Syntheses of Natural (–)-Osmundalactone and Its Epimer

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(–)-Osmundalactone, an aglycone of osmundalin, and its 5-epimer were synthesized from 3-triethylsiloxy-1-propyne and from (*S*)-1-methyl-2-oxoethyl benzoate, which was derived from 2,3-*O*-cyclohexylidene-D-glyceraldehyde.

Osmundalactone (**1**),¹⁾ an aglycone of osmundalin isolated from *Osmunda japonica* Thunberg (Akaboshi zenmai), is one of the non-benzenoid oligoketides bearing a 6-substituted-5,6-dihydro-5-hydroxy (or acyloxy)-2*H*-pyran-2-one moiety as shown in the structures of phomalactone (**2**),^{2,3)} acetylphomalactone (**3**),^{4,5)} asperlin (**4**),²⁾ olguin (**5**)⁶⁾ and phomopsolide (**6**).⁷⁾ The chemical structure, including the absolute stereochemistry of **1**, was elucidated in 1974.¹⁾ Recently, **1** was isolated as a feeding inhibitor for the larvae of butterfly *Eurema hecabe mandarina*.⁸⁾

In our continuing synthetic work on biologically active compounds, **1** was selected as a suitable target to establish the synthetic route to optically active 5,6-dihydro-5-hydroxy-2*H*-pyran-2-ones, since **1** has the simplest structure among them and an interesting biological activity.

This molecule **1** was constructed from two fragments, i.e. (*S*)-1-methyl-2-oxoethyl benzoate (**11**) and a protected propargyl alcohol. The former could be obtainable from ethyl L-lactate by a multi-step process, but was obtained more conveniently from (2*R*,3*S*)-1,2,3-butanetriol which was derived from 2,3-*O*-cyclohexylidene-D-glyceraldehyde.⁹⁾ A Grignard reaction on a glyceraldehyde derivative predominantly produces an *erythro* alcohol at the newly created chiral center when the reaction is carried out at low temperature.^{10a,b)} Thus, the reaction of methyl-

magnesium iodide with 2,3-*O*-cyclohexylidene-D-glyceraldehyde (**7**) gave a diastereomeric mixture (**8**) of *erythro* and *threo* isomers in the ratio of 3.2:1 by a gas chromatographic analysis. The *erythro* isomer was purified by fractional recrystallization of the 3,5-dinitrobenzoate of **8** and converted to the benzoate **9** in a 52% yield from the starting glyceraldehyde derivative **7**. The cyclohexylidene protective group was removed by refluxing in aqueous methanol in the presence of an acid catalyst to afford the diol-ester **10** in a 79% yield. The diol **10** was oxidized with sodium metaperiodate in an 82% yield to give the (*S*)-aldehyde **11**, which was immediately used for the next reaction because of its instability and vulnerability to moisture.

The reaction between **11** and 1-lithio-3-triethylsiloxy-1-propyne in tetrahydrofuran at low temperature gave a diastereomeric mixture

FIG. 1

FIG. 2

(12) in an 82% yield without affecting the benzoate protecting group. The mixture 12 was rapidly subjected to column chromatography on silica gel to avoid the possible migration of the benzoyl group to the free hydroxyl group on the adjacent carbon atom, but each diastereomer of 12 could not be separated. The hydroxyl group of 12 was protected with dihydropyran in dry benzene in the presence of an acid catalyst to give the ether 13 in a 93% yield. Both of the benzoyl and triethylsilyl groups were then removed by treating with methanolic sodium hydroxide to afford the diol 14 in a 76% yield. Partial hydrogenation of 14 over Lindlar's catalyst gave the (*Z*)-olefinic diol (15) in an 88% yield.

Oxidation of 15 with active manganese dioxide in dichloromethane according to the method by Yamamoto¹¹ yielded a mixture of the desired δ -lactones 16 and 17 in a good yield. Each of the δ -lactones was separated by preparative thin-layer chromatography developed with ether to give pure 16 (49%, *R*_f: 0.7) and 17 (46%, *R*_f: 0.5). The signal from the α -proton of the lactone carbonyl in the ¹H-NMR spectrum showed d-d splitting (*J*=1.7 and 10.0 Hz) for 16, while a simple doublet (*J*=10.0 Hz) was observed for 17. The presence of an allylic coupling (1.7 Hz) in 16 indicated the *trans* orientation of the substituents on the six-membered lactone ring as re-

ported by Perlin.¹² Therefore, 16 was determined to be a natural-form (5*R*,6*S*) isomer and 17 had diastereomeric (5*S*,6*S*)-stereochemistry. Finally, deprotection of the tetrahydropyranyl ether of 16 and 17 with ion exchange resin (Amberlyst-15) in dry methanol afforded (5*R*,6*S*)-5,6-dihydro-5-hydroxy-2*H*-pyran-2-one (osmundalactone, 1) and its diastereoisomer (5*S*,6*S*)-5,6-dihydro-2*H*-pyran-2-one (18) in 59 and 87% yields, respectively. Anhydrous conditions were necessary to prevent conversion of the δ -lactone into a γ -lactone during deprotection of the tetrahydropyranyl group.

The synthesized osmundalactone (1) was identical with the natural one in all spectral data, and its optical rotation ($[\alpha]_D^{20} - 70.3^\circ$ (*c*=0.56, H₂O)) was comparable with that of the natural compound ($[\alpha]_D^{22} - 70.6^\circ$ (*c*=2.0, H₂O)). Our synthetic procedure had fewer steps compared with the other procedures previously reported,^{11,14} and this strategy will be applicable to the synthesis of other chiral lactones having 6-substituted-5,6-dihydro-5-hydroxy- (or acyloxy)-2*H*-pyran-2-ones.

EXPERIMENTAL

All boiling points (bp) and melting points (mp) are uncorrected. ¹H-NMR spectra were recorded on a JEOL JNM FX-100 spectrometer, and IR spectra, on a JASCO IR-810 infrared spectrometer. Optical rotations were

measured on a JASCO DIP-4 polarimeter. Gas chromatographic analyses were performed on a Yanaco G 3800 instrument with a flame ionization detector, using a glass column (2 m × 3 mm) packed with 5% Carbowax (PEG) 20M on Chromosorb W (AW) (column temp., 145°C; N₂ flow rate, 20 ml/min).

(2*R*,3*S*)-1,2-*O*-Cyclohexylidene-1,2,3-butanetriol (**8e**).

To a solution of methylmagnesium iodide (prepared from 9.0 g of MeI (63 mmol) and 1.3 g of Mg turnings (53 mmol) in 200 ml of dry ether) was added dropwise 8.5 g of **7** (50 mmol) at –20°C, and the solution was stirred for 2 hr under N₂. The reaction mixture was then poured into aq. NH₄Cl and extracted with ether. The extract was washed with aq. NaHCO₃ and dried over anhyd. Na₂SO₄. After evaporating the ether, the residue was distilled to afford 9.0 g (96%) of (2*R*,3*RS*)-1,2-*O*-cyclohexylidene-1,2,3-butanetriol (bp 101°C (2.7 mmHg)), which consisted of the (2*R*,3*S*) and (2*R*,3*R*) isomers in the ratio of 3.2:1 by GLC analysis. Recrystallization of the 3,5-dinitrobenzoate of the mixture from MeOH gave 10.0 g of a pure ester of the (2*R*,3*S*)-isomer in a 52% yield from **7**. Subsequent alkaline hydrolysis and distillation afforded 4.7 g of the (2*R*,3*S*)-isomer **8e** as a colorless oil (bp 102°C (2.8 mmHg)). The physical data for the 3,5-dinitrobenzoate of **8e** are as follows: mp 104~105°C; $[\alpha]_D^{20} + 31.0^\circ$ ($c = 1.20$, CHCl₃); IR $\nu_{\max}^{\text{KBr}} \text{cm}^{-1}$: 3125, 3100, 1730, 1630, 1600, 1550, 1460, 1350, 1280, 1170, 1100, 1070, 1040, 930, 730, 720. ¹H-NMR (CDCl₃) δ : 1.45 (3H, d, $J = 6.6$ Hz), 1.59 (10H, br. s), 4.25 (2H, ddd, $J = 5.3, 6.4, 8.0$ Hz), 4.30 (1H, m), 5.30 (1H, dq, $J = 6.6, 6.6$ Hz), 9.17 (3H, m). *Anal.* Found: C, 53.71; H, 5.39; N, 7.31. Calcd. for C₁₇H₂₀O₈N₂: C, 53.68; H, 5.30; N, 7.38%.

(2*R*,3*S*)-1,2-*O*-Cyclohexylidene-1,2,3-butanetriol 3-benzoate (**9**). To a solution of 4.7 g of **8e** (25 mmol) in 50 ml of pyridine was added 3.7 g of benzoyl chloride (26 mmol), the mixture being stirred for 30 min at 0°C. The reaction mixture was poured into water and extracted with ether. The extract was successively washed with 5% aq. acetic acid, water, aq. NaHCO₃ and brine, and dried over anhyd. Na₂SO₄. After evaporating the ether *in vacuo*, the residue was purified by column chromatography on alumina to give 7.2 g (99%) of **9**. $[\alpha]_D^{20} + 39.0^\circ$ ($c = 1.53$, CHCl₃). IR $\nu_{\max}^{\text{film}} \text{cm}^{-1}$: 3060, 1720, 1600, 1585, 1450, 1270, 1160, 1118, 1100, 1070, 1040, 930, 720. ¹H-NMR (CDCl₃) δ : 1.39 (3H, d, $J = 6.4$ Hz), 1.59 (10H, br. s), 3.83~4.30 (3H, m), 5.19 (1H, quint, $J = 6.4$ Hz), 7.26~8.10 (5H, m). *Anal.* Found: C, 70.50; H, 7.63. Calcd. for C₁₇H₂₂O₄: C, 70.32; H, 7.64%.

(2*R*,3*S*)-1,2,3-Butanetriol 3-benzoate (**10**). A solution of 7.2 g of **9** (25 mmol) and 0.5 g of *p*-TsOH in 50 ml of aq. MeOH was refluxed for 1 hr. The reaction mixture was poured into aq. NaHCO₃ and extracted with ethyl acetate, before the extract was dried over anhyd. Na₂SO₄. After evaporating the solvent, the residue was chromatographed

on silica gel to afford 3.8 g (79%) of oily **10**. $[\alpha]_D^{20} + 18.9^\circ$ ($c = 1.20$, CHCl₃). IR $\nu_{\max}^{\text{film}} \text{cm}^{-1}$: 3400, 3070, 1720, 1600, 1580, 1450, 1280, 1120, 1070, 1050, 1030, 880, 720. ¹H-NMR (CDCl₃) δ : 1.45 (3H, d, $J = 6.6$ Hz), 2.60 (1H, br. t, $J = 6.6$ Hz), 2.75 (1H, br. d, $J = 6.6$ Hz), 3.69 (3H, m), 5.17 (1H, quintet, $J = 6.3$ Hz), 7.34~8.08 (5H, m). *Anal.* Found: C, 62.54; H, 6.83. Calcd. for C₁₁H₁₄O₄: C, 62.84; H, 6.71%.

(*S*)-1-Methyl-2-oxoethyl benzoate (**11**). A solution of 3.6 g of **10** (17 mmol), 4.0 g of sodium metaperiodate (19 mmol), 50 ml of THF, 100 ml of ether and 100 ml of water was stirred for 1 hr at room temperature. The reaction mixture was poured into 200 ml of water and extracted with ether, before the extract was dried over anhyd. Na₂SO₄. After evaporating the ether, the residue was distilled *in vacuo* to give 2.5 g (82%) of **11**, bp 112°C (5 mmHg). $[\alpha]_D^{20} - 28.0^\circ$ ($c = 2.80$, benzene), [lit.¹⁵] $[\alpha]_D^{20} - 30.8 \pm 1^\circ$ (benzene) as the estimated value for optically pure **11**. IR $\nu_{\max}^{\text{film}} \text{cm}^{-1}$: 2740, 1730, 1605, 1590, 1455, 1324, 1270, 1115, 1072, 1030, 715. ¹H-NMR (CDCl₃) δ : 1.53 (3H, d, $J = 7.3$ Hz), 5.29 (1H, q, $J = 7.3$ Hz), 7.30~8.10 (5H, m), 9.66 (1H, s). *Anal.* Found: C, 67.39; H, 5.67. Calcd. for C₁₀H₁₀O₃: C, 67.40; H, 5.66%.

(4*RS*,5*S*)-(Triethylsiloxy)-2-hexyne-1,4,5-triol 5-benzoate (**12**). To a solution of 2.7 g of 3-(triethylsiloxy)-1-propyne (16 mmol) in 100 ml of THF was added 10 ml of a 1.56M solution of *n*-butyllithium in *n*-hexane at –78°C, and the solution was stirred for 1 hr. Then, 2.5 g of **11** (14 mmol) was added dropwise and stirring was continued for 2 hr at that temperature. The reaction mixture was poured into 200 ml of water and extracted with ether, before the extract was dried over anhyd. Na₂SO₄. After evaporating the solvent *in vacuo*, the residue was subjected to column chromatography on silica gel to afford 4.1 g of oily **12** in an 82% yield. This diastereomeric mixture was used for the next reaction without further purification. IR $\nu_{\max}^{\text{film}} \text{cm}^{-1}$: 3425, 1725, 1710, 1600, 1455, 1275, 1120, 1100, 1070, 1030, 730, 715. ¹H-NMR (CDCl₃) δ : 0.89 (6H, m), 0.97 (9H, m), 1.46 (3H, d, $J = 6.4$ Hz), 2.68 (1H, br. d, $J = 6.8$ Hz), 4.36 (2H, d, $J = 1.7$ Hz), 4.58 (1H, dt, $J = 3.4, 1.7$ Hz), 5.22 (1H, dq, $J = 3.4, 4.6$ Hz), 7.33~8.12 (5H, m). *Anal.* Found: C, 65.08; H, 7.90. Calcd. for C₁₉H₂₈O₄Si: C, 65.48; H, 8.10%.

(3*RS*,2*S*)-3-Tetrahydropyranyloxy-6-triethylsiloxy-4-hexyn-2-ol benzoate (**13**). A solution of 2.8 g of **12** (8.0 mmol), 0.8 g of dihydropyran (9.5 mmol) and a catalytic amount of *p*-TsOH in 50 ml of dry benzene was stirred for 3 hr at room temperature. The reaction mixture was then poured into aq. NaHCO₃ and extracted with ether, before the extract was dried over anhyd. Na₂SO₄. After evaporating the solvent, the residue was purified by column chromatography on silica gel to afford 3.2 g (93%) of **13**. IR $\nu_{\max}^{\text{film}} \text{cm}^{-1}$: 3040, 1605, 1480, 1460, 1275, 1200, 1120, 1025, 970, 905, 870, 715, 680. ¹H-NMR (CDCl₃)

δ : 0.67 (6H, m), 0.94 (9H, m), 1.45 (3H, d, $J=6.6$ Hz), 1.45~1.90 (6H, m), 3.30~4.20 (2H, m), 4.63 (1H, m), 4.80~5.03 (1H, m), 5.32 (1H, m), 7.32~8.12 (5H, m). *Anal.* Found: C, 66.60; H, 8.39. Calcd. for $C_{24}H_{36}O_5Si$: C, 66.63; H, 8.39%.

(4*RS*,5*S*)-4-Tetrahydropyranyloxy-2-hexyne-1,5-diol (14). To a solution of 30 ml of 5% NaOH-MeOH was added 3.2 g of **13** (7.4 mmol), the mixture being stirred for 1 hr at room temperature. The reaction mixture was poured into 200 ml of water and extracted with ether, before the extract was dried over anhyd. Na_2SO_4 . After evaporating the ether, the residue was chromatographed on silica gel to afford 1.2 g (76%) of **14**. IR $\nu_{max}^{film} cm^{-1}$: 3400, 1445, 1360, 1205, 1120, 1020, 975, 905, 870, 815. 1H -NMR ($CDCl_3$) δ : 1.28 (3H, d, $J=6.4$ Hz), 1.53 (6H, m), 3.30 (1H, br. s), 3.40~4.20 (5H, m), 4.28 (2H, d, $J=1.7$ Hz), 4.80 (1H, m). Diacetate of **14**: IR $\nu_{max}^{film} cm^{-1}$: 1740, 1440, 1370, 1230, 1115, 1070, 1020, 965, 900, 870, 815. 1H -NMR ($CDCl_3$) δ : 1.36 (3H, d, $J=6.6$ Hz), 1.69 (6H, m), 2.07 (3H, s), 2.08 (3H, s), 3.40~4.20 (2H, m), 4.34~4.55 (1H, m), 4.69~4.73 (2H, m), 4.95~5.15 (2H, m). *Anal.* Found: C, 60.25; H, 7.86. Calcd. for $C_{15}H_{22}O_6$: C, 60.39; H, 7.43%. MS m/z : 299 ($M^+ + 1$, 1%), 211 (18), 197 (37), 113 (23), 85 (100).

(*Z*)-(4*RS*,5*S*)-4-Tetrahydropyranyloxy-2-hexene-1,5-diol (15). A solution of 0.9 g of **14** (4.4 mmol), 0.2 g of Lindlar's catalyst, 0.1 ml of quinoline and 50 ml of EtOH was stirred under H_2 . When 94 ml of H_2 had been absorbed, the reaction was stopped. The catalyst was filtered and washed well with EtOH, before the filtrate and washings were combined and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give 0.8 g (88%) of **15**. IR $\nu_{max}^{film} cm^{-1}$: 3390, 1200, 1130, 1120, 1020, 975, 905, 865, 810. 1H -NMR ($CDCl_3$) δ : 1.16 (3H, m), 1.62 (6H, m), 3.34~3.80 (5H, m), 4.12~4.35 (3H, m), 4.68~4.81 (1H, m), 5.21~6.20 (2H, m). *Anal.* Found: C, 60.41; H, 9.41. Calcd. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32%.

(5*R*,6*S*) and (5*S*,6*S*)-5,6-Dihydro-5-tetrahydropyranyloxy-6-methyl-2H-pyran-2-one (16 and 17). Active MnO_2 (5.6 g, 65 mmol) was added portionwise to a solution of 0.7 g of **15** (3.2 mmol) in CH_2Cl_2 at room temperature, and the reaction mixture was stirred for 12 hr. The reaction mixture was filtered, and the filter cake was washed well with ether. The filtrate and washings were combined and concentrated *in vacuo*, leaving a pale yellow oil which was subjected to chromatography on silica gel using ethyl acetate-hexane (1:4) as an eluent to give two isomeric compounds (**16** and **17**). Separation of each isomer was carried out by preparative TLC on silica gel developed with ether to afford 0.33 g (49%) of pure **16** (R_f : 0.7) and 0.31 g (46%) of pure **17** (R_f : 0.5).

16. IR $\nu_{max}^{film} cm^{-1}$: 3070, 1735, 1630, 1455, 1390, 1240, 1200, 1120, 1060, 1035, 965, 910, 870, 850, 820, 750. 1H -

NMR ($CDCl_3$) δ : 1.48 (3H, d, $J=6.2$ Hz), 1.30~1.83 (6H, m), 3.60~3.85 (2H, m), 4.73~4.84 (1H, m), 5.98 (1H, dd, $J=1.7$, 10.0 Hz). *Anal.* Found: C, 62.10; H, 7.62. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

17. IR $\nu_{max}^{film} cm^{-1}$: 3070, 1735, 1720, 1630, 1440, 1380, 1255, 1200, 1120, 1060, 1035, 1020, 1000, 965, 910, 830, 750. 1H -NMR ($CDCl_3$) δ : 1.48 (3H, d, $J=6.8$ Hz), 1.30~2.00 (6H, m), 3.42~3.90 (2H, m), 3.95~4.27 (1H, m), 4.45~4.75 (2H, m), 6.11 (1H, d, $J=10.0$ Hz), 7.11 (1H, dd, $J=5.6$, 10.0 Hz). *Anal.* Found: C, 61.86; H, 7.58. Calcd. for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60%.

(5*R*,6*S*)-5,6-Dihydro-5-hydroxy-6-methyl-2H-pyran-2-one (1, *osmundalactone*). The THP ether **16** (0.17 g, 0.8 mmol) was dissolved in dry MeOH and treated with a catalytic amount of Amberlyst-15 at room temperature. After stirring for 3 hr, the reaction mixture was filtered, and the filter cake was washed well with ethyl acetate. The filtrate and the washings were combined and concentrated *in vacuo* to leave a colorless oil, which was subjected to preparative TLC of silica gel developed with ethyl acetate-hexane (1:1) to afford 60 mg (59% yield) of the lactone **1**. mp 82.5°C (lit. 82~82.5°C).¹⁾ $[\alpha]_D^{20} - 70.3^\circ$ ($c=0.56$, H_2O) [lit.¹⁾ -70.6° ($c=2.0$, H_2O)]. IR $\nu_{max}^{KBr} cm^{-1}$: 3380, 1705, 1620, 1390, 1305, 1280, 1250, 1170, 1105, 1060, 1020, 965, 850, 810, 745. 1H -NMR ($CDCl_3$) δ : 1.48 (3H, d, $J=6.1$ Hz), 2.56 (1H, br. d, $J=6.4$ Hz), 4.00~4.50 (2H, m), 5.98 (1H, dd, $J=1.7$, 10.0 Hz), 6.85 (1H, dd, $J=2.2$, 10.0 Hz). *Anal.* Found: C, 56.00; H, 6.39. Calcd. for $C_6H_8O_3$: C, 56.24; H, 6.29%.

(5*S*,6*S*)-5,6-Dihydro-5-hydroxy-6-methyl-2H-pyran-2-one (18). The lactone (**17**, 0.15 g, 0.7 mmol) was treated as above to give 78 mg of the lactone (**18**) in an 87% yield. $[\alpha]_D^{20} + 142.8^\circ$ ($c=0.53$, H_2O). IR $\nu_{max}^{film} cm^{-1}$: 3400, 1710, 1630, 1380, 1260, 1175, 1115, 1060, 1020, 990, 960, 900, 830, 740. 1H -NMR ($CDCl_3$) δ : 1.50 (3H, d, $J=6.6$ Hz), 2.90 (1H, br. d, $J=10.0$ Hz), 4.20 (1H, ddd, $J=2.7$, 5.6, 10.0 Hz), 4.54 (1H, dq, $J=2.7$, 6.6 Hz), 6.09 (1H, d, $J=10.0$ Hz), 7.02 (1H, dd, $J=5.6$, 10.0 Hz).

The 3,5-dinitrobenzoate of **18**. mp 229~230°C. $[\alpha]_D^{20} + 273.6^\circ$ ($c=0.83$, CH_3CN). IR $\nu_{max}^{KBr} cm^{-1}$: 3080, 1730, 1705, 1630, 1550, 1350, 1285, 1260, 1170, 1100, 1080, 1060, 950, 925, 840, 720. 1H -NMR ($CDCl_3$) δ : 1.51 (3H, d, $J=6.4$ Hz), 5.00 (1H, dq, $J=2.4$, 6.4 Hz), 5.70 (1H, dd, $J=2.4$, 5.9 Hz), 6.30 (1H, d, $J=9.8$ Hz), 7.24 (1H, dd, $J=5.9$, 9.8 Hz). *Anal.* Found: C, 48.15; H, 3.14; N, 9.03. Calcd. for $C_{13}H_{10}O_8N_2$: C, 48.45; H, 3.13; N, 8.69%.

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