **2** to dehydroiridodial and chrysomelidial.[3] It is noteworthy that the easy access of cyclopentane derivatives from **2** in the latter case provided a new method of C_5-homologation leading to the higher terpenic cyclopentanes having correct head-to-tail arrangement.[4] Since the photochemical addition proceeds in a highly regioselective manner,[5] and is effective even with the conjugated olefins,[1,6] fundamental understanding of this cyclopentane formation is important. We wish herein to present experimental details of the formation of 1,2,3-substituted cyclopentane derivatives from the photoadducts, **1** and **2**, by the Mukaiyama-McMurry reaction.[7]



Scheme 1.

The Reductive Cyclization of Methyl 3-Methyl-3-vinyl-2,6-dioxoheptanoate (1). When methyl 3-methyl-3-vinyl-2,6-dioxoheptanoate (**1**) was treated with titanium(II) chloride in tetrahydrofuran (THF), prepared *in situ* from titanium(IV) chloride and zinc, four isomeric reductive cyclisates, 1,2-dihydroxy-2-methoxycarbonyl-1,3-dimethyl-3-vinylcyclopentanes, **5** (45%), **6** (1%), **7** (2%), and **8** (37%), were obtained. Two major products (**5** and **8**) afforded 2,2-dimethyl-1,3-dioxolane derivatives (**9** and **10**) by treatment with 2,2-dimethoxypropane (DMP) and pyridinium *p*-toluenesulfonate (PPTS) in benzene, while the other two (**6** and **7**) were recovered unchanged. Based on these facts, **5** and **8** are deduced to be *cis*-glycol derivatives, and **6** and **7** are thus *trans*-glycols.

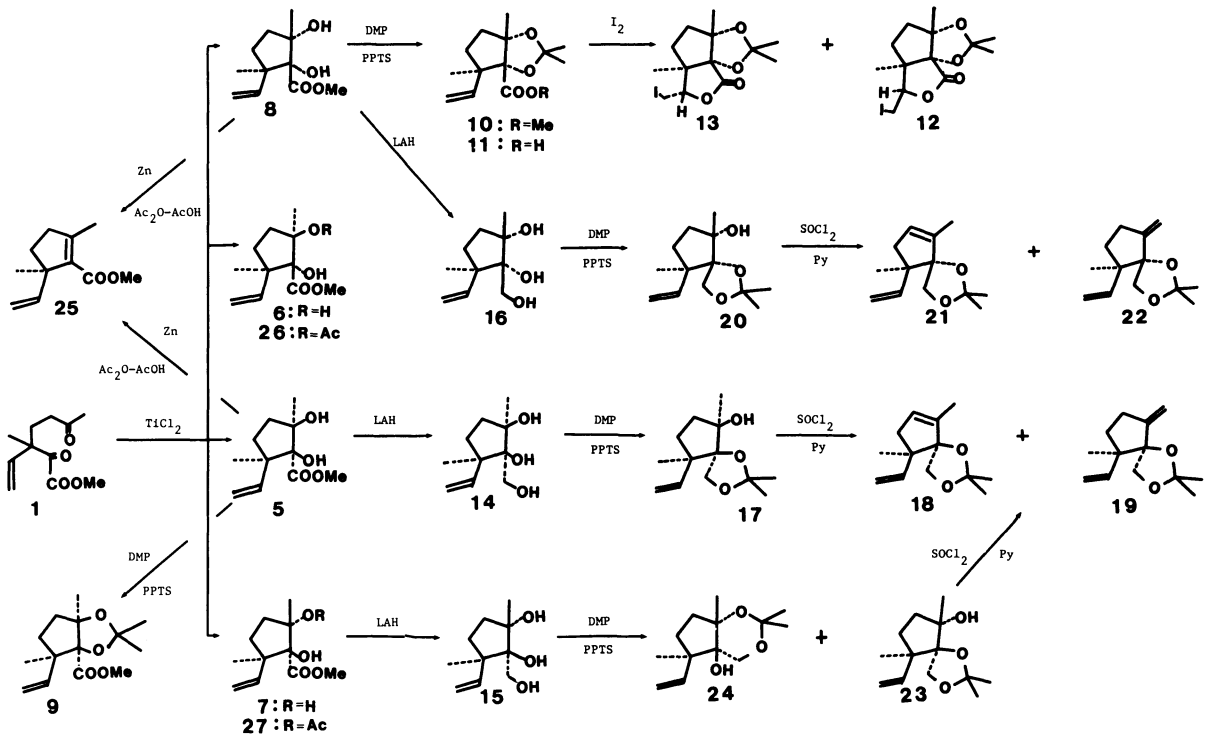
Consecutive treatments of **10** with sodium hydroxide in dimethyl sulfoxide (DMSO), and with iodine and sodium hydrogencarbonate in acetonitrile afforded, *via* the carboxylic acid (**11**), iodo γ-lactone derivatives (**12** and **13**), in 92 and 6% yields. Therefore, the ester and vinyl groups of **8** and **10** are in a *cis* relationship, and the full stereochemistry of **5** and **8** must be depicted as shown.

Moreover, the lithium aluminum hydride (LAH)-reduction of **5**, **7**, and **8** yielded the triol derivatives (**14**, **15**, and **16**) in good yields. Upon treatment of **14** with PPTS and DMP, the single dioxolane derivative (**17**) was obtained in 94% yield. Treatment of **17** with thionyl chloride in pyridine gave a 5:2-mixture of the unsaturated, anhydro 1,3-dioxolane derivatives (**18** and **19**), in 81% yield. On the other hand, the same treatment of **16** gave, *via* the 1,3-dioxolane (**20**), a 2:1-mixture of the unsaturated 1,3-dioxolane derivatives (**21** and **22**).

In the case of **15** (the triol derived from **7**), one of the *trans*-glycols, the DMP treatment afforded two acetals; one was the 1,3-dioxolane (**23**), and the other, a 1,3-dioxane (**24**). Treatment of **23** with thionyl chloride caused a facile dehydration to a mixture of unsaturated 1,3-dioxolanes, which consisted of **18** and **19** on the basis of NMR and gas-liquid chromatographic analyses. Therefore, the remaining products, **6** and **7**, must also have the configurations indicated.

Interestingly, the glycols, **5** and **8**, were reduced to the same cyclopentene derivative (**25**) by zinc in acetic acid and acetic anhydride, while the trans-isomers, **6** and **7**, merely formed monoacetates (**26** and **27**) under comparative conditions.

The Reductive Cyclization of Methyl 3-Isopropenyl-2,6-dioxoheptanoate (2). Methyl 3-isopropenyl-2,6-dioxoheptanoate (**2**) was treated with titanium(II) chloride to obtain three cyclopentanediols (**28**, **29**, and **30**) in a ratio of 1:1.5:9. By further reduction



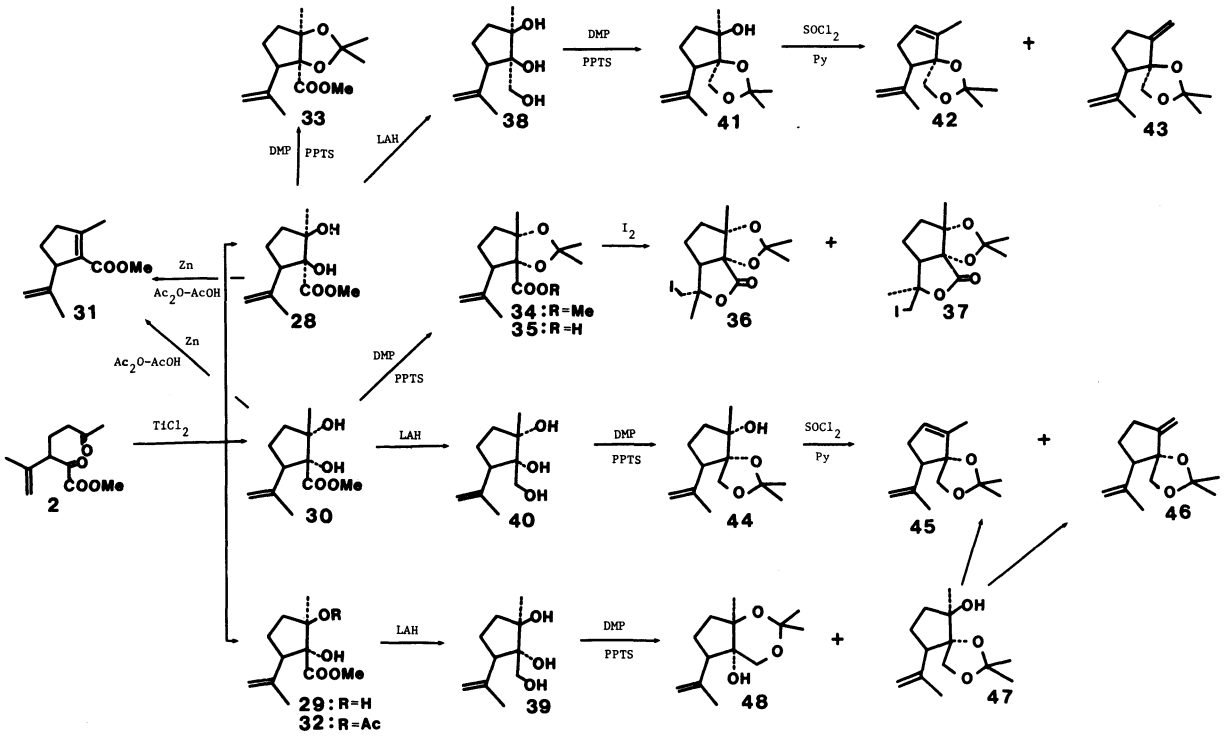
Scheme 2.

with zinc in acetic acid and acetic anhydride,[3] **28** and **30** yielded the same cyclopentene (**31**),[8] while the remaining **29** resulted in a monoacetylation to **32**, but not to **31**. By analogy with **6** and **7**, this might indicate the *trans* relationship for the glycol function of **29**. Indeed, **28** and **30** afforded the 2,2-dimethyl-1,3-dioxolane derivatives (**33** and **34**). The iodolactonization reaction of the acid (**35**) derived from **34** produced two iodo γ-lactones (**36** and **37**); the major product, **36**, colorless needles, showed an IR absorption due to $\nu_{C=O}$ at 1780 cm^{-1}. These two observations clarified the stereochemistry of **28** and **30** as depicted.

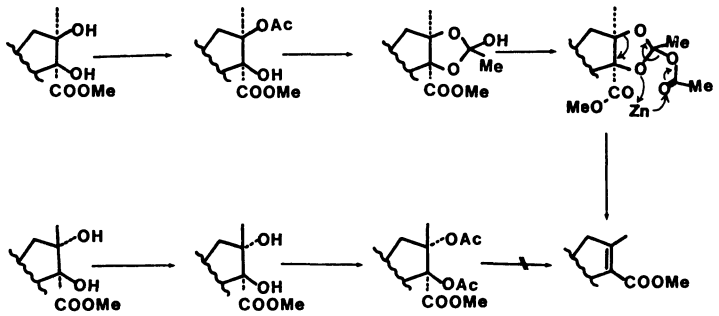
The stereochemistry of the minor product, **29**, was unambiguously elucidated by the following chemical correlations; the LAH-reduction of **28**, **29**, and **30** respectively afforded the triol derivatives (**38**, **39**, and **40**) in good yields. Treatment of **38** with DMP and PPTS in THF gave the 1,3-dioxolane (**41**), which upon treatment with thionyl chloride in pyridine afforded an isomeric pair of unsaturated 1,3-dioxolanes (**42** and **43**). Similarly, the DMP-treatment of **40** with PPTS afforded another 1,3-dioxolane (**44**), which was converted to a mixture of unsaturated 1,3-dioxolanes (**45** and **46**).

Subsequently, the DMP-treatment of the remaining triol (**39**) with PPTS was carried out to obtain two products, **47**, 40%, and **48**, 49%; the NMR analysis indicated that **47** was the expected 1,3-dioxolane, while **48** was the 1,3-dioxane. The similar dehydration of **47** as in the cases of **41** and **44**, afforded a mixture of the unsaturated 1,3-dioxolanes. This mixture was indeed identical with **45** and **46** in respect of NMR spectral and gas-liquid chromatographic analyses. Therefore, **39** and **40** mutually differ in the stereochemistry of the methyl and hydroxyl groups at C-1; the structure of **29** should be as shown.

In conclusion, it is particularly noteworthy that, for both series, the major cyclopentanediols were *cis*-derivatives. And the highly specific conversion to cyclopentene derivatives from only *cis*-glycols has supported the correctness of the orthoacetate mechanism already proposed.[9] Namely, the difference between the *cis*- and *trans*-glycols can be explained in of the structural difference of "diacetates"; it is well known that even hindered *cis*-glycols form diacetates by acetyl migration *via* bridged intermediates, while the *trans*-glycols can not make such an intermediate. It is true that in this case no *cis*-diacetate could be detected, and probably, they should have been rapidly reduced to olefins under the reaction conditions. On the other hand, the *trans*-diacetate, whose formation was in fact identified,[10] must suffer a severe steric hindrance. Should the reduction proceed *via* the *trans* elimination like ordinary debromination, the *trans*-isomers must be more favorable than the *cis*-isomers. But, this was not the case. Therefore, the reduction should occur from the orthoester acetates, 2-acetoxy-2-methyl-1,3-dioxolanes, which should be formed from the immediate precursors by the acid-catalyzed solvolysis.[11] Furthermore, this cyclopentene formation is to be expectable only with the photoadducts of **4** but not with those of acetylacetone, due to their readiness to give the cyclohexenones.[12] The relative unreactivity of the pho-



Scheme 3.



Scheme 4.

toadducts of **4** towards acid and base should have become favorable for this reductive cyclization.

Experimental

The mps were measured with Yanagimoto Micro-mp apparatus, and not corrected. The elemental analyses were performed by Miss S. Hirashima of this Institute. All the NMR spectra were taken on a JEOL FX 100 Model spectrometer in $CDCl_3$ solutions, and the chemical shifts expressed in δ unit were from the internal Me_4Si. Mass spectra were measured on a JEOL 01SG-2 Model apparatus. The IR spectra were measured on a Jasco IRA 102 Model spectrophotometer. The gas-liquid chromatographic analyses were performed on a JEOL JGC 20 K Model apparatus with a 200 cm column of 20% DOP on Uniport B (temperatures of column and injection chamber were 140 °C and 160 °C, and carrier gas (N_2) flow was 32 cm³/min), and the retention times measured under those conditions were designated by the term, *RT*.

$TiCl_2$-reduction of 1. To a THF-complex of $TiCl_4$ (prepared from 1.65 cm³) in anhydrous THF (200 cm³), Zn (2.0 g) was added at 0 °C under stirring. After a yellow coloration of the complex faded out completely, pyridine (1.2 cm³) was added. Then, into the resultant suspension, **1** (2.12 g) was added dropwise over a period of 30 min. After additional stirring for 1 h at 15—25 °C, the mixture was quenched with aqueous 30%-K_2CO_3, and fractionated with ether. After removing the precipitates through a short Celite column, the filtrate was evaporated, and chromatographed on a silica-gel (Wakogel C 300) column. From the least polar fractions from hexane-EtOAc (6:1), colorless granules, mp 59.5—60.5 °C, 960 mg (45%), **5** [Found: C, 61.47; H, 8.51%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%. ^{1}H-NMR δ=1.10 (3H, s), 1.28 (3H, s), 1.6—2.3 (4H, m), 2.90 (1H, br. s, OH), 3.71 (3H, s), 3.84 (1H, s, OH), 4.92 (1H, dd, J=10.3, 1.6 Hz), 4.98 (1H, dd, J=17.8, 1.6 Hz), and 5.78 (1H, dd, J=17.8, 10.3 Hz). ^{13}C-NMR δ=24.2, 24.9, 33.3, 35.7, 50.5, 52.4, 80.6, 88.8, 112.6, 144.0, and 175.3. ν: 3475, 3400, 2955, 1730, 1637, 1438, 1248, 1154, 1132, 1006, and 901 cm^{-1}. *m/z*: 214 (M^+)], was obtained. Subsequently, colorless

prisms, mp 66—66.5 °C, **6** [Found: C, 61.93; H, 8.50%. ^{1}H-NMR δ=1.26 (3H, s), 1.33 (3H, s), 1.7—2.1 (4H, m), 2.70 (1H, s, OH), 3.78 (3H, s), 3.94 (1H, br. s, OH), 5.17 (1H, dd, J=17.3, 1.6 Hz), 5.25 (1H, dd, J=10.9, 1.6 Hz), and 5.94 (1H, dd, J=17.3, 10.9 Hz). ^{13}C-NMR δ=23.5, 26.0, 34.2, 37.2, 51.7, 52.1, 84.0, 86.0, 115.8, 142.3, and 174.3. ν: 3500, 3400, 2965, 1706, 1640, 1451, 1383, 1252, 1198, 1042, 1029, and 906 cm^{-1}. m/z: 214 (M^+)], 19 mg (1%), and colorless needles, mp 105.5—106 °C, **7** [Found: C, 61.65; H, 8.52%. ^{1}H-NMR δ=1.20 (3H, s), 1.34 (3H, s), 1.4—2.3 (4H, m), 2.98 (1H, s, OH), 3.58 (1H, br. s, OH), 3.71 (3H, s), 4.87 (1H, dd, J=11, 1.4 Hz), 4.91 (1H, dd, J=17.4, 1.4 Hz), and 6.17 (1H, dd, J=17.4, 11 Hz). ^{13}C-NMR δ=20.5, 23.5, 36.8, 37.3, 51.2, 52.2, 83.9, 88.5, 111.3, 145.9, and 174.0. ν: 3470, 3340, 2975, 1712, 1634, 1390, 1251, 1068, 1036, 907, and 865 cm^{-1}. m/z: 214 (M^+)], 45 mg (2%), were obtained. The most polar fractions eluted with hexane-EtOAc (4:1) were colorless plates, mp 25 °C, **8** [Found: M^+, 214.1196. Calcd for $C_{11}H_{18}O_4$: 214.1204. ^{1}H-NMR δ=1.03 (3H, s), 1.13 (3H, s), 1.7—2.2 (4H, m), 2.64 (1H, br. s, OH), 3.64 (1H, s, OH), 3.80 (3H, s), 5.02 (1H, dd, J=11.1, 1.4 Hz), 5.04 (1H, dd, J=17.4, 1.4 Hz), and 6.33 (1H, dd, J=17.4, 11.1 Hz). ^{13}C-NMR δ=21.9, 24.2, 33.4, 36.2, 50.2, 52.4, 81.0, 89.2, 111.5, 144.3, and 174.5. ν: 3470, 3410, 2950, 1724, 1633, 1244, and 1138 cm^{-1}], 790 mg (37%).

DMP-acetalization of 5 to 9. A mixture of **5** (86 mg), DMP (1 cm^3), and PPTS (15 mg) in benzene (2 cm^3) was refluxed on an oil bath for 15 h. The mixture was then poured into $NaHCO_3$ solution, extracted with ether, and chromatographed on a silica-gel column with hexane-EtOAc (15:1) to give a colorless oil, 92 mg (90%), **9** [Found: M^+, 254.1512. Calcd for $C_{14}H_{22}O_4$: 254.1517. ^{1}H-NMR δ=1.21 (3H, s), 1.32 (3H, br. s), 1.50 (3H, br. s), 1.58 (3H, s), 1.6—2.0 (4H, m), 3.70 (3H, s), 5.00 (1H, dd, J=10.1, 1.3 Hz), 5.02 (1H, dd, J=18.0, 1.3 Hz), and 5.91 (1H, dd, J=18.0, 10.1 Hz). ν: 2990, 1738, 1637, 1460, 1380, 1267, 1086, 1058, 1043, 998, and 914 cm^{-1}].

DMP-acetalization of 8 to 10. Similarly, a benzene solution of **8** (67 mg) was refluxed for 15 h with DMP (1 cm^3) and PPTS (15 mg). Chromatographic purification of the product afforded a colorless oil, 77 mg (98%), **10** [Found: M^+, 254.1506. ^{1}H-NMR δ=1.01 (3H, br. s), 1.28 (3H, br. s), 1.47 (3H, br. s), 1.61 (3H, s), 1.7—2.4 (4H, m), 3.73 (3H, s), 4.99 (1H, dd, J=17.4, 1.4 Hz), 5.07 (1H, dd, J=10.9, 1.4 Hz), and 6.08 (1H, dd, J=17.4, 10.9 Hz). ν: 2990, 1738, 1637, 1454, 1380, 1265, 1088, 1046, 913, and 848 cm^{-1}].

Saponification and Iodolactonization of 10 to 12 and 13 via 11. To a DMSO solution (1 cm^3) of **10** (47 mg), an aqueous 20%-NaOH (0.6 cm^3) was added and refluxed for 2 h. The mixture was acidified with dil HCl, and extracted with ether to give colorless needles, mp 60.5—61.5 °C, **11**, 44 mg (100%) [Found: C, 64.78; H, 8.40%. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39%. ^{1}H-NMR δ=1.09 (3H, br. s), 1.37 (3H, br. s), 1.49 (3H, br. s), 1.60 (3H, s), 1.7—2.4 (4H, m), 5.06 (1H, dd, J=17.3, 1.3 Hz), 5.11 (1H, dd, J=11.0, 1.3 Hz), and 5.98 (1H, dd, J=17.3, 11.0 Hz). ν: 3500—2500, 2990, 1705, 1638, 1450, 1378, 1272, 1090, 1073, 1030, and 910 cm^{-1}. m/z: 240 (M^+)].

This acid, **11**, was then treated with I_2 (100 mg) in MeCN (2 cm^3) in the presence of $NaHCO_3$ (100 mg). After being stirred at 15—25 °C for 15 h, excess I_2 was decomposed with aqueous $NaHSO_3$, and extracted with ether. Silica-gel column chromatography (hexane-EtOAc=6:1) gave two epimeric iodo lactones, the major isomer, 62 mg (92%), colorless prisms, mp 84.5—85 °C, **12** [Found: C, 42.85; H, 5.34%. Calcd for $C_{13}H_{19}O_4I$: C, 42.64; H, 5.23%. ^{1}H-NMR δ=1.11 (3H, br. s), 1.41 (3H, br. s), 1.45 (3H, br. s), 1.62 (1H, m), 1.63 (3H, s), 2.1—2.3 (3H, m), 3.06 (1H, dd, J=11, 10 Hz), 3.38 (1H, dd, J=10, 5.5 Hz), and 5.01 (1H, dd, J=11, 5.5 Hz). ν: 2975, 1790, 1380, 1332, 1164, 1045, 1026, 915, 875, and 846 cm^{-1}. m/z: 366 (M^+)], and the minor, 4 mg (6%), a colorless oil, **13** [^{1}H-NMR δ=1.33 (3H, s), 1.42 (3H, br. s), 1.51 (3H, br. s), 1.61 (3H, s), 2.2—2.5 (4H, m), 3.59 (1H, dd, J=10, 6.5 Hz), 3.78 (1H, dd, J=10, 8.5 Hz), and 4.45 (1H, dd, J=8.5, 6.5 Hz)].

The LAH-reduction of 5 to 14. An anhydrous THF solution of **5** (214 mg) was treated with LAH (150 mg) at 15—25 °C for 1 h. The mixture was treated with EtOAc, diluted with aqueous NH_4Cl, and extracted with ether. Silica-gel column chromatography (hexane-EtOAc=1:1) of the extract gave colorless needles, mp 123—123.5 °C, 170 mg (91%), **14** [Found: C, 64.68; H, 9.57%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%. ^{1}H-NMR δ=1.15 (3H, s), 1.39 (3H, s), 1.6—2.0 (4H, m), 2.21 (1H, dd, J=7.3, 6.2 Hz, OH), 2.60 (1H, s, OH), 3.61 (1H, dd, J=11.8, 6.2 Hz), 3.66 (1H, dd, J=11.8, 7.3 Hz), 3.77 (1H, s, OH), 5.01 (1H, dd, J=10.1, 1.3 Hz), 5.05 (1H, dd, J=17.8, 1.3 Hz), and 5.84 (1H, dd, J=17.8, 10.1 Hz). ν: 3440, 3380, 2980, 1657, 1373, 1042, 1004, and 927 cm^{-1}. m/z: 186 (M^+)].

The LAH-reduction of 7 to 15. An anhydrous THF solution (5 cm^3) of **7** (74 mg) was reduced similarly with LAH (60 mg) to give colorless prisms, mp 69—70 °C, 53 mg (82%) **15** [Found: C, 64.51; H, 9.70%. ^{1}H-NMR δ=1.12 (3H, s), 1.36 (3H, s), 1.6—2.1 (4H, m), 2.14 (1H, br. s, OH), 2.43 (1H, br. m, OH), 2.78 (1H, s, OH), 3.57 (1H, dd, J=11.5, 5 Hz), 3.88 (1H, dd, J=11.5, 4 Hz), 5.01 (1H, dd, J=10.5, 1.4 Hz), 5.07 (1H, dd, J=17.7, 1.4 Hz), and 6.13 (1H, dd, J=17.7, 10.5 Hz). ν: 3545, 3390, 2970, 2950, 1630, 1467, 1058, 1006, 994, and 902 cm^{-1}. m/z: 168 (M^+−18)].

The LAH-reduction of 8 to 16. Similarly, **8** (214 mg) was reduced with LAH (150 mg) to give colorless needles, mp 90—91 °C, 148 mg (80%) **16** [Found: C, 64.23; H, 9.69%. ^{1}H-NMR δ=1.08 (3H, s), 1.33 (1H, m), 1.44 (3H, s), 1.7—2.1 (3H, m), 2.10 (1H, dd, J=7.6, 5.5 Hz, OH), 2.82 (1H, s,, OH), 3.43 (1H, s, OH), 3.63 (1H, dd, J=11.0, 5.5 Hz), 3.69 (1H, dd, J=11.0, 7.6 Hz), 5.05 (1H, dd, J=17.3, 1.4 Hz), 5.11 (1H, dd, J=11.0, 1.4 Hz), and 6.15 (1H, dd, J=17.3, 11.0 Hz). ν: 3430, 3370, 2970, 1636, 1379, 1121, 1009, and 975 cm^{-1}. m/z: 168 (M^+−18)].

Reaction of 14 with DMP and PPTS. An anhydrous THF solution (5 cm^3) of **14** (170 mg) was treated with DMP (0.5 cm^3) and PPTS (30 mg), and kept at 15—25 °C for 3 h. The mixture was diluted with aqueous K_2CO_3 and extracted with ether. Silica-gel column chromatography (hexane-EtOAc=8:1) gave a colorless oil, **17**, 195 mg (94%) [Found: M^+, 226.1558. Calcd for $C_{13}H_{22}O_3$: 226.1568. ^{1}H-NMR δ=1.16 (3H, s), 1.25 (3H, s), 1.42 (3H, br. s), 1.46 (3H, br. s), 1.5—1.9 (4H, m), 3.13 (1H, br. s, OH), 3.88 (2H, s), 5.01 (1H, dd, J=10.6, 1.3 Hz), 5.03 (1H, dd, J=17.5, 1.3 Hz), and 5.83 (1H, dd, J=17.5, 10.6 Hz). ν: 3530, 2990, 1635, 1460, 1382, 1372, 1243, 1215, 1048, 914, 875, and 852 cm^{-1}].

Dehydration of 17 to 18 and 19. A pyridine solution (1 cm^3) of **17** (35 mg) was treated with $SOCl_2$ (30 mg) at 0 °C for 1 h. Then the mixture was poured into $NaHCO_3$ solu-

tion, and extracted with ether. The extract was rapidly passed through a silica-gel column with hexane–ether (15:1) to give a colorless oil, 26 mg (81%), whose gas-liquid chromatogram showed the presence of two compounds, **18** [Found: M+, 208.1482. Calcd for $C_{13}H_{20}O_2$: 208.1462. *RT*=23.4 min], and **19** [Found: M+, 208.1478. *RT*=23.9 min], in a ratio of 5:2. This was further confirmed by the ^{1}H-NMR spectral analysis of the mixture [δ=1.15 (3H, s), 1.42 (6H, s), 1.73 (3H, q, *J*=2 Hz), 2.0—2.4 (2H, m), 3.62 (1H, d, *J*=9 Hz), 3.87 (1H, d, *J*=9 Hz), 5.02 (1H, dd, *J*=11.0, 1.5 Hz), 5.05 (1H, dd, *J*=17.3, 1.5 Hz), 5.49 (1H, m), and 5.98 (1H, dd, *J*=17.3, 11.0 Hz) for **18**; δ=1.03 (3H, s), 1.44 (6H, s), 1.5—1.7 (2H, m), 2.3—2.5 (2H, m), 3.66 (1H, d, *J*=8.5 Hz), 3.96 (1H, d, *J*=8.5 Hz), 5.01 (1H, td, *J*=2.5, 0.8 Hz), 5.02 (1H, dd, *J*=17.2, 1.6 Hz), 5.05 (1H, dd, *J*=11.0, 1.6 Hz), 5.25 (1H, br. t, *J*=2.5 Hz), and 5.97 (1H, dd, *J*=17.2, 11.0 Hz) for **19**].

Acetal Formation of 16 with DMP. An anhydrous THF solution (5 cm^3) of **16** (148 mg) was treated with DMP (0.5 cm^3) and PPTS (30 mg) at 15—25 °C for 4 h. The extraction and silica-gel column chromatography of the mixture afforded a colorless oil, **20**, 166 mg (92%) [Found: M+, 226.1578. ^{1}H-NMR δ=1.02 (3H, s), 1.33 (3H, s), 1.37 (3H, br. s), 1.44 (3H, br. s), 1.7—2.1 (4H, m), 3.41 (1H, s, OH), 3.85 (1H, d, *J*=9.5 Hz), 3.98 (1H, d, *J*=9.5 Hz), 4.97 (1H, dd, *J*=17.1, 1.4 Hz), 5.03 (1H, dd, *J*=11.2, 1.4 Hz), and 6.10 (1H, dd, *J*=17.1, 11.2 Hz). ν: 3510, 2990, 1638, 1460, 1382, 1372, 1243, 1050, 878, and 854 cm^{-1}].

Dehydration of 20 to 21 and 22. A pyridine solution (1 cm^3) of **20** (30 mg) was treated with $SOCl_2$ (30 mg) at 0 °C for 1 h. The mixture was poured into $NaHCO_3$ solution, extracted with ether, and passed through a silica-gel column to give colorless oils, **21**, 13 mg (46%) [Found: M+, 208.1445. Calcd for $C_{13}H_{20}O_2$: 208.1462. *RT*=25.6 min. δ=1.08 (3H, s), 1.32 (3H, br. s), 1.43 (3H, br. s), 1.75 (3H, q, *J*=2 Hz), 1.93 (1H, d of quint, *J*=16, 2 Hz), 2.48 (1H, d of quint, *J*=16, 2 Hz), 3.78 (1H, d, *J*=9 Hz), 3.90 (1H, d, *J*=9 Hz), 5.03 (1H, dd, *J*=17.6, 1.6 Hz), 5.03 (1H, dd, *J*=10.7, 1.6 Hz), 5.52 (1H, m), and 6.18 (1H, dd, *J*=17.6, 10.7 Hz)], and **22**, 7 mg (24%) [Found: M+, 208.1483. *RT*=22.5 min. δ=0.92 (3H, s), 1.35 (3H, br. s), 1.40 (3H, br. s), 1.40 (1H, m), 1.96 (1H, ddd, *J*=13, 10, 7 Hz), 2.2—2.7 (2H, m), 3.86 (1H, d, *J*=9 Hz), 3.90 (1H, d, *J*=9 Hz), 5.00 (1H, td, *J*=2.5, 0.8 Hz), 5.02 (1H, dd, *J*=17.2, 1.6 Hz), 5.09 (1H, dd, *J*=11.1, 1.6 Hz), 5.27 (1H, br. t, *J*=2.5 Hz), and 6.09 (1H, dd, *J*=17.2, 11.1 Hz)].

Acetal Formation of 15 with DMP. An anhydrous THF solution (2 cm^3) of **15** (49 mg) was treated with DMP (0.2 cm^3) and PPTS (20 mg) at 15—25 °C for 1 h. The mixture was diluted with aqueous $NaHCO_3$, ether extracted, and chromatographed on a silica-gel column to give a colorless oil, **24**, 17 mg (29%) [Found: M+, 226.1557. ^{1}H-NMR δ=1.05 (3H, s), 1.25 (3H, br. s), 1.39 (3H, s), 1.43 (3H, br. s), 1.6—2.0 (4H, m), 2.28 (1H, br. s, OH), 3.18 (1H, d, *J*=12 Hz), 3.61 (1H, d, *J*=12 Hz), 5.01 (1H, dd, *J*=17.6, 1.4 Hz), 5.02 (1H, dd, *J*=10.5, 1.4 Hz), and 5.89 (1H, dd, *J*=17.6, 10.5 Hz). ν: 3485, 2980, 2950, 1640, 1467, 1448, 1376, 1225, 1052, 913, and 834 cm^{-1}], and a colorless oil, **23**, 35 mg (59%) [Found: M+, 226.1557. ^{1}H-NMR δ=1.12 (3H, s), 1.31 (3H, s), 1.37 (3H, br. s), 1.44 (3H, br. s), 1.6—2.0 (4H, m), 1.80 (1H, s, OH), 3.86 (1H, d, *J*=10 Hz), 4.19 (1H, d, *J*=10 Hz), 5.01 (1H, dd, *J*=10.5, 1.4 Hz), 5.10 (1H, dd, *J*=17.7, 1.4 Hz), and 6.04 (1H, dd, *J*=17.7, 10.5 Hz). ν: 3500, 2990, 1634, 1454, 1381, 1372, 1209, 1049, 1021, 913, and 857 cm^{-1}].

Dehydration of 23 to 18 and 19. A pyridine solution of **23** (33 mg) was treated with $SOCl_2$ (30 mg) at 0 °C for 1 h. The mixture was washed with aqueous $NaHCO_3$, and extracted with ether to give a colorless oil, 25 mg (82%), whose NMR was identical with that of the products, a mixture of **18** and **19**, obtained from **17**, and the gas-liquid chromatograms from the both sources were mutually indistinguishable other than for a small difference in the ratio of **18** and **19**.

Reduction of 5 with Zn to 25. A mixed solution of AcOH (2 cm^3) and Ac_2O (1 cm^3) of **5** (21 mg) was refluxed with powdered Zn (300 mg) for 8 h. Zn was removed by filtration and the filtrate was poured into $NaHCO_3$, and extracted with benzene. The extract was rapidly passed through a silica-gel column to give a colorless liquid, 17 mg (95%), **25** [Found: M+, 180.1155. Calcd for $C_{11}H_{16}O_2$: 180.1149. ^{1}H-NMR δ=1.31 (3H, s), 1.6—2.0 (2H, m), 2.05 (3H, br. s), 2.39 (2H, br. t, *J*=7 Hz), 3.67 (3H, s), 4.88 (1H, dd, *J*=10.8, 1.6 Hz), 4.90 (1H, dd, *J*=17.0, 1.6 Hz), and 5.96 (1H, dd, *J*=17.0, 10.8 Hz). ^{13}C-NMR δ=16.9, 24.4, 37.3, 38.0, 50.6, 52.4, 110.3, 133.6, 145.2, 155.0, and 166.4. ν: 2955, 1710, 1637, 1435, 1340, 1263, 1220, 1062, 908, and 788 cm^{-1}].

Reduction of 8 to 25. Similarly, **8** (21 mg) gave **25**, 16 mg (90%).

Attempted Reduction of 6 or 7. Mixed solutions of AcOH (1.3 cm^3) and Ac_2O (0.7 cm^3) respectively containing **6** (20 mg) and **7** (16 mg) were refluxed for 7 h with powdered Zn (200 mg); only the products isolated after the ordinary work-up and silica-gel column chromatography (hexane–EtOAc=8:1) were colorless oily monoacetates, **26**, 18 mg (77%) [Found: M+, 256.1313. Calcd for $C_{13}H_{20}O_5$: 256.1310. ^{1}H-NMR δ=1.00 (3H, s), 1.49 (3H, s), 1.92 (3H, s), 2.0—2.5 (4H, m), 3.76 (3H, s), 4.01 (1H, s, OH), 5.05 (1H, dd, *J*=10.9, 1.2 Hz), 5.05 (1H, dd, *J*=17.7, 1.2 Hz), and 6.07 (1H, dd, *J*=17.7, 10.9 Hz). ν: 3500, 2955, 1740, 1730, 1638, 1439, 1371, 1256, 1212, 1143, 1020, and 908 cm^{-1}],[10] and **27**, 15 mg (78%) [Found: M+, 256.1317. ^{1}H-NMR δ=1.16 (3H, s), 1.60 (3H, s), 1.91 (3H, s), 2.0—2.6 (4H, m), 3.67 (3H, s), 3.90 (1H, s, OH), 4.94 (1H, dd, *J*=10.3, 1.2 Hz), 4.98 (1H, dd, *J*=17.8, 1.2 Hz), and 5.83 (1H, dd, *J*=17.8, 10.3 Hz). ν: 3500, 2990, 2955, 1741, 1730, 1640, 1438, 1376, 1370, 1258, 1242, 1143, 1019, and 916 cm^{-1}].

$TiCl_2$-reduction of 2 to 28, 29, and 30. To an anhydrous THF suspension (300 cm^3) of pyridine complex of $TiCl_2$, prepared from $TiCl_4$ (3.3 cm^3), Zn (4 g), and pyridine (2.4 cm^3), a THF solution (20 cm^3) of **2** (4.25 g) was added dropwise over a period of 1 h under cooling with water. After continued stirring for 30 min at 15—25 °C, the mixture was treated with 30%-aqueous K_2CO_3 (300 cm^3), to which ether was added, and the precipitates were filtered off. The filtrate was extracted with ether and chromatographed on a silica-gel column. A colorless oil, 320 mg (8%), **28** [Found: C, 61.52; H, 8.51%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%. ^{1}H-NMR δ=1.08 (3H, s), 1.74 (3H, br. s), 1.9—2.0 (4H, m), 2.88 (1H, br. s, OH), 3.10 (1H, br. m), 3.75 (3H, s), 3.79 (1H, s, OH), and 4.79 (2H, m). ^{13}C-NMR δ=22.8, 23.1, 23.6, 34.9, 51.7, 52.3, 80.9, 88.5, 110.7, 143.9, and 174.5. ν: 3510, 2955, 1728, 1646, 1442, 1245, 1227, 1123,

1089, 951, and 890 cm^{-1}. *m/z*: 214 (M^+)], was eluted at first.

Subsequently, colorless needles, mp 57.5—58 °C, 470 mg (11%), **29** [Found: C, 61.54; H, 8.31%. ^{1}H-NMR δ=1.28 (3H, s), 1.69 (3H, br. s), 1.7—2.2 (4H, m), 2.83 (1H, s, OH), 3.28 (1H, br. s, OH), 3.43 (1H, m), 3.80 (3H, s), 4.89 (1H, br. s), and 5.00 (1H, m). ^{13}C-NMR δ=21.8, 23.5, 25.7, 37.5, 52.0, 52.6, 84.3, 85.1, 113.2, 140.9, and 175.4. *ν*: 3470, 3340, 2950, 1700, 1645, 1400, 1292, 1254, 1142, 1110, 1040, 928, and 893 cm^{-1}. *m/z*: 214 (M^+)], and a colorless oil, 2.91 g (68%), **30** [Found: C, 61.53; H, 8.50%. ^{1}H-NMR δ=1.26 (3H, s), 1.72 (3H, br. s), 1.7—2.1 (4H, m), 3.07 (1H, br. s, OH), 3.18 (1H, br. m), 3.61 (1H, s, OH), 3.80 (3H, s), 4.80 (1H, br. s), and 4.89 (1H, br. s). ^{13}C-NMR δ=22.5, 25.0, 25.1, 38.9, 51.0, 52.3, 81.6, 85.2, 112.9, 143.4, and 174.7. *ν*: 3490, 2950, 1725, 1641, 1440, 1376, 1257, 1121, 1047, and 892 cm^{-1}. *m/z*: 214 (M^+)], were obtained from the elutions with hexane–EtOAc (3:1).

Reduction of 28 with Zn to 31. A mixture of AcOH (4 cm^3), Ac_2O (2 cm^3), and **28** (60 mg) was refluxed with powdered Zn (600 mg) for 8 h. The mixture was filtered to remove Zn, washed with $NaHCO_3$, and extracted with ether. Silica-gel column chromatography of the extract gave a colorless oil, **31**,[8] 22 mg (44%) [^{1}H-NMR δ=1.65 (1H, m), 1.68 (3H, dd, *J*=1.3, 1.0 Hz), 2.10 (1H, m), 2.11 (3H, q, *J*=1.2 Hz), 2.3—2.6 (2H, m), 3.56 (1H, br. m), 3.66 (3H, s), 4.61 (1H, m), and 4.64 (1H, m). ^{13}C-NMR δ=16.3, 20.6, 28.7, 39.2, 50.8, 53.2, 109.1, 129.5, 148.0, 156.4, and 166.5. *ν*: 2950, 1714, 1648, 1435, 1218, 1117, 1062, and 885 cm^{-1}].

Reduction of 30 with Zn to 31. Similarly, **30** (150 mg) was reduced with Zn to **31**, 68 mg (54%), identical with the sample prepared from **28**.

Attempted Reduction of 29. To a mixed solution of AcOH (1.3 cm^3) and Ac_2O (0.7 cm^3) of **29** (19 mg) was similarly refluxed with powdered Zn (200 mg) for 7 h. After the work-up the product isolated was **32**, 19 mg (83%) [Found: M^+, 256.1316. Calcd for $C_{13}H_{20}O_5$: 256.1310. ^{1}H-NMR δ=1.55 (3H, s), 1.74 (3H, br. s), 1.96 (3H, s), 1.8—2.4 (4H, m), 3.27 (1H, br. s, OH), 3.37 (1H, br. t, *J*=9 Hz), 3.79 (3H, s), 4.82 (1H, br. s), and 4.91 (1H, m). *ν*: 3510, 2955, 1742, 1730, 1642, 1439, 1370, 1246, 1116, 1022, and 892 cm^{-1}].

DMP-treatment of 28. A mixture of **28** (45 mg), DMP (1 cm^3), and PPTS (10 mg) in benzene (1 cm^3) was refluxed for 25 h. The mixture was distilled *in vacuo*, and the residue was passed through a silica-gel column to give a colorless oil, **33**, 46 mg (86%) [Found: M^+ 254.1502. Calcd for $C_{14}H_{22}O_4$: 254.1517. ^{1}H-NMR δ=1.40 (3H, s), 1.45 (3H, br. s), 1.55 (3H, br. s), 1.75 (3H, br. s), 1.7—2.3 (4H, m), 2.90 (1H, br. m), 3.68 (3H, s), 5.71 (1H, br. s), and 5.79 (1H, m). *ν*: 2990, 1755, 1738, 1649, 1447, 1436, 1376, 1228, 1125, 1089, 1002, 887, and 870 cm^{-1}].

DMP-treatment of 30. Similarly, a benzene solution (5 cm^3) of **30** (160 mg), DMP (2 cm^3), and PPTS (25 mg) was refluxed for 14 h to afford a colorless oil, **34**, 171 mg (90%) [Found: M^+, 254.1529. ^{1}H-NMR δ=1.38 (3H, s), 1.45 (6H, br. s), 1.71 (3H, br. s), 1.5—2.1 (4H, m), 3.03 (1H, br. m), 3.77 (3H, s), 4.72 (1H, br. s), and 4.82 (1H, m). *ν*: 2990, 1757, 1732, 1648, 1456, 1438, 1378, 1265, 1127, 1055, 1022, and 887 cm^{-1}].

Saponification and Iodolactonization of 34 to 36 and 37 via *35*. Into a DMSO solution (1 cm^3) of **34** (53 mg), 20%-NaOH solution (0.6 cm^3) was added and refluxed for 2 h. The mixture was then acidified with dil HCl, and extracted with ether to give 50 mg (100%), **35**, colorless granules, mp 86.5—87.5 °C [Found: C, 64.78; H, 8.37%. Calcd for $C_{13}H_{20}O_4$: C, 64.98; H, 8.39%. ^{1}H-NMR δ=1.48 (6H, s), 1.51 (3H, br. s), 1.73 (3H, br. s), 1.6—2.1 (4H, m), 3.06 (1H, br. m), 4.77 (1H, br. s), and 4.87 (1H, m). *ν*: 3400—2500, 2980, 1713, 1692, 1648, 1377, 1278, 1259, 1122, 1009, and 886 cm^{-1}. *m/z*: 240 (M^+)].

Then, **35** was treated with excess of I_2 (100 mg) in MeCN (2 cm^3) in the presence of $NaHCO_3$ (100 mg). After stirring at 15—25 °C for 15 h, I_2 was decomposed by $NaHSO_3$ solution, and extracted with ether. From the aqueous layer, starting **35** (25 mg) was recovered. Silica-gel column chromatography of the neutral extract afforded two isomeric iodo lactones, **36**, colorless prisms, mp 117.5—188 °C, 19 mg (50%) [Found: C, 42.76; H, 5.24%. Calcd for $C_{13}H_{19}O_4I$: C, 42.64; H, 5.23%. ^{1}H-NMR δ=1.48 (6H, s), 1.52 (3H, s), 1.77 (3H, s), 1.8—2.4 (5H, m), and 3.35 (2H, br. s). *ν*: 2990, 1780, 1371, 1285, 1185, and 1012 cm^{-1}. *m/z*: 366 (M^+)], and **37**, a colorless oil, 7 mg (18%) [^{1}H-NMR δ=1.48 (6H, s), 1.51 (3H, s), 1.69 (3H, s), 1.7—2.4 (5H, m), 3.63 (1H, d, *J*=11 Hz), and 3.76 (1H, d, *J*=11 Hz). *ν*: 2990, 1787, 1382, and 1000 cm^{-1}].

LAH-reduction of 28 to 38. An anhydrous THF solution (7.5 cm^3) of **28** (118 mg) was treated with LAH (100 mg) at 15—25 °C for 1 h. Purification of the products by silica-gel column chromatography gave a colorless oil, 94 mg (92%) **38** [Found: C, 64.26; H, 9.78%. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74%. ^{1}H-NMR δ=1.25 (3H, s), 1.6—1.9 (4H, m), 1.88 (3H, br. s), 2.41 (1H, br. m, OH), 2.79 (1H, br. s, OH), 2.90 (1H, br. t, *J*=9 Hz), 3.44 (1H, s, OH), 3.46 (1H, dd, *J*=12, 7 Hz), 3.64 (1H, dd, *J*=12, 5 Hz), 4.84 (1H, br. s), and 4.93 (1H, m). *ν*: 3400, 2790, 1642, 1450, 1380, 1120, 1045, 928, and 892 cm^{-1}. *m/z*: 168 (M^+−18)].

LAH-reduction of 29 to 39. An anhydrous THF solution (5 cm^3) of **29** (70 mg) was treated with LAH (60 mg) at 15—25 °C for 1 h. From the mixture, a colorless oil, 47 mg (77%), **39** [Found: C, 64.27; H, 9.68%. ^{1}H-NMR δ=1.37 (3H, s), 1.5—2.1 (4H, m), 1.88 (3H, br. s), 1.99 (1H, s, OH), 2.15 (1H, br. s, OH), 2.83 (1H, dd, *J*=9, 3 Hz, OH), 3.09 (1H, br. t, *J*=9 Hz), 3.49 (1H, dd, *J*=11, 9 Hz), 3.74 (1H, dd, *J*=11, 3 Hz), 4.89 (1H, br. s), and 5.07 (1H, m). *ν*: 3400, 2975, 1638, 1375, 1106, 1032, 926, and 895 cm^{-1}. *m/z*: 168 (M^+−18)], was obtained.

LAH-reduction of 30 to 40. Similarly, **30** (210 mg) in THF (10 cm^3) was reduced by LAH (150 mg) to colorless needles, mp 106.5—107 °C, 157 mg (86%), **40** [Found: C, 64.37; H, 9.95%. ^{1}H-NMR δ=1.35 (3H, s), 1.83 (3H, br. s), 1.5—2.1 (4H, m), 2.40 (1H, br. m, OH), 2.48 (1H, m), 2.75 (1H, br. s, OH), 3.17 (1H, br. s, OH), 3.65 (2H, br. d, *J*=4 Hz), 4.81 (1H, br. s), and 4.93 (1H, m). *ν*: 3445, 3400, 2955, 1633, 1377, 1343, 1120, 1097, 934, and 899 cm^{-1}. *m/z*: 168 (M^+−18)].

DMP-treatment of 38 to 41. An anhydrous THF solution (2 cm^3) of **38** (53 mg) was treated with DMP (0.2 cm^3) and PPTS (20 mg) at 15—25 °C for 3 h. Extraction and silica-gel chromatographic purification afforded a colorless oil, 63 mg (98%), **41** [Found: M^+, 226.1569. Calcd for $C_{13}H_{22}O_3$: 226.1568. ^{1}H-NMR δ=1.23 (3H, s), 1.36 (3H, br. s), 1.46 (3H, br, s), 1.4—1.9 (4H, m), 1.82 (3H, br. s), 2.56 (1H, br. s, OH), 3.12 (1H, br. m), 3.76 (1H, d, *J*=9.5 Hz),

3.88 (1H, d, J=9.5 Hz), 4.77 (1H, br. s), and 5.03 (1H, m). ν: 3550, 2990, 1645, 1454, 1382, 1372, 1211, 1146, 1068, 888, 877, and 853 cm^{-1}].

*Dehydration of **41** to **42** and **43**.* A pyridine solution (1 cm^3) of **41** (27 mg) was treated with $SOCl_2$ (30 mg) at 0 °C for 1 h. The mixture was then quenched with $NaHCO_3$ solution and extracted with a 1:1-mixture of hexane–ether to give a colorless oil, 21 mg (85%), a 3:1-mixture of **42** [Found: M^+, 208.1465. Calcd for $C_{13}H_{20}O_2$: 208.1462. ^{1}H-NMR δ=1.37 (3H, br. s), 1.44 (3H, br. s), 1.55 (3H, dd, J=1.5, 0.8 Hz), 1.72 (3H, q, J=2 Hz), 2.08 (1H, dm, J=17 Hz), 2.64 (1H, dd of quint, J=17, 8, 2 Hz), 3.09 (1H, dd, J=8, 3.5 Hz), 3.81 (1H, d, J=9 Hz), 4.01 (1H, d, J=9 Hz), 4.81 (2H, m), and 5.57 (1H, m). RT= 30.4 min], and **43** [Found: M^+, 208.1477. ^{1}H-NMR δ= 1.40 (3H, br. s), 1.47 (3H, br. s), 1.78 (3H, dd, J= 1.5, 0.8 Hz), 1.5—2.1 (2H, m), 2.3—2.6 (2H, m), 2.69 (1H, dd, J=9.5, 7 Hz), 3.79 (1H, d, J=9 Hz), 4.06 (1H, d, J=9 Hz), 4.77 (1H, br. s), 4.91 (1H, m), 4.97 (1H, td, J=2.5, 0.8 Hz), and 5.22 (1H, br. t, J=2.5 Hz). RT=29.7 min].

*DMP-treatment of **40** to **44**.* An anhydrous THF solution (3 cm^3) of **40** (90 mg) was treated with DMP (0.3 cm^3) and PPTS (30 mg) at 15—25 °C for 3 h. The work-up gave a colorless oil, 105 mg (96%), **44** [Found: M^+, 226.1573. ^{1}H-NMR δ=1.24 (3H, s), 1.35 (3H, br. s), 1.4—2.1 (4H, m), 1.43 (3H, br. s), 1.82 (3H, br. s), 2.43 (1H, m), 2.87 (1H, br. s, OH), 3.84 (1H, d, J=9 Hz), 4.04 (1H, d, J=9 Hz), 4.76 (1H, br. s), and 4.87 (1H, m). ν: 3520, 2980, 1642, 1453, 1382, 1372, 1217, 1068, 890, and 860 cm^{-1}].

*Dehydration of **44** to **45** and **46**.* A pyridine solution (1.5 cm^3) of **44** (47 mg) was treated with $SOCl_2$ (45 mg) at 0 °C for 1 h. The reaction mixture was poured into aqueous $NaHCO_3$ and extracted with a 1:1-mixture of hexane–ether. The extract was passed through a silica-gel column with hexane–ether (15:1) to give a colorless oil, 36 mg (83%), a 3:1-mixture of **45** [Found: M^+, 208.1445. RT=23.9 min. ^{1}H-NMR δ=1.33 (3H, br. s), 1.42 (3H, br. s), 1.73 (3H, q, J=2 Hz), 1.75 (1H, dd, J=1.5, 0.8 Hz), 2.2—2.4 (2H, m), 2.74 (1H, dd, J=7.5, 5.5 Hz), 3.87 (2H, s), 4.78 (2H, m), and 5.52 (1H, m)] and **46** [Found: M^+, 208.1471. RT=26.9 min. ^{1}H-NMR δ=1.36 (3H, br. s), 1.45 (3H, br. s), 1.80 (3H, dd, J=1.5, 0.8 Hz), 1.6—2.0 (2H, m), 2.2—2.4 (3H, m), 3.85 (1H, d, J=8.5 Hz), 3.96 (1H, d, J=8.5 Hz), 4.71 (1H, br. s), 4.85 (1H, m), 5.01 (1H, td, J=2.5, 0.8 Hz), and 5.26 (1H, br. t, J=2.5 Hz)].

*DMP-treatment of **39** to **47** and **48**.* An anhydrous THF solution (1.5 cm^3) of **39** (37 mg) was treated with DMP (0.15 cm^3) and PPTS (15 mg^3) at 15—25 °C for 1 h, after which, the mixture was diluted with aqueous $NaHCO_3$, extracted with ether, and chromatographed on a silica-gel column. The fractions eluted from hexane–ether (4:1) were a colorless oil, 22 mg (49%), **48** [Found: C, 68.96; H, 9.88%. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80%. ^{1}H-NMR δ=1.37 (3H, br. s), 1.41 (3H, s), 1.48 (3H, br. s), 1.84 (3H, br. s), 1.6—2.0 (5H, m), 3.18 (1H, br. m), 3.52 (1H, d, J=12 Hz), 3.73 (1H, d, J=12 Hz), 4.89 (1H, br. s), and 5.08 (1H, m). ν: 3530, 2995, 2950, 1638, 1453, 1379, 1191, 1075, and 891 cm^{-1}. m/z: 211 (M^+−15)]. Subsequently, a colorless oil, 18 mg (40%), **47** [Found: M^+, 226.1564. ^{1}H-NMR δ=1.28 (3H, br. s), 1.33 (3H, s), 1.41 (3H, br. s), 1.84 (3H, br. s), 1.5—2.1 (5H, m), 2.84 (1H, br. m), 3.88 (1H, d, J=9 Hz), 4.21 (1H, d, J=9 Hz), 4.78 (1H, br. s), and 4.93 (1H, m). ν: 3495, 2960, 1638, 1455, 1381, 1371, 1207, 1060, 880, and 851 cm^{-1}], was obtained.

*Dehydration of **47** to **45** and **46**.* A pyridine solution (0.5 cm^3) of **47** (16 mg) was treated with $SOCl_2$ (15 mg) at 0 °C for 1 h. The mixture was diluted with aqueous $NaHCO_3$, extracted with ether, and chromatographed on a silica-gel column to give a colorless oil, 12 mg (81%), which proved to be a 6:1-mixture of **45** and **46** from the NMR spectral and gas-liquid chromatographic analyses.

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10) Formation of diacetates from the *trans*-glycols might gradually occur under the conditions; indeed as the by-product of **26** from **6**, a colorless oily diacetate [δ=1.44 (3H, s), 1.70 (3H, s), 1.95 (3H, s), 2.00 (3H, s), 2.0—2.6 (4H, m), 3.71 (3H, s), 4.95 (1H, dd, J=11, 1.5 Hz), 4.96 (1H, dd, J=17.5, 1.5 Hz), and 6.07 (1H, dd, J=17.5, 11 Hz)] was isolated in 8% yield.

11) This formation of these orthoester derivatives by solvolysis was employed for optical resolution of these iridoids. This will be reported in the near future.

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