JOC*Note*

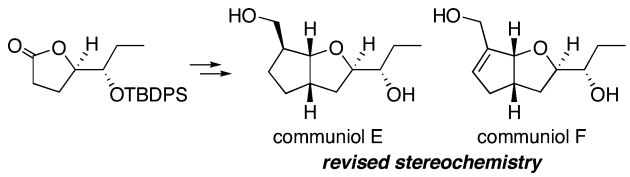
Enantioselective Total Synthesis and Stereochemical Revision of Communiols E and F

Masaru Enomoto and Shigefumi Kuwahara*

Laboratory of Applied Bioorganic Chemistry, Graduate School of Agricultural Science, Tohoku University, Tsutsumidori-Amamiyamachi, Aoba-ku, Sendai 981-8555, Japan

skuwahar@biochem.tohoku.ac.jp

Received April 28, 2006



The enantioselective total synthesis of candidate structures for communiols E and F, novel bicyclic polyketides of fungal origin, was accomplished using a Lewis acid-mediated ring closure reaction of an allylsilane intermediate as the key step. Comparison of the spectral data of the synthetic materials with those of natural communiols E and F, coupled with biosynthetic considerations, led to the conclusion that the stereochemistry of communiols E and F should be (2*S*,5*S*,7*R*,8*S*,11*R*)- and (5*S*,7*R*,8*S*,11*R*)-forms, respectively.

In the course of screening for bioactive metabolites from coprophilous (dung-colonizing) fungi, Gloer and co-workers isolated novel bicyclic polyketides, communiols E and F, along with biosynthetically related monocyclic polyketides (communiols G and H) from the culture broth of the horse dung-inhabiting fungus *Podospora communis*, and proposed their structures as **1b** and **2b**, respectively (Figure 1). [1] Their stereochemical assignment for communiols E and F was based mainly on the following three grounds: (1) strong NOESY correlations between 2-H and 7-H, and 5-H and 11-H to support the relative stereochemical assignment among the stereogenic centers on the bicyclic system, (2) the similarity of the 7-H−8-H vicinal coupling constant ($J = 3.6$ Hz) to that observed for analogous polyketides (communiols A−D)[2] of the same microbial origin to rationalize the threo stereochemistry between the C7 and C8 positions (the C7−C8 threo relative stereochemistry of communiols A−D had previously been deduced on the basis of Born's empirical rule),[2,3] and (3) the biogenetically acceptable presumption that the absolute configuration at the C8-position

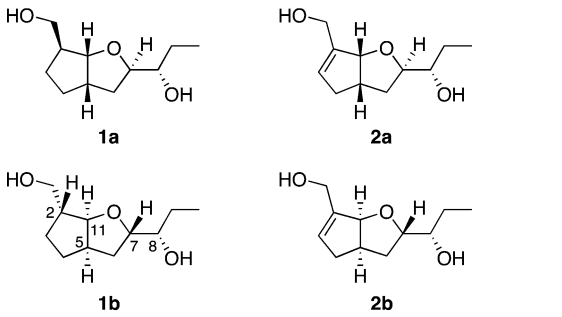


FIGURE 1. Newly proposed stereochemistry for communiols E and F (**1a** and **2a**, respectively) and their original stereochemistry (**1b** and **2b**, respectively).

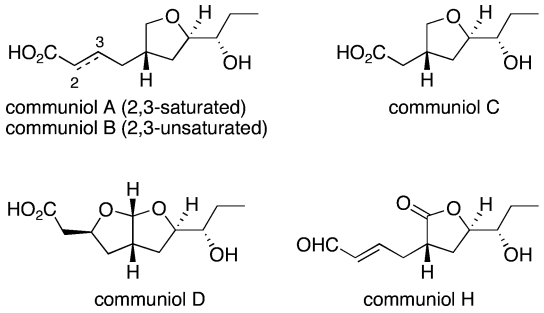


FIGURE 2. Revised stereochemistry for communiols A−D and H.

of communiols E and F should be the same as that of communiol A, which in turn was unambiguously determined to be *S* by the modified Mosher method.[4] Our previous synthetic studies on optically active forms of communiols A−D and H, however, enabled us to conclude that the relative stereochemical assignment between the C7 and C8 positions by Gloer et al. was incorrect, and that the stereochemistry of communiols A−D and H should all be altered as shown in Figure 2.[5,6] This stereochemical revision led us to suppose that the genuine stereochemistry for communiols E and F should also be altered to structures **1a** (*ent*-8-*epi*-**1b**) and **2a** (*ent*-8-*epi*-**2b**), respectively. In this note, we describe the enantioselective total synthesis of **1a** and **2a**, which culminated in the stereochemical revison of communiols E and F.

Our retrosynthetic analysis of **1a** and **2a** is shown in Scheme 1. For the construction of the 2-oxabicyclo[3.3.0]octane framework incorporated in **1a** and **2a**, we planned to utilize a Lewis acid-mediated cyclization of **4** containing a lactol functionality as the electrophilic site and an allylsilane moiety as the nucleophilic site. The bicyclic product **3** would be convertible into either **1a** or **2a** via oxidative cleavage of the double bond. The lactol **4** would be readily obtainable from **5** through diastereoselective trans alkylation and subsequent reduction of the lactone group.

(1) Che, Y.; Araujo, A. R.; Gloer, J. B.; Scott, J. A.; Malloch, D. *J. Nat. Prod.* **2005**, *68*, 435−438.

(2) Che, Y.; Gloer, J. B.; Scott, J. A.; Malloch, D. *Tetrahedron Lett.* **2004**, *45*, 6891−6894.

(3) (a) Born, L.; Lieb, F.; Lorentzen, J. P.; Moeschler, H.; Nonfon, M.; Söllner, R.; Wendisch, D. *Planta Med.* **1990**, *56*, 312−316. (b) Chávez, D. C.; Acevedo, L. A.; Mata, R. *J. Nat. Prod.* **1998**, *61*, 419−421. (c) Fujimoto, Y.; Murasaki, C.; Shimada, H.; Nishioka, S.; Kakinuma, K.; Singh, S.; Singh, M.; Gupta, Y. K.; Sahai, M. *Chem. Pharm. Bull.* **1994**, *42*, 1175−1184.

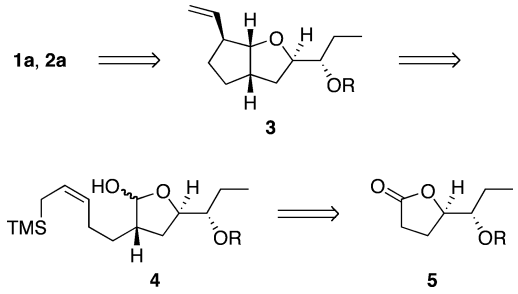
(4) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092−4096.

(5) (a) Kuwahara, S.; Enomoto, M. *Tetrahedron Lett.* **2005**, *46*, 6297−6300. (b) Enomoto, M.; Nakahata, T.; Kuwahara, S. *Tetrahedron* **2006**, *62*, 1102−1109.

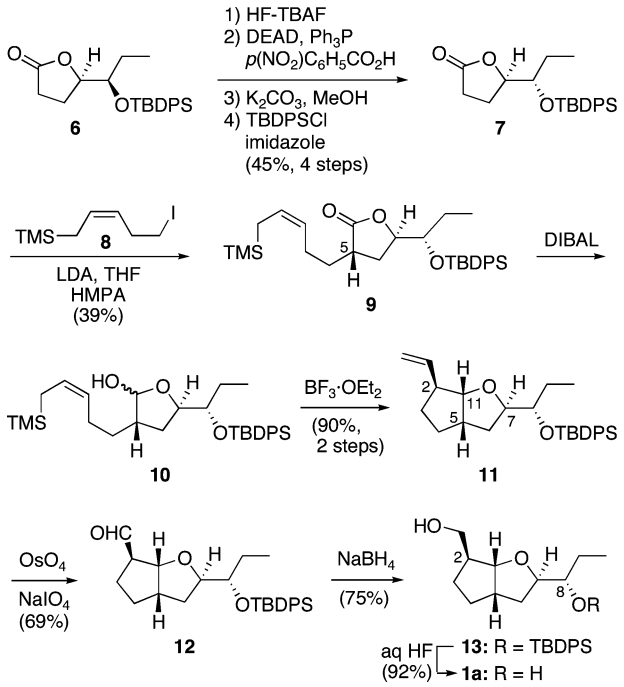
(6) For the synthesis of ent-communiols A−C which led to the same stereochemical revision as our studies, see the following: Murga, J.; Falomir, E.; Carda, M.; Marco, J. A. *Tetrahedron Lett.* **2005**, *46*, 8199−8202.

10.1021/jo0608927 CCC: $33.50
Published on Web 07/07/2006

SCHEME 1. Retrosynthetic Analysis of 1a and 2a

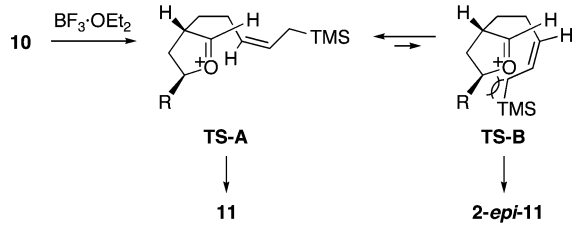


SCHEME 2. Synthesis of Communiol E (1a)



As shown in Scheme 2, our synthesis of the newly proposed candidate structure for communiol E (**1a**) began with a four-step inversion of the stereochemistry at the chiral center on the side chain of known lactone **6** to afford its epimer **7**. The starting lactone **6**, in turn, was prepared in enantiomerically pure form from ethyl (*E*)-4-heptenoate according to our previously reported three-step procedure consisting of the Sharpless asymmetric dihydroxylation, acid-catalyzed lactonization, and protection followed by recrystallization.[5b] The trans-selective alkylation of **7** with known silylated iodoalkene **8**[7] gave a 15.2:1 mixture of **9** and its C5-epimer in 44% yield along with recovered starting lactone **7** (16%).[8,9] After isolation of **9** by repeated silica gel column chromatography (39% isolated yield), the lactone was reduced with DIBAL to lactol **10**, which was then exposed to $BF_3{\cdot}OEt_2$ in CH_2Cl_2 to induce the formation of the bicyclic ring system in an intramolecular manner.[10] Fortunately, the C2-vinyl substituent of the cyclization product **11** preferred the desired exo orientation (**11**/2-*epi*-**11** = 6.4:1), as determined by observation of NOE correlations between 2-H and 7-H, and

SCHEME 3. Preferential Formation of 11



5-H and 11-H. This desirable diastereoselectivity could be explained by considering the thermodynamic stability of two types of transition states, **TS-A** and **TS-B**, leading to **11** and 2-*epi*-**11**, respectively (Scheme 3). The reaction must have taken place mainly through the less sterically demanding transition state **TS-A** rather than **TS-B** wherein severe steric repulsion between the side-chain moiety and the ring portion was anticipated, giving the desired product **11** preferentially. The double bond of **11** was cleaved by the Lemieux-Johnson reaction, and the resulting aldehyde **12** was reduced to alcohol **13**. The C2-epimer of **13** originating from the incomplete stereoselectivity in the formation of **11** (6.4:1, as mentioned above) was readily removed at this stage by SiO_2 chromatography. Finally, removal of the silyl protecting group of **13** with aq HF furnished the target bicyclic diol **1a**. Direct comparison of the ^1H and ^{13}C NMR spectra of **1a** with those of natural communiol E indicated them to be identical, which enabled us to confirm that the relative stereochemistry of communiol E should be represented by structure **1a**. Quite curiously, however, the specific rotation value of **1a** ($[\alpha]^{22}_D$ −8.3 (*c* 0.12, CH_2Cl_2)) was far different from that reported for natural communiol E ($[\alpha]_D$ +129 (*c* 0.075, CH_2Cl_2)).[1] Although this discrepancy prevented us from straightforwardly assigning the absolute stereochemistry of communiol E, the fact that structurally related metabolites of the same microbial origin (communiols A−D and H, see Figure 2) all had (*S*)-absolute configuration in common at the side chain asymmetric center (C8-position in **1a**)[1,2,5,6] strongly supported the stereochemical assignment of communiol E as **1a**, including its absolute configuration.

The candidate structure for communiol F (**2a**), which corresponds to 2,3-dehydrocommuniol E, was synthesized as shown in Scheme 4. The aldehydic intermediate **12** used for the synthesis of **1a** was subjected to α-selenylation with $PhSeNEt_2$,[11] and the resulting α-selenoaldehyde **14** was treated in situ with aq $NaIO_4$ to give α,*β*-unsaturated aldehyde **15**. Reduction of **15** to allylic alcohol **16** with DIBAL and subsequent deprotection of its TBDPS-protecting group afforded the target compound **2a**. The ^1H and ^{13}C NMR spectral data of **2a** were identical with those of natural communiol F. In this case also,

(7) (a) Schinzer, D.; Allagiannis, C.; Wichmann, S. *Tetrahedron* **1988**, *44*, 3851−3868. (b) Frank, K. E.; Aubé, J. *J. Org. Chem.* **2000**, *65*, 655−666.

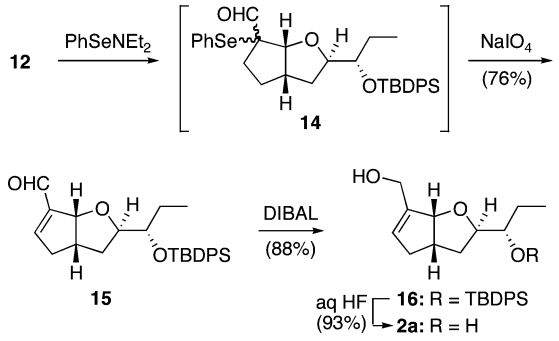
(8) For examples of the *trans*-selective alkylation of *γ*-substituted-*γ*-butyrolactones, see the following: (a) Sells, T. B.; Nair, V. *Tetrahedron* **1994**, *50*, 117−138. (b) Davidson, A. H.; Moloney, B. A. *J. Chem. Soc., Chem. Commun.* **1989**, 445−446.

(9) The modest chemical yield of this conversion is ascribable, in part, to the formation of a conjugated diene through *β*-elimination of **8**, in which the lithium enolate generated from **7** functioned as a base. Attempts to improve the yield of this step by using a zinc enolate of **7** (to reduce the basicity of the nucleophile) or a more reactive alkylating agent [$TMSCH_2CH{=}CH(CH_2)_2OTf$] were unsuccessful. For successful application of these methodologies, see the following: (a) Kuwahara, S.; Hamade, S.; Leal, W. S.; Ishikawa, J.; Kadama, O. *Tetrahedron* **2000**, *56*, 8111−8117. (b) Uenishi, J.; Tatsumi, Y.; Kobayashi, N.; Yonemitsu, O. *Tetrahedron Lett.* **1995**, *36*, 5909−5912.

(10) (a) Schmitt, A.; Rei*β*ig, H.-U. *Eur. J. Org, Chem.* **2000**, 3893−3901. (b) Lee, T. V.; Roden, F. S.; Yeoh, H. T−L. *Tetrahedron Lett.* **1990**, *31*, 2063−2066.

(11) (a) Jefson, M.; Meinwald, J. *Tetrahedron Lett.* **1981**, *22*, 3561−3564. (b) Keck, G. E.; Cressman, E. N. K.; Enholm, E. J. *J. Org. Chem.* **1989**, *54*, 4345−4349.

SCHEME 4. Synthesis of Commuiol F (2a)



however, the specific rotation of **2a** ($[\alpha]^{22}_D$ +21 (*c* 0.21, CH_2Cl_2)) disagreed with that of natural communiol F ($[\alpha]_D$ +137 (*c* 0.058, CH_2Cl_2)).[1] Despite this disagreement, the same argument on biogenetic similarity as described for communiol E led us to the conclusion that the stereochemistry of communiol F should also be revised to **2a**.

In summary, on the basis of our previous synthetic studies on communiols A−D and H, which culminated in their stereochemical revision, we proposed the most probable stereochemistry for communiols E and F, and synthesized the candidate structures (**1a** and **2a**). The complete agreement of **1a** and **2a** with natural communiols E and F, respectively, in ^{1}H and ^{13}C NMR, coupled with the fact that structurally related communiols A−D and H isolated from the same microbial origin have (*S*)-absolute configuration in common at the side chain asymmetric center, strongly suggested that the originally proposed structures for cummuniols E and F (**1b** and **2b**, respectively) should be revised to **1a** and **2a**, respectively.

Experimental Section

(2*S*,4*R*,5*S*)-5-(*tert*-Butyldiphenylsilyloxy)-2-[(*Z*)-5-trimethylsilyl-3-pentenyl]-4-heptanolide (9). To a stirred solution of LDA [prepared by treating a solution of *i*Pr$_2$NH (22 μL, 0.16 mmol) and HMPA (50 μL) in THF (0.50 mL) with *n*BuLi (1.6 M in hexane, 90 μL, 0.14 mmol) at −10 °C] was added a solution of **7** (50.2 mg, 0.131 mmol) in THF (0.50 mL) at −65 °C. After 15 min, a solution of **8** (70.4 mg, 0.262 mmol) in THF (0.30 mL) was added, and the resulting mixture was stirred for 1 h at −78 °C. The reaction was quenched with saturated aq NH_4Cl, and the mixture was extracted with Et_2O. The extract was successively washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed over SiO_2 (hexane/EtOAc, 50:1−4:1) to give a 15.2:1 mixture of **9** and its cis isomer (31.8 mg, 44%) along with recovered starting lactone **7** (16%). Repeated SiO_2 column chromatography (hexane/EtOAc, 40:1) of the mixture afforded 26.5 mg (39%) of pure **9** as a colorless oil: $[\alpha]^{22}_D$ −19 (*c* 0.27, $CHCl_3$). IR (film) ν_{max}: 3020 (w), 1770 (s), 1110 (s), 700 (vs). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.01 (9H, s), 0.68 (3H, t, *J* = 7.4 Hz), 1.03 (9H, s), 1.36−1.52 (5H, m), 1.80−1.93 (2H, m), 2.02−2.13 (2H, m), 2.47 (1H, ddd, *J* = 12.6, 9.3, 4.1 Hz), 2.54−2.61 (1H, m), 3.81−3.89 (1H, m), 4.45 (1H, dt, *J* = 8.2, 4.1 Hz), 5.21 (1H, dt, *J* = 10.7, 7.4 Hz), 5.45 (1H, dt, *J* = 10.7, 8.8 Hz), 7.35−7.47 (6H, m), 7.64−7.70 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$): δ −1.8 (3C), 9.1, 18.6, 19.4, 24.7, 26.2, 27.0 (3C), 28.0, 31.4, 39.0, 74.9, 79.1, 125.6, 127.0, 127.5 (2C), 127.7 (2C), 129.7, 129.9, 132.8, 134.2, 135.8 (2C), 136.0 (2C), 179.6. HRMS (FAB): *m*/*z* calcd for $C_{31}H_{47}O_3Si_2$ ($[M + H]^+$), 523.3064; found, 523.3068.

(2*R*,3a*S*,6*S*,6a*R*)-2-[(*S*)-1-(*tert*-Butyldiphenylsilyloxy)propyl]-5-vinylhexahydrocyclopenta[*b*]furan (11). To a stirred solution of **9** (42.3 mg, 81 μmol) in CH_2Cl_2 (1 mL) was added dropwise a solution of DIBAL (0.94 M in hexane, 95 μL, 89 μmol) at −78 °C. After 10 min, the reaction was quenched with saturated aq Rochelle's salt, and the mixture was stirred for 1 h at room temperature before being extracted with EtOAc. The extract was washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give **10** (49.6 mg) as a colorless oil, which was then dissolved in CH_2Cl_2 (1 mL). To the solution was added BF_3·OEt_2 (12 μL, 97 μmol) at −78 °C, and the resulting mixture was gradually warmed to −15 °C over a period of 45 min before being quenched with a suspension of $NaHCO_3$ in MeOH. The reaction mixture was filtered through a pad of Celite, and the filter cake was washed with EtOAc. The combined filtrate and washings were concentrated in vacuo, and the residue was chromatographed over SiO_2 (hexane/EtOAc, 10:1) to give 31.5 mg (90% from **9**) of a 6.4:1 mixture of **11** and its epimer as a colorless oil: $[\alpha]^{22}_D$ −35.4 (*c* 1.28, $CHCl_3$). IR (film) ν_{max}: 3070 (m), 1640 (w), 1110 (s), 700 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.78 (3H, t, *J* = 7.5 Hz), 1.05 (9H, s), 1.22−1.51 (4H, m), 1.56 (1H, ddd, *J* = 12.1, 5.5, 2.2 Hz), 1.74−1.91 (2H, m), 1.93 (1H, dt, *J* = 12.4, 8.7 Hz), 2.42−2.63 (2H, m), 3.76 (1H, dt, *J* = 5.4, 5.1 Hz), 3.94 (1H, ddd, *J* = 9.0, 5.1, 4.5 Hz), 4.11 (1H, dd, *J* = 6.9, 3.8 Hz), 4.96 (1H, d, *J* = 10.4 Hz), 5.01 (1H, d, *J* = 18.3 Hz), 5.78 (1H, ddd, *J* = 18.3, 10.4, 6.9 Hz), 7.33−7.43 (6H, m), 7.67−7.73 (4H, m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.2, 19.4, 26.8, 27.0 (3C), 30.8, 31.6, 34.4, 42.2, 50.4, 75.5, 80.6, 89.5, 113.8, 127.40 (2C), 127.43 (2C), 129.46, 129.47, 134.4, 134.8, 136.1 (2C), 136.2 (2C), 140.4. HRMS (FAB): *m*/*z* calcd for $C_{28}H_{38}O_2SiNa$ ($[M + Na]^+$), 457.2539; found, 457.2540.

(*S*)-1-[(2*R*,3a*S*,6*S*,6a*R*)-6-Hydroxymethylhexahydrocyclopenta-[*b*]furan-2-yl]-1-propanol (1a). To a stirred solution of **13** (5.7 mg 13 μmol) in CH_3CN (0.175 mL) was added 40% aq HF (75 μL) at 0 °C. After 8.5 h, the reaction was quenched with saturated aq $NaHCO_3$, and the mixture was extracted with EtOAc. The extract was dried ($MgSO_4$) and concentrated in vacuo. The residue was chromatographed over SiO_2 (EtOAc only) to give 2.4 mg (92%) of **1a** as a colorless oil: $[\alpha]^{22}_D$ −8.3 (*c* 0.12, CH_2Cl_2). IR (film) ν_{max}: 3410 (s), 2940 (vs), 2875 (s), 1455 (m), 1045 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.99 (3H, t, *J* = 7.4 Hz), 1.20−1.39 (2H, m), 1.42 (2H, qui, *J* = 7.3 Hz), 1.52 (1H, br dd, *J* = 12.6, 5.6 Hz), 1.58 (1H, br s, OH), 1.78−1.88 (1H, m), 1.89−2.00 (2H, m), 2.02−2.11 (1H, m), 2.10 (1H, br s, OH), 2.69 (1H, qui, *J* = 7.4 Hz), 3.56−3.70 (2H, m), 3.72−3.81 (1H, m), 3.93 (1H, ddd, *J* = 9.9, 5.4, 3.4 Hz), 4.34 (1H, dd, *J* = 7.2, 4.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.5, 25.8, 28.5, 31.2, 31.8, 43.0, 49.9, 65.2, 72.8, 80.9, 88.1. HRMS (FAB): *m*/*z* calcd for $C_{11}H_{21}O_3$ ($[M + H]^+$), 201.1491; found, 201.1493.

(2*R*,3a*S*,6a*R*)-2-[(*S*)-1-(*tert*-Butyldiphenylsilyloxy)propyl]-3,-3a,4,6a-tetrahydro-2*H*-cyclopenta[*b*]furan-6-carbaldehyde (15). To a stirred and ice-cooled solution of **12** (10.2 mg, 23.4 μmol) in THF (0.25 mL) was added a solution of $PhSeNEt_2$ [prepared by treating a solution of PhSeCl (9.0 mg, 47 μmol) in hexane (0.25 mL) with Et_2NH (10 μL, 94 μmol) at 0 °C for 15 min], and the mixture was stirred at room temperature for 4 h until compound **12** was completely consumed (TLC analysis). Water (0.2 mL) and $NaIO_4$ (22.5 mg, 0.105 mmol) were then added, and the resulting mixture was stirred at room temperature for 7 h, during which time 10.4 mg (49 μmol) and 20.0 mg (94 μmol) of additional $NaIO_4$ were added to bring the oxidative elimination to completion. The reaction was quenched with saturated aq $Na_2S_2O_3$ and extracted with EtOAc. The extract was dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed over SiO_2 (hexane/EtOAc, 7:1) to give 7.8 mg (76%) of **15** as a colorless oil: $[\alpha]^{22}_D$ −31 (*c* 0.17, $CHCl_3$). IR (film) ν_{max}: 3070 (w), 3050 (w), 1690 (s), 1110 (m), 740 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.75 (3H, t, *J* = 7.5 Hz), 1.05 (9H, s), 1.35−1.62 (3H, m), 2.00 (1H, dt, *J* = 12.5, 9.1 Hz), 2.31 (1H, dm, *J* = 19.8 Hz), 2.80 (1H, ddd, *J* = 19.8, 8.5, 2.6 Hz), 2.88−2.99 (1H, m), 3.73 (1H, dt, *J* = 9.5, 5.1 Hz), 3.79 (1H, q, *J* = 5.1 Hz), 5.18 (1H, dd, *J* = 7.1, 1.7 Hz), 6.89 (1H, t, *J* = 2.6 Hz), 7.32−7.44 (6H, m), 7.66−7.74 (4H, m), 9.78 (1H, s). ^{13}C NMR (300 MHz, $CDCl_3$): δ 9.3, 19.6, 27.1 (3C), 27.2, 35.4, 40.1, 40.3,

75.2, 79.5, 84.1, 127.4 (4C), 129.4 (2C), 134.1, 134.6, 136.06 (2C), 136.14 (2C), 145.4, 153.2, 189.1. HRMS (FAB): *m*/*z* calcd for $C_{27}H_{34}O_3SiNa$ ($[M + Na]^+$), 457.2175; found, 457.2181.

(*S*)-1-[(2*R*,3a*S*,6a*R*)-6-Hydroxymethyl-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*b*]furan-2-yl]-1-propanol (2a). To a stirred solution **16** (9.7 mg 0.022 mmol) in CH_3CN (0.37 mL) was added 40% aq HF (0.17 mL) at 0 °C. After 10 h, the reaction was quenched with saturated aq $NaHCO_3$ and extracted with EtOAc. The extract was dried ($MgSO_4$) and concentrated in vacuo. The residue was chromatographed over SiO_2 (EtOAc only) to give 4.1 mg (93%) of **2a** as a colorless oil: $[\alpha]^{22}_D$ +21 (*c* 0.21, CH_2Cl_2). IR (film) ν_{max}: 3735 (s), 3400 (br s), 1700 (w), 1505 (m), 1035 (m). ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.98 (3H, t, J = 7.4 Hz), 1.42 (2H, qui, J = 7.1 Hz), 1.51 (1H, ddd, J = 12.6, 5.0, 1.5 Hz), 2.04 (1H, dt, J = 12.6, 9.6 Hz), 2.15 (1H, br d, 17.7 Hz), 1.95−2.26 (2H, br, OH), 2.67 (1H, br dd, J = 17.7, 8.6 Hz), 2.94−3.06 (1H, m), 3.71−3.80 (2H, m), 4.21−4.34 (2H, m), 5.16 (1H, br d, J = 7.3 Hz), 5.80 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 10.2, 26.0, 33.1, 39.3, 39.7, 60.9, 72.4, 79.4, 89.2, 130.5, 141.1; HRMS (FAB): *m*/*z* calcd for $C_{11}H_{19}O_3$ ($[M + H]^+$), 199.1334; found, 199.1336.

Acknowledgment. This work was financially supported, in part, by a Grant-in-Aid for Scientific Research (B) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (Grant No. 16380075). We also thank Ms. Yamada (Tohoku University) for measuring the NMR and mass spectra.

Supporting Information Available: Experimental procedures for compounds **7**, **12**, **13**, and **16**, and ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0608927