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Studies on the Synthesis of Myriaporones: Stereoselective Synthesis of the C5–C13 Fragment Starting from D-Glucose *via* Regioselective Reductive Opening of Methoxybenzylidene Acetal

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A stereoselective synthesis is described of the C5–C13 fragment (4) of myriaporone 4 (1) starting from D-glucose by a coupling of the C5–C9 aldehyde (5), prepared using a regioselective reductive ring-opening of methoxybenzylidene acetal, with the C10–C13 iodoolefin (6).

Key words stereoselective synthesis; marine product; protecting group; benzylidene acetal

Myriaporone 4 (**1**), a cytotoxic marine product (IC_{50}=100 ng/ml *vs.* L-1210), was isolated as an equilibrium mixture with myriaporone 3 (**2**) from a bryozoan, *Myriapora truncata*, by Rinehart in 1995.[1] The synthesis of **1** is of great interest because of its structural similarity to the C10–C23 part of the marine sponge macrolide, tedanolide (**3**),[2] the synthesis of which is currently under study by several research groups.[3] Recently, we reported the synthesis of the C13–C23 part of **3** starting from (*R*)- and (*S*)-3-hydroxy-2-methylpropionates,[3f] and this synthetic methodology can be applied to the synthesis of **1**. However, we are now investigating an alternative approach by the use of an intermediate (**8**) in the synthetic work of erythronolide A,[4] and this report presents a synthesis of the C5—C13 fragment (**4**) of **1**,[5] corresponding to the C13—C21 part of **3**, starting from D-glucose (**9**)[6] *via* the regioselective reductive opening of methoxybenzylidene (MP) acetals.[7]

A retrosynthetic analysis of **1** is shown in Chart 1. The key intermediate is **4**, from which **1** will be derived *via* elongation of the C1–C4 and C14–C15 units and epoxidation of the C10–C11 double bond, and **4** was planned to be synthesized by coupling between the C5–C9 aldehyde (**5**) and the known C10–C13 iodoalkene (**6**).[3f,8] The synthesis of **5** would be achieved starting from **9** *via* **8**, and attention was paid to the construction of the C6 chiral center and the regioselective opening of the MP acetal of **11** (see Chart 2).

During the course of synthetic work on erythronolide A, the olefin (**8**) was already synthesized starting from **9** *via* the secondary alcohol (**12**).[4] A stereoselective hydroboration of **8** was presumed to be a good way to give **5**. However, it was required to improve the conversion of **10**,[4] readily available from **9**, into **12**, since the overall yield of three steps (tosylation, epoxidation, MPMONa treatment) was only 39%, which is too low to complete the total synthesis of **1**.

Direct and selective protection of the primary alcohol of **10** was first examined by treatment with 4-methoxybenzyl chloride (MPMCl) and silver oxide (Ag_2O),[9] but only a poor result to give **12** in 32% yield was obtained. Quite recently, we reported a facile reductive opening of MP acetals with tri-*n*-butyltin hydride (Bu_3SnH) in the presence of magnesium bromide ($MgBr_2$).[7] This method is characterized by the reverse regioselectivity to the usual selectivity of reduction mainly with diisobutylaluminum hydride (DIBAH). When a

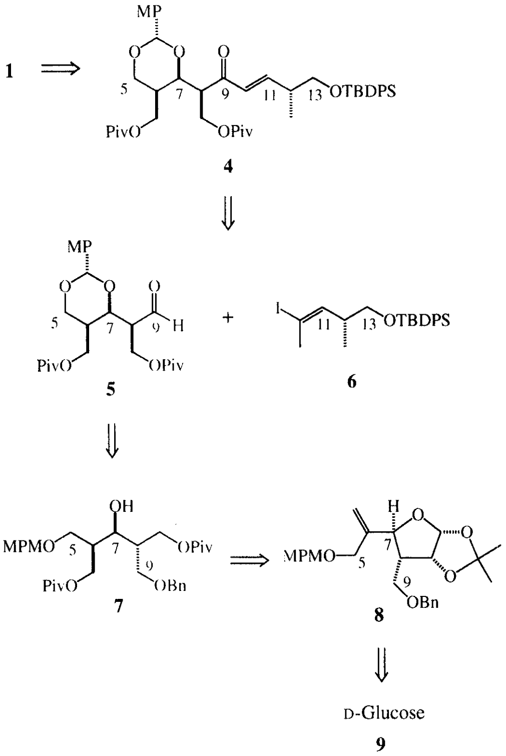
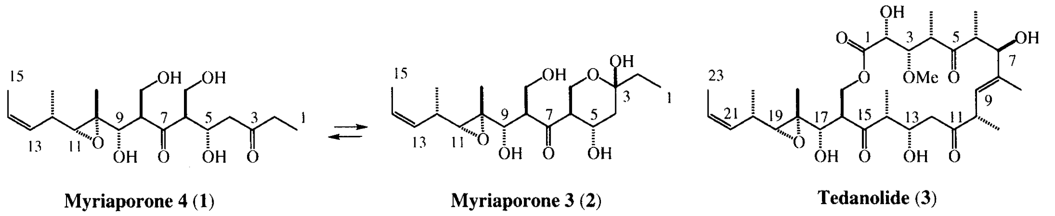


Chart 1



Myriaporone 4 (1) **Myriaporone 3 (2)** **Tedanolide (3)**

Fig. 1

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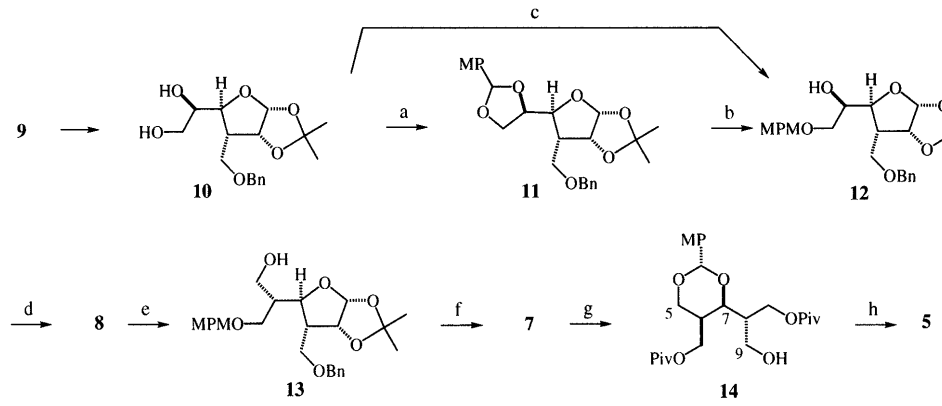
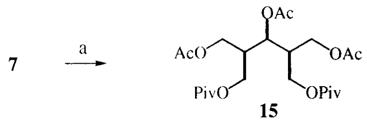


(a) p-MeOC$_6$H$_4$CH(OMe)$_2$, TsOH(cat). DMF, 55°C (86%). (b) MgBr$_2$. Bu$_3$SnH, CH$_2$Cl$_2$, r.t. (95%). (c) MPMCl, Ag$_2$O, KI, toluene, reflux (32%). (d) 1) (COCl)$_2$, DMSO, Et$_3$N, CH$_2$Cl$_2$, -78°C (87%); 2) Ph$_3$PMe$^+$Br$^-$, BuLi, THF, 0°C (83%). (e) BH$_3$·SMe$_2$, toluene, r.t., then NaOH, H$_2$O$_2$ (63%, 5:1) [9-BBN, THF, r.t., then NaOH, H$_2$O$_2$ (66%, 45:1)]. (f) 1) PivCl, Et$_3$N, DMAP, CH$_2$Cl$_2$, r.t. (99%,); 2) 4N-HCl, THF, 55°C (86%); 3) Pb(OAc)$_4$, C$_6$H$_6$, r.t.; 4) LiAlH$_4$, Et$_2$O, 0°C (2 steps 89%); 5) PivCl, Et$_3$N, DMAP, CH$_2$Cl$_2$, r.t. (100%). (g) 1) Raney Ni (W2), H$_2$, EtOH, r.t. (91%); 2) DDQ, MS3A, CH$_2$Cl$_2$, r.t. (89%). (h) Dess-Martin periofinane, pyridine, CH$_2$Cl$_2$, r.t. (88%).

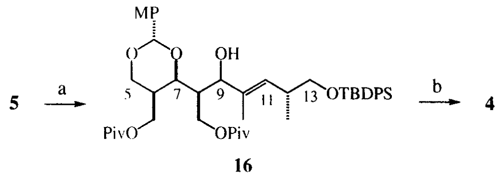
Chart 2

5 : 4 mixture of MP acetals (**11**), readily converted from **10** in the usual way, was treated with Bu$_3$SnH and MgBr$_2$ in dichloromethane (CH$_2$Cl$_2$) at room temperature, complete regioselective reduction proceeded quite smoothly to give the expected **12** in 95% yield.[7] Swern oxidation of **12** followed by Wittig methylenation easily gave **8**. Hydroboration of **8** with a borane dimethyl sulfide complex (BH$_3$·Me$_2$S) in toluene gave a 5 : 1 mixture of the expected alcohol (**13**) and its C6 isomer. The reaction with 9-borabicyclo[3.3.1]nonane (9-BBN) took place slowly and **13** was isolated with excellent stereoselectivity (45 : 1).[10] Although its selectivity was not so good, BH$_3$·Me$_2$S was useful in practical syntheses. After protection of the primary alcohol of crude **13** with a pivaloyl (Piv) group, selective hydrolysis of the acetonide was carefully examined under several acidic conditions, and a good result was obtained when the pivaloate was warmed at 50 °C with 4 N HCl in THF.[11] The resulting diol was cleaved with lead tetraacetate [Pb(OAc)$_4$], and the lithium aluminum hydride (LiAlH$_4$) reduction gave the triol, whose two primary alcohols were protected with PivCl to give a 5 : 1 mixture of **7** and its C6 isomer (**7a**), which were readily separated by silica gel chromatography. Selective hydrogenolysis of the benzyl (Bn) group over Raney nickel (Ni) proceeded very smoothly without any detectable cleavage of the MPM group.[12] Oxidation of the resulting diol with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in the presence of molecular sieves (MS) gave the MP acetal (**14**)[13] as a single product, whose primary alcohol was oxidized with Dess–Martin periodinane[14] to give the C5–C9 aldehyde (**5**), which was immediately used in the next reaction without purification. The overall yield of 13 steps from **10** to **5** was 20%. The configuration at C6 was substantiated as follows; hydrogenolysis of **7**, after conversion to a MP acetal, over palladium charcoal (Pd-C) gave the triol, which was treated with acetic anhydride (Ac$_2$O) to give the meso triacetate (**15**).



(a) 1) DDQ, MS3A, CH$_2$Cl$_2$, r.t. (89%); 2) 10%Pd-C, H$_2$, EtOH, r.t. (100%); 3) Ac$_2$O, DMAP, CH$_2$Cl$_2$, r.t. (100%).

Chart 3



(a) 1) **6**, t-BuLi. Et$_2$O, -78°C; 2) PivCl, Et$_3$N, DMAP, CH$_2$Cl$_2$, r.t. (2 steps 79%, 2:1). (b) Dess-Martin periodinane, pyridine, CH$_2$Cl$_2$, r.t. (100%).

Chart 4

Excess **6**[3f] was first lithiated with *tert*-butyllithium (t-BuLi) and allowed to react with crude **5**. The coupling reaction proceeded smoothly at −78 °C, and, after reprotection of the primary alcohols with PivCl, gave a 2 : 1 mixture of C9 alcohols (**16**), which was finally oxidized with Dess–Martin periodinane[14] to the title compound (**4**). The results presented here, though in small-scale experiments, may possibly lead to the total synthesis of **1**.

Experimental

3-*C*-Benzyloxymethyl-3-deoxy-1,2-*O*-isopropylidene-5,6-*O*-(4-methoxybenzylidene)-α-D-allofuranose (11) p-Anisaldehyde dimethyl acetal (3.8 ml, 22.50 mmol) and p-toluenesulfonic acid (TsOH·H$_2$O) (643 mg, 3.38 mmol) were added to a solution of **10**[4] [^{1}H-NMR (500 MHz, CDCl$_3$) δ: 7.35—7.24 (5H, m), 5.75 (1H, d, J=3.7 Hz), 4.66 (1H, dd, J=4.0, 3.7 Hz), 4.59 (1H, d, J=11.6 Hz), 4.50 (1H, d, J=11.6 Hz), 3.92 (1H, t, J=8.7 Hz), 3.87 (1H, dd, J=9.0, 3.7 Hz), 3.77 (1H, dd, J=11.6, 3.7 Hz), 3.77 (1H, dd, J=11.6, 3.1 Hz), 3.67 (1H, d, J=5.6 Hz), 3.65 (1H, d, J=9.0 Hz), 3.54 (1H, m), 2.10—2.18 (1H, m), 1.46 (3H, s), 1.26 (3H, s). ^{13}C-NMR (125 MHz, CDCl$_3$) δ: 136.5, 128.6, 128.2, 128.0, 112.2, 104.5, 82.4, 81.8, 73.8, 67.4, 64.2, 49.1, 26.6, 26.2] (3.65 g, 11.25 mmol) in DMF (100 ml) at 55 °C. After 4 h, the reaction was quenched with saturated aqueous NH$_4$Cl, and the mixture was extracted with EtOAc (100 ml×5). The extract was washed with saturated aqueous NH$_4$Cl (20 ml×2) and brine (20 ml) , then dried over Na$_2$SO$_4$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with n-hexane-Et$_2$O (3 : 2), to give a 5 : 4 mixture of **11** as a colorless oil (4.28 g, 86%). ^{1}H-NMR (500 MHz, CDCl$_3$) δ: 7.36—7.25 (5H, m), 7.31 (8/9H, d, J=8.5 Hz), 7.30 (10/9H, d, J=8.5 Hz), 6.88 (8/9H, d,

$J=8.5$ Hz), 6.86 (10/9H, d, $J=8.5$ Hz), 5.85 (4/9H, s), 5.82 (4/9H, d, $J=3.4$ Hz), 5.79 (5/9H, d, $J=3.4$ Hz), 5.69 (5/9H, s), 4.77 (5/9H, dd, $J=4.3$, 3.4 Hz), 4.75 (4/9H, dd, $J=4.3$, 3.4 Hz), 4.52 (1H, s), 4.49 (1H, d, $J=2.4$ Hz), 4.27 (4/9H, dd, $J=12.2$, 6.7 Hz), 4.21 (5/9H, dd, $J=12.2$, 6.7 Hz), 4.18 (1H, dd, $J=6.7$, 4.9 Hz), 4.11 (1H, dd, $J=8.5$, 4.9 Hz), 4.07 (1H, ddd, $J=8.5$, 6.7, 4.9 Hz), 3.95 (5/9H, dd, $J=8.5$, 6.7 Hz), 3.91 (4/9H, dd, $J=8.5$, 6.7 Hz), 3.80 (12/9H, s), 3.79 (15/9H, s), 3.73 (1H, m), 2.27 (5/9H, m), 2.15 (4/9H, m), 1.51 (12/9H, s), 1.50 (15/9H, s), 1.33 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 160.4, 160.2, 138.3, 138.1, 128.3, 128.2, 128.1, 127.8, 127.6, 127.5, 127.5, 127.4, 113.6, 112.2, 112.1 , 105.2, 105.1, 104.3, 103.9, 81.2, 81.0, 80.1, 79.6, 77.9, 73.3, 73.2, 68.0, 67.2, 66.1, 66.0 , 55.2, 48.7, 48.2, 26.8, 26.7, 26.4 , 26.3. IR (neat) cm^{-1}: 2935, 1615, 1516, 1455, 1077, 753. FAB-MS *m/z* (%): 443 (M$^+$+1, 28), 441 (21), 385 (23), 277 (11), 186 (9.1), 185 (100), 179 (17), 137 (38), 135 (59), 121 (40), 93 (100), 91 (100), 75 (29). HR-MS Calcd for $C_{25}H_{31}O_7$ (M$^+$+1): 443.2070. Found: 443.2058.

3-*C*-Benzyloxymethyl-3-deoxy-1,2-*O*-isopropylidene-6-*O*-(4-methoxybenzyl)-*α*-D-allofuranose (12) *a*) To a stirred solution of **11** (1.33 g, 3.01 mmol) in CH_2Cl_2 (15 ml) was added *n*-Bu_3SnH (1.8 ml, 9.03 mmol) and $MgBr_2$ (1.11 g, 6.02 mmol) at room temperature under argon. After 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with EtOAc (100 ml×2). The extract was washed with saturated aqueous NH_4Cl (10 ml), H_2O (10 ml) and brine (10 ml), dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 2), to give **12** as a colorless oil (1.28 g, 95%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.35—7.26 (5H, m), 7.25 (2H, d, $J=8.5$ Hz), 6.84 (2H, d, $J=8.5$ Hz), 5.74 (1H, d, $J=3.7$ Hz), 4.69 (1H, t, $J=4.3$ Hz), 4.58 (1H, d, $J=11.6$ Hz), 4.49 (1H, d, $J=11.6$ Hz), 4.48 (2H, dd, $J=11.6$, 9.5 Hz), 3.93 (1H, dd, $J=9.5$, 7.6 Hz), 3.83 (1H, dd, $J=9.5$, 5.2 Hz), 3.78 (3H, s), 3.73—3.66 (3H, m), 3.51 (1H, dd, $J=9.5$, 6.6 Hz), 2.22—2.16 (1H, m), 1.48 (3H, s), 1.29 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.1, 137.1, 130.3, 129.4, 128.5, 127.9, 127.9, 113.7, 112.0, 104.5, 81.9, 81.0, 73.6, 73.0, 72.6, 71.2, 67.1, 55.2, 48.9, 26.7, 26.4.

b) A suspension of **10** (289 mg, 0.82 mmol), Ag_2O (475 mg, 2.05 mmol), KI (68 mg, 0.41 mmol) and MPM chloride (0.17 ml, 1.23 mmol) in toluene (8 ml) was heated under reflux for 15 h. After the reaction mixture was passed through a florisil pad (Et_2O), the filtrate was concentrated *in vacuo*, and the residue was chromatographed as described above to give **12** (115 mg, 32%) and recovered **10** (179 mg, 62%).

3-*C*-Benzyloxymethyl-3,5,6-trideoxy-1,2-*O*-isopropylidene-5-*C*-(4-methoxybenzyloxymethyl)-*α*-D-*ribo*-hex-5-enofuranose (8) DMSO (2.02 ml, 28.4 mmol) was added to a stirred solution of $(COCl)_2$ (1.24 ml, 14.2 mmol) in CH_2Cl_2 (30 ml) at −78 °C under argon. After 15 min, a solution of **12** (3.16 g, 3.19 mmol) in CH_2Cl_2 (30 ml) was added, and the stirring was continued for 1 h. After dropwise addition of Et_3N (6.96 ml, 49.7 mmol), the solution was allowed to warm to 0 °C over 1.5 h, and the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc (100 ml×3). The extract was washed with saturated aqueous NH_4Cl (20 ml×3), H_2O (20 ml×2) and brine (20 ml), then dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (7 : 3), to give 3-*C*-benzyloxymethyl-3-deoxy-1,2-*O*-isopropylidene-6-*O*-(4-methoxybenzyl)-*α*-D-*ribo*-hexofuranos-5-ulose as a colorless oil (2.73 g, 87%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.32—7.22 (5H, m), 7.23 (2H, d, $J=8.5$ Hz), 6.84 (2H, d, $J=8.5$ Hz), 5.84 (1H, d, $J=3.4$ Hz), 4.72 (1H, t, $J=4.0$ Hz), 4.48 (2H, d, $J=1.8$ Hz), 4.45 (2H, d, $J=11.0$ Hz), 4.33 (2H, d, $J=5.2$ Hz), 4.25 (1H, d, $J=10.7$ Hz), 3.77 (3H, s), 3.79—3.75 (1H, m), 3.67 (2H, dd, $J=9.3$, 5.7 Hz), 2.39—2.33 (1H, m), 1.46 (3H, s), 1.31 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 205.7, 159.4, 138.0, 129.6, 129.2, 128.3, 127.6, 127.6, 113.8, 112.6, 105.8, 81.5, 80.3, 73.3, 72.8, 72.0, 65.6, 55.2, 48.2, 26.8, 26.3; IR (neat) cm^{-1}: 2935, 1732, 1612, 1513, 1455, 1373, 1246, 1116.

A 1.53 M solution of *n*-BuLi in hexane (8.9 ml, 13.5 mmol) was added to a stirred suspension of $Ph_3PCH_3^+Br^-$ (4.85 g, 13.5 mmol) in THF (40 ml) at 0 °C under argon. After 30 min, a solution of the ketone (2.73 g, 6.17 mmol) in THF (20 ml) was added dropwise. After 6 h, the reaction was quenched with H_2O, and the mixture was extracted with EtOAc (100 ml×2). The extract was washed with saturated aqueous NH_4Cl (20 ml×3), H_2O (20 ml×2) and brine (20 ml), dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 1), to give **8** as a colorless oil (2.27 g, 83%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.34—7.26 (5H, m), 7.24 (2H, d, $J=8.5$ Hz), 6.85 (2H, d, $J=8.5$ Hz), 5.81 (1H, d, $J=3.7$ Hz), 5.31 (2H, d, $J=1.2$ Hz), 5.22 (1H, brs), 4.75 (1H, t, $J=4.0$ Hz), 4.52 (1H, d, $J=11.9$ Hz), 4.48 (1H, d, $J=11.9$ Hz), 4.45 (1H, d, $J=11.6$ Hz), 4.38 (1H, d, $J=11.6$ Hz), 4.32 (1H, d, $J=10.4$ Hz), 4.12 (1H, d, $J=12.8$ Hz), 3.98 (1H, d, $J=12.8$ Hz), 7.80—3.74 (1H, m), 3.77 (3H, s), 3.47 (1H, dd, $J=9.3$, 4.8 Hz), 2.46—2.40 (1H, m), 1.52 (3H, s), 1.35 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.0, 142.4, 138.2, 130.2, 129.2, 128.1, 127.4, 127.4, 116.3, 113.6, 111.5, 104.8, 80.8, 80.5, 73.1, 71.7, 69.0, 65.8, 55.1, 48.2, 26.6, 26.3.

3-*C*-Benzyloxymethyl-3,5-dideoxy-1,2-*O*-isopropylidene-6-*O*-(4-methoxybenzyl)-5-*C*-hydroxymethyl-*β*-L-talofuranose (13) *a*) A 1.0 M solution of $BH_3\cdot Me_2S$ in toluene (12.3 ml, 12.33 mmol) was added to a stirred solution of **8** (2.17 g, 4.93 mmol) in toluene (30 ml) at room temperature under argon. After 20 min, the reaction mixture was cooled to 0 °C, and quenched with H_2O. After addition of 3 N NaOH (30 ml) and 30% H_2O_2 (25 ml), vigorous stirring was continued for 30 min, and the mixture was extracted with ether (100 ml×3). The extract was washed with saturated aqueous NH_4Cl (20 ml×3) and brine (20 ml), then dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 2), to give a 5 : 1 mixture of **13** and its C6 isomer as a colorless oil (1.43 g, 63%). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.34—7.26 (5H, m), 7.23 (10/6H, d, $J=8.6$ Hz), 7.22 (2/6H, d, $J=8.6$ Hz), 6.86 (10/6H, d, $J=8.6$ Hz), 6.85 (2/6H, d, $J=8.6$ Hz), 5.76 (5/6H, d, $J=3.7$ Hz), 5.73 (1/6H, d, $J=3.7$ Hz), 4.71 (5/6H, t, $J=4.3$ Hz), 4.69 (1/6H, t, $J=4.3$ Hz), 4.52 (1H, d, $J=12.2$ Hz), 4.50 (1H, d, $J=12.2$ Hz), 4.43 (1H, d, $J=11.2$ Hz), 4.42 (1H, d, $J=11.2$ Hz), 4.09 (5/6H, dd, $J=10.5$, 2.8 Hz), 4.06 (1/6H, dd, $J=10.5$, 3.4 Hz), 3.83—3.75 (2H, m), 3.79 (15/6H, s), 3.77 (3/6H, s), 3.68 (1/6H, dd, $J=9.5$, 5.5 Hz), 3.66 (5/6H, dd, $J=9.2$, 7.6 Hz), 3.60 (1/6H, dd, $J=9.5$, 6.7 Hz), 3.59 (5/6H, dd, $J=9.5$, 6.1 Hz), 3.54 (1/6H, dd, $J=9.5$, 5.5 Hz), 3.48 (5/6H, dd, $J=9.5$, 6.4 Hz), 2.71 (5/6H, dd, $J=7.6$, 3.7 Hz), 2.63 (1/6H, dd, $J=7.6$, 4.0 Hz), 2.42—2.35 (1H, m), 2.13—2.07 (1H, m), 1.48 (3H, s), 1.31 (3H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 159.1, 138.1 (1/6C), 137.9 (5/6C), 130.2 (5/6C), 130.1 (1/6C), 129.2 (5/6C), 129.1 (1/6C), 128.3 (5/6C), 128.2 (1/6C), 127.6, 127.5 (5/6C), 127.4 (1/6C), 113.7, 111.8 (5/6C), 111.7 (1/6C), 104.6 (1/6C), 104.4 (5/6C), 80.9 (5/6C), 80.8 (1/6C), 80.1 (5/6C), 80.0 (1/6C), 73.3 (5/6C), 73.2 (1/6C), 72.9, 70.4 (5/6C), 68.4 (1/6C), 66.4 (5/6C), 66.3 (1/6C), 64.4 (1/6C), 61.2 (5/6C), 55.2, 46.4 (5/6C), 46.3 (1/6C), 42.5 (5/6C), 42.4 (1/6C), 26.6 (1/6C), 26.5 (5/6C), 26.3 (1/6C), 26.2 (5/6C). IR (neat) cm^{-1}: 3476, 2934, 1612, 1512, 1454, 1371, 1303, 1249.

b) A 0.5 M solution of 9-BBN in THF (0.36 ml, 0.18 mmol) was added dropwise to a stirred solution of **8** (40.1 mg, 0.09 mmol) in THF (0.5 ml) at room temperature under argon. After 24 h, the reaction was quenched with H_2O, then 4 N KOH (0.2 ml) and 30% H_2O_2 (0.2 ml) were added, and the mixture was stirred vigorously for 30 min. After concentration *in vacuo*, the residue was extracted with Et_2O (10 ml×3). The extract was washed with saturated aqueous NH_4Cl (2 ml×3) and brine (2 ml), dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed as described above to give a 45 : 1 mixture of **13** and its C6 isomer (27.4 mg, 66%).

(2*S*,3*S*,4*R*)-1-Benzyloxy-2,4-bis(2,2-dimethylpropanoyloxymethyl)-3-hydroxy-5-(4-methoxybenzyloxy)pentane (7) and (2*S*,3*S*,4*S*)-1-Benzyloxy-2,4-bis(2,2-dimethylpropanoyloxymethyl)-3-hydroxy-5-(4-methoxybenzyloxy)pentane (7a) Et_3N (1.15 ml, 8.20 mmol), DMAP (40 mg, 0.33 mmol) and PivCl (404 μl, 3.28 mmol) were added to a stirred solution of the 5 : 1 mixture of **13** and its C6 isomer (752 mg, 1.64 mmol) in CH_2Cl_2 (16 ml) at 0 °C under argon. After 3 h at room temperature, the reaction was quenched with cold saturated aqueous NH_4Cl, and the mixture was extracted with EtOAc (50 ml×2). The extract was washed with saturated aqueous NH_4Cl (5 ml×2), H_2O (10 ml×2) and brine (10 ml), then dried over $MgSO_4$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 1), to give 5 : 1 mixture of 3-*O*-benzyloxymethyl-3,5-dideoxy-1,2-*O*-isopropylidene-6-*O*-(4-methoxybenzyl)-5-*C*-(2,2-dimethylpropanoyloxymethyl)-*β*-L-talofuranose and its C6 isomer as a colorless oil (884 mg, 99%.). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 7.32—7.24 (5H, m), 7.22 (10/6H, d, $J=8.5$ Hz), 7.21 (2/6H, d, $J=8.5$ Hz), 6.85 (10/6H, d, $J=8.5$ Hz), 6.84 (2/6H, d, $J=8.5$ Hz), 5.74 (5/6H, d, $J=3.7$ Hz), 5.72 (1/6H, d, $J=3.7$ Hz), 4.71 (5/6H, t, $J=4.3$ Hz), 4.69 (1/6H, t, $J=4.3$ Hz), 4.52 (1H, d, $J=12.2$ Hz), 4.49 (1H, d, $J=12.2$ Hz), 4.41 (1H, d, $J=12.2$ Hz), 4.39 (1H, d, $J=12.2$ Hz), 4.17 (1H, dd, $J=5.8$, 2.7 Hz), 4.10 (5/6H, dd, $J=10.4$, 2.7 Hz), 4.05 (1/6H, dd, $J=10.5$, 2.7 Hz), 3.78 (15/6H, s), 3.76 (3/6H, s), 3.75 (5/6H, dd, $J=9.8$, 6.1 Hz), 3.64 (1/6H, dd, $J=9.8$, 6.1 Hz), 3.55—3.51 (2H, m), 3.50 (5/6H, dd, $J=9.5$, 6.1 Hz), 3.40 (1/6H, dd, $J=9.5$, 6.1 Hz), 2.47—2.43 (1/6H, m), 2.43—2.37 (5/6H, m), 2.33—2.29 (1/6H, m), 2.28—2.22 (5/6H, m), 1.48 (15/6H, s), 1.47 (3/6H, s), 1.32 (3H, s), 1.16 (9/6H, s), 1.15 (45/6H, s). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 178.2, 159.0, 138.2, 130.2 (5/6C), 130.1 (1/6C), 129.2 (5/6C), 129.1 (1/6C), 128.3 (5/6C), 128.2 (1/6C), 127.6, 127.5 (1/6C), 127.4 (5/6C), 113.7 (5/6C), 111.5 (1/6C), 104.6 (1/6C), 104.5 (5/6C), 80.9 (5/6C), 78.1 (5/6C), 78.0 (1/6C), 77.2 (1/6C), 73.1 (5/6C), 73.2 (1/6C), 72.6 (5/6C), 72.5 (1/6C), 68.6 (5/6C), 66.4 (1/6C), 63.3, 61.4 (5/6C), 60.3 (1/6C), 55.1, 46.3 (5/6C), 46.2 (1/6C), 40.5 (1/6C), 40.1 (1/6C), 38.6

(1/6C), 38.5 (5/6C), 27.0 (5/6C), 26.9 (1/6C), 26.6 (5/6C), 26.5 (1/6C), 26.4 (1/6C), 26.3 (5/6C). IR (neat) cm^{-1}: 2975, 1728, 1612, 1513, 1480, 1455, 1370. FAB-MS *m/z* (%): 543 ($\mathrm{M^+}+1$, 12), 485 (20), 461 (22), 369 (64), 365 (13), 278 (26), 277 (100), 275 (26), 241 (16), 187 (28), 186 (100), 185 (100), 165 (23), 149 (21), 137 (38), 135 (40), 122 (88), 121 (100), 107 (39), 94 (56), 93 (100), 91 (100), 75 (100). HR-MS Calcd for $\mathrm{C_{35}H_{43}O_5}$ ($\mathrm{M^+}+1$): 543.3111. Found: 543.2942.

4 N HCl (0.60 ml) was added to a stirred solution of the pivaloate (139 mg, 0.26 mmol) in THF (3 ml) at 55 °C. After 6 h, the reaction mixture was neutralized with saturated aqueous $\mathrm{NaHCO_3}$, and extracted with $\mathrm{CH_2Cl_2}$ (50 ml×2). The extract was washed with saturated aqueous $\mathrm{NH_4Cl}$ (5 ml×2) and brine (10 ml), then dried over $\mathrm{MgSO_4}$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 2), to give a 5 : 1 mixture of diols as a colorless oil (111 mg, 86%).

$\mathrm{Pb(OAc)_4}$ (106 mg, 0.24 mmol) was added to a stirred solution of the diol (111 mg, 0.22 mmol) in benzene (2 ml) at room temperature. After 10 min, the reaction mixture was filtered with florisil, and the filtrate, after concentration, was used for the next step without purification.

$\mathrm{LiAlH_4}$ (16.7 mg, 0.44 mmol) was added to a stirred solution of the aldehyde (110 mg, 0.22 mmol) in ether (2 ml) at 0 °C under argon. After 20 min, the reaction was quenched with saturated aqueous $\mathrm{NH_4Cl}$. The mixture was diluted with ether (2 ml), vigorously stirred for 10 min, and extracted with $\mathrm{CHCl_3}$ (50 ml×2). The extract was washed with saturated aqueous $\mathrm{NH_4Cl}$ (5 ml×2) and brine (10 ml), then dried over $\mathrm{MgSO_4}$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (2 : 3), to give a 5 : 1 mixture of (2*R*,3*S*,4*S*)-1-benzyloxy-2,4-dihydroxymethyl-3-hydroxy-5-(4-methoxybenzyloxy)pentane and its C6 isomer as a colorless oil (76.8 mg, 89%). FAB-MS *m/z* (%): 391 ($\mathrm{M^+}+1$, 27), 281 (12), 241 (15), 233 (10), 211 (20), 165 (11), 154 (14), 151 (14), 137 (100), 122 (100), 121 (100), 107 (44), 91 (100). HR-MS (FAB) *m/z* Calcd for $\mathrm{C_{22}H_{31}O_6}$: 391.2121 ($\mathrm{M^+}+\mathrm{H}$). Found: 391.2133.

$\mathrm{Et_3N}$ (168 μl, 1.20 mmol), DMAP (18.3 mg, 0.15 mmol) and PivCl (81 μl, 0.66 mmol) were added to a stirred solution of the triol (116 mg, 0.30 mmol) in $\mathrm{CH_2Cl_2}$ (3 ml) at 0 °C under argon. After 1 h at room temperature, the reaction was quenched with MeOH, and the mixture was extracted with ether (30 ml×2). The extract was washed with saturated aqueous $\mathrm{NH_4Cl}$, $\mathrm{H_2O}$ and brine, then dried over $\mathrm{MgSO_4}$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (6 : 1), to give **7** (139 mg, 84%) and **7a** (27 mg, 16%) as colorless oils. **7**: ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$) δ: 7.34—7.26 (5H, m), 7.21 (2H, d, *J*=8.9 Hz), 6.85 (2H, d, *J*=8.9 Hz), 4.48 (2H, s), 4.41 (2H, s), 4.36 (2H, dt, *J*=12.5, 4.6 Hz), 4.29 (1H, dd, *J*=7.3, 4.9 Hz), 4.26 (1H, dd, *J*=7.3, 4.9 Hz), 3.95—3.91 (1H, m), 3.79 (3H, s), 3.61 (1H, dd, *J*=9.3, 4.6 Hz), 3.58 (1H, dd, *J*=9.3, 4.6 Hz), 3.55 (1H, dd, *J*=9.5, 4.6 Hz), 3.52 (1H, dd, *J*=9.5, 4.6 Hz), 3.22 (1H, d, *J*=3.1 Hz), 2.17—2.10 (2H, m), 1.15 (18H, s). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$) δ: 178.5, 159.2, 137.9, 129.9, 129.3, 129.2, 128.4, 127.7, 127.5, 113.8, 113.7, 73.4, 73.0, 71.0, 69.1, 68.9, 61.8, 55.2, 41.0, 40.9, 38.7, 27.2, 27.1, 27.1; IR (neat) cm^{-1} 3359, 2868, 1728. FAB-MS *m/z* (%): 559 ($\mathrm{M^+}+1$, 76), 558 ($\mathrm{M^+}$, 12), 451 (11), 289 (11), 228 (9.5), 138 (47), 107 (59), 91 (100). HR-MS (FAB) Calcd for $\mathrm{C_{32}H_{46}O_8}$: 559.3271 ($\mathrm{M^+}+\mathrm{H}$). Found: 559.3250. **7a**: ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$) δ: 7.35—7.26 (5H, m), 7.21 (2H, d, *J*=8.9 Hz), 6.85 (2H, d, *J*=8.9 Hz), 4.65 (1H, dd, *J*=12.8, 0.9 Hz), 4.58 (1H, dd, *J*=12.8, 0.9 Hz), 4.47 (2H, d, *J*=2.7 Hz), 4.40 (2H, d, *J*=0.9 Hz), 4.13—4.06 (4H, m), 3.80 (3H, s), 3.44—3.38 (2H, m), 3.09—3.02 (1H, m), 1.59 (1H, s), 1.18 (9H, s), 1.15 (9H, s). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$) δ: 178.3, 178.0, 159.1, 138.0, 134.7, 130.1, 129.8, 129.1, 128.4, 128.3, 127.7, 127.6, 113.7, 72.8, 72.4, 69.8, 66.0, 65.6, 64.5, 55.2, 38.8, 38.7, 37.9, 27.2, 27.1.

(2*S*,3*S*,4*R*)-2,4-Bis(2,2-dimethylpropanoyloxymethyl)-3,5-[(*S*)-4-methoxybenzylidenedioxy]pentan-1-ol (14) To a stirred solution of **7** (41.4 mg, 74.1 μmol) in EtOH (1 ml) was added Raney-Ni (W2) at room temperature under $\mathrm{H_2}$, and stirring was continued for 26 h. After filtration, the filtrate was concentrated *in vacuo*, and the residue was chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 2), to give (2*S*,3*S*,4*R*)-2,4-bis(2,2-dimethylpropanoyloxymethyl)-5-(4-methoxybenzyloxy)pentane-1,3-diol as a colorless oil (31.5 mg, 91%). ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$) δ: 7.23 (2H, d, *J*=8.5 Hz), 6.87 (2H, d, *J*=8.5 Hz), 4.46 (1H, d, *J*=7.9 Hz), 4.43 (1H, d, *J*=6.7 Hz), 4.36 (1H, ddd, *J*=11.3, 8.9, 4.3 Hz), 4.29 (1H, dd, *J*=11.3, 7.0 Hz), 3.95—3.92 (1H, m), 3.80 (3H, s), 3.71—3.69 (2H, m), 3.62 (1H, dd, *J*=9.2, 4.3 Hz), 3.55 (1H, dd, *J*=9.2, 4.3 Hz), 3.44 (1H, d, *J*=2.7 Hz), 2.63 (1H, dd, *J*=6.1, 5.8 Hz), 2.18—2.13 (1H, m), 2.02—1.97 (1H, m), 1.21 (9H, s), 1.02 (9H, s). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$) δ: 179.5, 178.8, 129.7, 129.4, 129.3, 113.9, 113.8, 73.1, 71.6, 69.4, 61.7, 61.5, 55.2, 42.6, 40.9, 38.8, 38.7, 27.2, 27.1. FAB-MS *m/z* (%): 469 ($\mathrm{M^+}+1$, 12), 461 (11), 369 (33), 277 (100), 186 (84), 185 (100), 165 (14), 149 (17), 122 (26), 121 (100), 94 (62), 93 (100), 91 (48), 75 (100). HR-MS Calcd for $\mathrm{C_{25}H_{41}O_8}$ ($\mathrm{M^+}+1$): 469.2954. Found: 469.2808.

MS 3A (10 mg) and DDQ (12 mg, 51.6 μmol) was added to a stirred solution of the diol (22 mg, 46.9 μmol) in $\mathrm{CH_2Cl_2}$ (1 ml) at room temperature under argon. After 4 h, the reaction was quenched with saturated aqueous $\mathrm{NaHCO_3}$, and the mixture was extracted with ether (10 ml×2). The extract was washed with saturated aqueous $\mathrm{NH_4Cl}$ (5 ml×2), $\mathrm{H_2O}$ (10 ml×2) and brine (10 ml), then dried over $\mathrm{Na_2SO_4}$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 2), to give **14** as a colorless oil (19.5 mg, 89%). ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$) δ: 7.39 (2H, d, *J*=8.5 Hz), 6.89 (2H, d, *J*=8.5 Hz), 5.49 (1H, s), 4.52 (1H, dd, *J*=11.0, 5.0 Hz), 4.47 (1H, dd, *J*=11.3, 7.9 Hz), 4.41 (1H, dd, *J*=11.0, 9.5 Hz), 4.33 (1H, dd, *J*=11.3, 3.4 Hz), 4.11 (1H, dd, *J*=10.7, 2.1 Hz), 4.05 (1H, dd, *J*=11.0, 7.0 Hz), 4.01 (1H, dd, *J*=10.7, 1.0 Hz), 3.80 (3H, s), 3.81 (1H, m), 3.75 (1H, dd, *J*=11.0, 4.6 Hz), 2.54 (1H, brs), 2.17—2.11 (1H, m), 2.02—2.00 (1H, m), 1.21 (9H, s), 1.20 (9H, s). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$) δ: 179.4, 178.4, 159.7, 130.4, 127.0, 113.3, 101.9, 76.3, 68.4, 61.2, 60.8, 57.8, 55.0, 41.7, 38.7, 38.5, 34.3, 27.0, 26.9.

(2*S*,3*R*,4*R*)-2,4-Bis(2,2-dimethylpropanoyloxymethyl)-3,5-[(*S*)-4-methoxybenylidenedioxy]pentanal (5) A solution of **14** (21.9 mg, 46.9 μmol) in $\mathrm{CH_2Cl_2}$ (0.5 ml) was added to a mixture of pyridine (9.5 μl, 117 μmol) and Dess–Martin periodinane (39.8 mg, 93.9 μmol) in $\mathrm{CH_2Cl_2}$ (0.5ml) at room temperature under argon. After 20 min, the mixture was diluted with ether (1 ml), and quenched with saturated aqueous $\mathrm{NaHCO_3}$ (1 ml) and saturated aqueous $\mathrm{Na_2S_2O_3}$ (1 ml). The mixture was extracted with ether (10 ml), and washed with saturated aqueous $\mathrm{NH_4Cl}$ (5 ml×2), $\mathrm{H_2O}$ (5 ml×2) and brine (10 ml), then dried over $\mathrm{Na_2SO_4}$. The extract was concentrated *in vacuo*, and the residue was chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (7 : 3), to give **5** as a colorless oil (19.2 mg, 88%) [^{1}H-NMR δ: 9.82 (1H, s)], which was immediately used to the next reaction.

(2*R*,3*s*,4*S*)-2,4-Bis(2,2-dimethylpropanoyloxymethyl)-1,3,5-triacetoxypentane (15) To a stirred solution of **7** (22 mg, 46.9 μmol) in $\mathrm{CH_2Cl_2}$ (1 ml) was added MS 3A (10 mg) and DDQ (12 mg, 51.6 μmol) at room temperature under argon. After 4 h, the reaction was quenched with saturated aqueous $\mathrm{NaHCO_3}$. The mixture was diluted with ether (1 ml), extracted with ether (10 ml×2), and washed with saturated aqueous $\mathrm{NH_4Cl}$ (5 ml×2), $\mathrm{H_2O}$ (10 ml×2) and brine (10 ml), then dried over $\mathrm{Na_2SO_4}$. The extract was concentrated *in vacuo*, and the residue was chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (3 : 2), to give an acetal as a colorless oil (19.5 mg, 89%). ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$) δ: 7.38 (2H, d, *J*=8.5 Hz), 7.35—7.26 (5H, m), 6.88 (2H, d, *J*=8.5 Hz), 5.47 (1H, s), 4.49 (2H, d, *J*=4.6 Hz), 4.47 (1H, dd, *J*=5.1, 2.1 Hz), 4.40 (1H, dd, *J*=11.3, 9.2 Hz), 4.33 (1H, dd, *J*=10.7, 3.4 Hz), 4.30 (1H, dd, *J*=11.3, 1.0 Hz), 4.27 (1H, dd, *J*=10.7, 7.9 Hz), 4.10 (1H, dd, *J*=10.7, 1.8 Hz), 3.96 (1H, dd, *J*=11.6, 1.8 Hz), 3.80 (3H, s), 3.64 (1H, dd, *J*=9.8, 4.3 Hz), 3.61 (1H, dd, *J*=9.8, 3.7 Hz), 2.28—2.22 (1H, m), 1.89—1.84 (1H, m), 1.19 (9H, s), 1.13 (9H, s). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$) δ: 178.4, 178.1, 159.9, 138.0, 1306, 128.4, 127.7, 127.2, 114.2, 113.6, 113.5, 102.1, 76.9, 73.3, 73.1, 68.5, 65.6, 61.7, 61.0, 55.3, 40.1, 38.8, 34.6, 27.2. FAB-MS *m/z* (%): 556 ($\mathrm{M^+}$, 43), 449 (8.8), 188 (5.4), 165 (8.5), 148 (4.9), 134 (6.4), 121 (24), 107 (18), 91 (100). HR-MS (FAB) *m/z* Calcd for $\mathrm{C_{32}H_{46}O_8}$: 557.3115 ($\mathrm{M^+}+\mathrm{H}$). Found: 557.3089.

To a stirred solution of the acetal (20 mg, 35.9 μmol) in EtOH (1 ml) was added 10% Pd/C at room temperature under $\mathrm{H_2}$. The stirring was continued for 2 h. After careful filtration through a celite layer, the filtrate was concentrated *in vacuo*, and the residue was chromatographed on a silica gel column, eluting with EtOAc, to give a triol as a colorless oil (12.5 mg, 100%).

To a stirred solution of the triol (10 mg, 28.7 μmol) in $\mathrm{CH_2Cl_2}$ (0.5 ml) was added DMAP (7.0 mg, 57.4 μmol) and $\mathrm{Ac_2O}$ (8.9 μl, 94.7 μmol) at room temperature. After 10 min, the reaction was quenched with saturated aqueous $\mathrm{NH_4Cl}$, and then the mixture was extracted with ether (20 ml) and washed with $\mathrm{H_2O}$ (2 ml×2) and brine (2 ml), then dried over $\mathrm{MgSO_4}$, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (2 : 3), to give **15** as a colorless oil (13.6 mg, 100%). ^{1}H-NMR (500 MHz, $\mathrm{CDCl_3}$)δ: 5.31 (1H, t, *J*=6.1 Hz), 4.23 (2H, dd, *J*=11.6, 4.6 Hz), 4.14—4.12 (4H, m), 4.03 (2H, dd, *J*=11.6, 6.7 Hz), 2.46—2.41 (2H, m), 2.07 (9H, s), 1.20 (18H, s). ^{13}C-NMR (125 MHz, $\mathrm{CDCl_3}$) δ: 178.2, 170.6, 169.8, 68.8, 61.9, 60.7, 39.2, 38.8, 27.1, 20.7, 20.6.

(2*R*,3*E*,6*S*,7*R*,8*R*-)-6,8-Bis(2,2-dimethylpropanoyloxymethyl)-1-[1,1-(dimethylethyl)diphenylsilyloxy]-2,4-dimethyl-7,9-[(*S*)-4-methoxybenzylidenedioxy]-3-nonen-5-one (4) A 1.64 M solution of *tert*-BuLi in pentane (90.9 μl, 149 μmol) was added to a stirred solution of **6** (33.3 mg, 71.6 μmol) in ether (0.5 ml) at −78 °C under argon. The mixture was stirred for 1 h at $-78\,°C$ and for 1 h at room temperature, then cooled again to $-78\,°C$, and a solution of **5** (12.9 mg, 27.8 μmol) in ether (0.5 ml) was added dropwise. The stirring was continued for 1 h at $-78\,°C$, then the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with ether (10 ml). The extract was washed with saturated aqueous NH_4Cl (5 ml×2), H_2O (5 ml×2) and brine (10 ml), then dried over Na_2SO_4, and concentrated *in vacuo*. The residue (26.2 mg) was dissolved in CH_2Cl_2, and to this stirred solution were added Et_3N (23.1 μl, 0.17 mmol), DMAP (2.5 mg, 20.6 μmol) and PivCl (10.2 μl, 82.5 μmol) at 0 °C. After 1 h at room temperature, the reaction was quenched with saturated aqueous NH_4Cl, and the mixture was extracted with ether (10 ml×2). The extract was washed with saturated aqueous NH_4Cl and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give a 2 : 1 mixture of crude alcohols (**16**) (17.7 mg, 79%).

A solution of the alcohols (**16**) (9 mg, 11.2 μmol) in CH_2Cl_2 (0.5 ml) was added to a mixture of pyridine (1.8 μl, 22.4 μmol) and Dess–Martin periodinane (5.2 mg, 12.3 μmol) in CH_2Cl_2 (0.5 ml) at room temperature under argon. After 1 h, the mixture was diluted with ether (1 ml), and quenched with saturated aqueous $NaHCO_3$ (1 ml) and saturated aqueous $Na_2S_2O_3$ (1 ml). The mixture was extracted with ether (10 ml). The extract was washed with saturated aqueous NH_4Cl (5 ml×2), H_2O (5 ml×2) and brine (10 ml×1), then dried over Na_2SO_4, concentrated *in vacuo*, and chromatographed on a silica gel column, eluting with *n*-hexane–EtOAc (4 : 1), to give **4** as a colorless oil (9 mg, 100%). $[\alpha]_D^{20}$ +24.9° (c=1.0, $CHCl_3$). ^{1}H-NMR (500 MHz, C_6D_6) δ: 7.81—7.78 (5H, m), 7.54 (2H, d, J=8.5 Hz), 7.31—7.22 (5H, m), 6.79 (2H, d, J=8.5 Hz), 6.49 (1H, d, J=9.3 Hz), 5.39 (1H, s), 4.66 (1H, dd, J=10.8, 7.3 Hz), 4.64 (1H, dd, J=10.8, 5.5 Hz), 4.59 (1H, dd, J=10.8, 3.7 Hz), 4.44 (1H, dd, J=10.2, 2.3 Hz), 4.43 (1H, dd, J=10.2, 3.7 Hz), 4.26 (1H, dd, J=11.6, 1.0 Hz), 3.80 (1H, ddd, J=10.2, 7.3, 3.7 Hz), 3.71 (1H, dd, J=9.8, 5.5 Hz), 3.64 (1H, dd, J=9.8, 7.3 Hz), 3.57 (1H, d, J=11.6 Hz), 3.24 (3H, s), 2.79—2.73 (1H, m), 1.89 (3H, s), 1.86—1.82 (1H, m), 1.20 (9H, s), 1.12 (9H, s), 1.04 (3H, d, J=6.7 Hz), 1.00 (9H, s). ^{13}C-NMR (125 MHz, C_6D_6) δ: 200.0, 177.5, 177.3, 160.5, 145.3, 138.5, 136.0, 135.9, 131.4, 130.1, 130.0, 128.3, 128.2, 127.8, 113.8, 102.5, 77.7, 67.9, 67.5, 64.3, 60.6, 54.7, 46.4, 38.8, 38.6, 37.1, 35.1, 27.3, 27.1, 27.0, 19.5, 16.6, 12.0. FAB-MS m/z (%): 801 (M^++1, 3.0), 743 (1.1), 563 (2.3), 553 (1.7), 369 (9.3), 365 (3.4), 337 (2.4), 307 (2.3), 283 (6.3), 278 (4.1), 277 (35), 275 (5.3), 259 (2.4), 239 (5.0), 223 (4.1), 215 (4.3), 207 (4.6), 199 (8.7), 197 (10), 186 (24), 185 (100), 183 (11), 167 (6.4), 165 (6.6), 137 (6.6), 135 (16), 121 (6.2), 115 (7.8), 94 (10), 93 (100), 75 (53). HR-MS Calcd for $C_{47}H_{65}O_9Si$ (M^++1): 801.4396. Found: 801.4393.

References and Notes

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6) In this synthesis, five out of six carbons in D-glucose (**9**) were incorporated in the title compound (**4**).

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10) $BH_3 \cdot THF$ also gave a good result (82% yield, 11 : 1 selectivity), but the reproducibility was poor..

11) The TBDPS protecting group instead of the pivaloyl group was rather labile under acidic conditions.

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