A Stereoselective Total Synthesis of Verbalactone[1])

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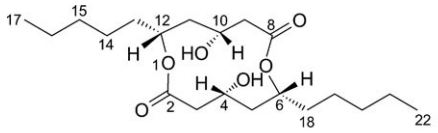
A stereoselective total synthesis of verbalactone has been achieved starting from commercially available hexanal. The sequence involves *Maruoka* allylation, diastereoselective iodine-induced electrophillic cyclization, ring opening of epoxide, and *Yamaguchi* macrolactonization as the key steps.

Introduction. – Verbalactone (**1**), a macrocyclic dimer lactone with C_2-symmetry, was isolated by *Mitaku et al.* from the roots of *Verbascum undulatum* LAM. a biennial plant of the genus *Verbascum* that belongs to the family Scrophulariaceae. The compound exhibited interesting antibacterial activity against various *Gram*-positive ($MIC = 62.5$ μg/ml) and *Gram*-negative bacteria ($MIC = 125$ μg/ml) [1][2]. This macrocycle is a symmetrical dimeric lactone of (+)-(3*R*,5*R*)-3-hydroxy-5-decanolide (=(4*R*,6*R*)-tetrahydro-4-hydroxy-6-pentyl-2*H*-pyran-2-one; **2**) [3]. The absolute configuration of **1** was determined as (4*R*,6*R*,10*R*,12*R*) by spectroscopic (1D- and 2D-NMR) methods and chemical correlation [1]. It is the first example of a 1,7-dioxacyclododecane unit being present in the ring system of a naturally occurring compound. The total synthesis of **1** was reported earlier [4–8]. Due to its interesting structural pattern and impressive activity, we have synthesized **1** with an alternative approach, which we would like to mention here.



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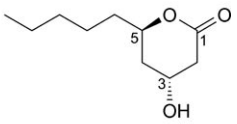

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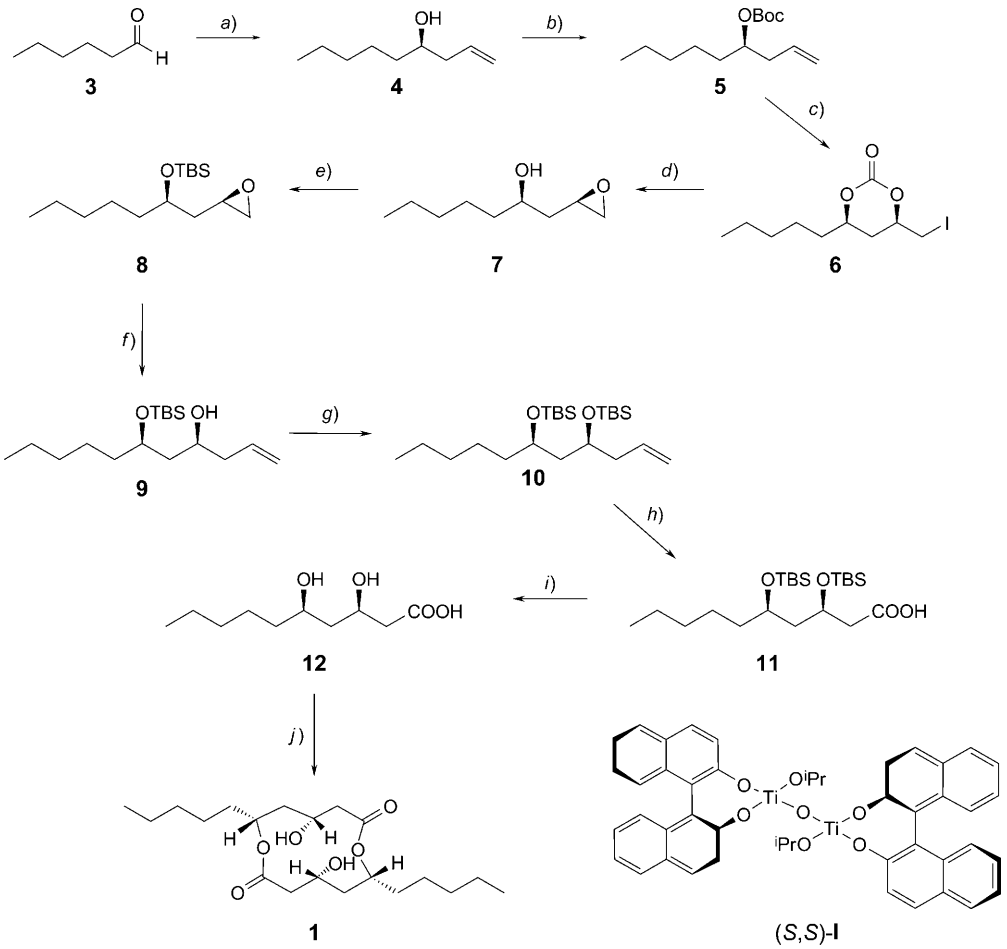
Results and Discussion. – The synthesis (*Scheme*) was started from the commercially available hexanal **3**, which was subjected to an enantioselective *Maruoka* allylation [9][10] using the titanium complex (*S*,*S*)-**I** and allyl(tributyl)tin to furnish the homoallyl alcohol **4** in 83% yield with an enantioselectivity of 97% (determined by chiral HPLC). The latter was treated with di(*tert*-butyl) dicarbonate in the presence of DMAP in MeCN forming the homoallylic *tert*-butyl carbonate **5** in 81% yield [11], which was prepared for the diastereoselective I_2-induced electrophilic cyclization to introduce the required stereogenic centre. The treatment of **5** with I_2 in MeCN at $-20°$

[1]) Part 32 in the series 'Synthetical studies on natural products'.

formed the iodocarbonate **6** (72%) [12][13], which was subsequently treated with K_2CO_3 in MeOH to give the desired *syn*-epoxy alcohol **7** in 82% yield [12]. The alcohol **7** was protected with ^{t}BuMe$_2$SiCl (TBS-Cl) to form the TBS-protected epoxide **8**, which, on reaction with vinyl magnesium bromide in the presence of CuCN, yielded the corresponding homoallylalcohol **9** in 85% yield [14]. The alcohol **9** was again reacted with TBS-Cl to furnish **10**. Oxidation of the latter with $RuCl_3/NaIO_4$, in the presence of CCl_4/MeCN/H_2O resulted in the formation of an acid **11** in 75% yield [15].

Scheme



a) (*S,S*)-**I** (10 mol%), $Bu_3SnCH_2CH{=}CH_2$, CH_2Cl_2, −15–0°, 20 h, 83%. *b*) Boc_2O, 4-(dimethylamino)pyridine (DMAP), MeCN, 5 h, 81%. *c*) I_2, MeCN, −20°, 6 h, 72%. *d*) K_2CO_3, MeOH, 20°, 30 min, 82%. *e*) ^{t}BuMe$_2$SiCl (TBS-Cl), 1*H*-imidazole, CH_2Cl_2, 4 h, 91%. *f*) Vinylmagnesium bromide, CuCN, −20°– r.t., 3 h, 85%. *g*) TBS-Cl, 1*H*-imidazole, CH_2Cl_2, 6 h, 88%. *h*) $RuCl_3$, $NaIO_4$, CCl_4/MeCN/H_2O 2:2:3, 3 h, 75%. *i*) TBAF, THF, 5 h, 76%. *j*) 1. 2,4,6-trichlorobenzoyl chloride, Et_3N, THF, r.t., 4 h, 2. DMAP (30 equiv), toluene, reflux, 4 h, 45% (over two steps).

The deprotection of **11** was achieved by TBAF in THF to produce the dihydroxyacid **12**. The compound **12** was utilized immediately for *Yamaguchi*'s macrolactonization [4][6][16] to complete the synthesis of **1**. Verbalactone (**1**) was formed in 45% yield accompanied by monomeric lactone **2** in 25% yield. All the spectroscopic data (^{1}H- and ^{13}C-NMR, and MS) and optical rotation ($[\alpha]_D^{20} = +9.1$ ($c = 0.3$, $CHCl_3$), ([1]: $[\alpha]_D^{20} = +7.3$ ($c = 0.9$, $CHCl_3$)) of **1** were identical to those reported [1][4–6][8].

A brief comparison of our synthetic strategy with the methods reported [4–8] for the synthesis of verbalactone is given here. The intermediate **4** was prepared [6] previously from hexanal using allyl magnesium chloride and (−)-allyl $(Icp)_2B$. This compound has now been prepared from hexanal by treatment with allyltributyltin in the presence of the titanium complex (*S*,*S*)-**I** (*Maruoka* allylation). The epoxy alcohol **7** (employed earlier in one synthesis [4] in acetate form) has been prepared here following an entirely different route involving the iodo carbonate **6** prepared from **4** through Boc-protection and subsequent treatment with I_2. The conversion of **7** into the TBS-protected diol **10** has also not been utilized earlier. However, the conversion of **10** into **11** has been carried out analogously in an earlier synthesis [6], where two OH groups were protected as acetonide. Deprotection of **11** yielded **12** which is a suitable precursor for *Yamaguchi* macrolactonization (a general procedure used in different syntheses [4][6][7] for macrolactonization of a 3,5-dihydroxy aliphatic acid) to form the desired compound, verbalactone (**1**). Thus several steps involved in the present synthesis are entirely new.

In summary, a stereoselective synthesis of verbalactone **1** was achieved *via Maruoka* asymmetric allylation, diastereoselective I_2-induced electrophillic cyclization, epoxide ring opening, and *Yamaguchi* macrolactonization as key steps.

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Experimental Part

Commercial reagents were used without further purification. All solvents were purified by standard techniques. Column chromatography (CC): silica gel (SiO_2; 60–120 mesh). Optical rotation: *Jasco Dip 360* digital polarimeter. NMR Spectra: in $CDCl_3$; *Varian Gemini 200*, *Bruker 300*, or *Varian Unity 400* NMR spectrometers; chemical shifts (δ) in ppm; referenced to Me_4Si as internal standard; coupling constants (J) given in Hz. MS: *Finnigan MAT 1020B* or *micro mass VG 70-70 H* spectrometers operating at 70 eV using a direct inlet system.

*(4*R*)-Non-1-en-4-ol* (**4**). To a stirred soln. of $TiCl_4$ (0.274 g, 1.5 mmol) in CH_2Cl_2 (10 ml) was added dried $Ti(O^iPr)_4$ (1.27 g, 4.5 mmol) at 0° under N_2 atmosphere and was allowed to warm to r.t. After 1 h, silver(I)oxide (0.695 g, 3 mmol) was added at r.t., and the mixture was stirred for 5 h under exclusion of direct light. The mixture was diluted with CH_2Cl_2 (50 ml), and treated with (*S*)-BINOL (1.716 g, 6 mmol) at r.t. for 2 h to furnish the chiral bis-Ti(IV) oxide (*S,S*)-**I**. The *in situ* generated (*S,S*)-**I** was cooled to −15° and treated sequentially with aldehyde **3** (3 g, 30 mmol) and allyltributyltin (= tributyl(prop-2-en-1-yl)stannane; 12.90 g, 39 mmol) at the same temp. The mixture was allowed to warm to 0° and stirred for 20 h. Then, the mixture was quenched with sat. aq. $NaHCO_3$ (60 ml), and extracted with Et_2O (3 × 60 ml). The org. extracts were dried (anh. Na_2SO_4). Evaporation of the solvents and purification of the residue by CC on SiO_2 (2% AcOEt/hexane) gave **4** (3.53 g, 83% yield) as colorless oil. $[\alpha]_D^{25} = +8.9$ ($c = 1.1$, $CHCl_3$). ^{1}H-NMR: ($CDCl_3$, 200 MHz): 5.80–5.74 (*m*, 1 H); 5.13–5.00 (*m*, 2 H); 3.66–3.52 (*m*, 1 H); 2.33–2.00 (*m*, 2 H); 1.53–1.30 (*m*, 8 H); 0.90 (*t*, $J = 6.0$, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 134.9; 117.9; 70.6; 41.8; 36.7; 31.8; 25.2; 22.5; 13.9. EI-MS: 143 ($[M+H]^+$).

tert-*Butyl (4*R*)-Non-1-en-4-yl Carbonate* (**5**). To a soln. of **4** (3.5 g, 24.64 mmol) in MeCN (50 ml) were added Boc_2O (8.05 g, 36.96 mmol) and DMAP (1.20 g, 9.85 mmol) at 0°. After 5 h of stirring, the solvent was evaporated under reduced pressure. The residue was taken up in EtOH (50 ml), and imidazole (8.13 g, 123.2 mmol) was added. The resulting mixture was stirred at r.t. for 15 min and CH_2Cl_2 was added. The org. phase was washed with 5% HCl soln., dried (anh. Na_2SO_4), filtered, and concentrated *in vacuo*. Purification of the residue by CC on SiO_2 (1% AcOEt/hexane) gave **5** (4.82 g, 81%) as colorless oil. $[\alpha]_D^{25} = -12.13$ ($c = 0.75$, $CHCl_3$). ^{1}H-NMR: ($CDCl_3$, 200 MHz): 5.82–5.70 (*m*, 1 H); 5.13–5.03 (*m*, 2 H); 4.66–4.61 (*m*, 1 H); 2.35–2.29 (*m*, 2 H); 1.54–1.29 (*m*, 17 H); 0.89 (*t*, $J = 6.0$, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 153.6; 133.5; 117.5; 81.4; 76.5; 38.6; 33.5; 31.5; 29.6; 27.7 (2×); 24.8; 22.4; 13.9. ESI-MS: 265 ($[M+Na]^+$).

*(4*R*,6*R*)-4-(Iodomethyl)-6-pentyl-1,3-dioxan-2-one* (**6**). A mixture of **5** (4 g, 16.5 mmol) and I_2 (12.9 g, 51.15 mmol) in 100 ml of dry MeCN was stirred mechanically under N_2 at −20° for 6 h. The mixture was partitioned between 300 ml of 20% aq. $Na_2S_2O_3$/5% aq. $NaHCO_3$ and 500 ml of Et_2O. The org. layer was washed with sat. aq. NaCl, dried (anh. Na_2SO_4), and evaporated. The crude product was purified by CC on SiO_2 (10% AcOEt/hexane) to give **6** (3.71 g, 72%) as a reddish oil. $[\alpha]_D^{25} = -42.7$ ($c = 1.4$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.62–4.56 (*m*, 1 H); 4.51–4.47 (*m*, 1 H); 3.44 (*dd*, $J = 9.8, 5.2$, 1 H); 3.27 (*dd*, $J = 9.8, 2.0$, 1 H); 2.24–2.11 (*m*, 2 H); 1.82–1.78 (*m*, 1 H); 1.64–1.25 (*m*, 7 H); 0.91 (*t*, $J = 6.0$, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 148.5; 78.4; 77.0; 34.9; 33.1; 31.3; 23.9; 22.3; 13.8; 5.7. ESI-MS: 313 ($[M+H]^+$). HR-MS: 335.0106 ($[M+Na]^+$, $C_{10}H_{17}INaO_3^+$; calc. 335.0120).

*(2*R*)-1-[(2*R*)-Oxiran-2-yl]heptan-2-ol* (**7**). A mixture of **6** (3.5 g, 11.2 mmol) and K_2CO_3 (4.63 g, 33.6 mmol) in 25 ml of dry MeOH was stirred at 20° for 30 min. Et_2O was added and the mixture was washed with 20% aq. $Na_2S_2O_3$/5% aq. $NaHCO_3$, the org. portion was separated, dried (anh. Na_2SO_4), and evaporated. The crude product was purified by CC on SiO_2 (30% AcOEt/hexane) to give **7** (1.45 g, 82%) as a colorless liquid. $[\alpha]_D^{25} = +31.3$ ($c = 1.7$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.82–3.80 (*m*, 1 H); 3.07–3.01 (*m*, 1 H); 2.73 (*dd*, $J = 4.5, 3.0$, 1 H); 2.45 (*dd*, $J = 3.0, 2.2$, 1 H); 2.36 (br. *s*, 1 H); 1.81–1.77 (*m*, 1 H); 1.52–1.25 (*m*, 9 H); 0.90 (*t*, $J = 6.0$, 3 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 70.4; 50.3; 46.5; 39.7; 37.1; 31.6; 24.9; 22.4; 13.8. EI-MS: 159 ($[M+H]^+$).

tert-*Butyl(dimethyl)({(2*R*)-1-[(2*R*)-Oxiran-2-yl]heptan-2-yl}oxy)silane* (**8**). To a stirred soln. of **7** (1.25 g, 7.91 mmol) and imidazole (1.07 g, 15.82 mmol) in dry CH_2Cl_2 (30 ml) was added *tert*-butyl chloro(dimethyl)silane (TBS-Cl) (2.38 g, 15.82 mmol) slowly at 0°. The mixture was then kept at r.t. for 4 h, and then quenched with H_2O. The CH_2Cl_2 layer was separated and the aq. layer was extracted with CH_2Cl_2 (2 × 10 ml). The combined org. layers were washed with H_2O, brine, and dried (anh. Na_2SO_4). The solvent was removed *in vacuo*, and the residue was purified by CC on SiO_2 (2% AcOEt/hexane) to form **8** (1.95 g, 91%) as a colorless liquid. $[\alpha]_D^{25} = +4.1$ ($c = 2.0$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 3.86–3.78 (*m*, 1 H); 3.02–2.89 (*m*, 1 H); 2.69 (*dd*, $J = 4.5, 2.2$, 1 H); 2.37 (*dd*, $J = 3.0, 2.2$, 1 H); 1.62 (*t*, $J = 5.2$, 2 H); 1.51–1.25 (*m*, 8 H); 0.90–0.80 (*m*, 12 H); 0.04 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 70.3; 49.4; 46.7; 40.0; 37.1; 31.8; 25.7; 25.0; 22.5; 17.9; 13.9; −4.6. ESI-MS: 273 ($[M+H]^+$).

*(4*S*,6*R*)-6-{[*tert*-Butyl(dimethyl)silyl]oxy}undec-1-en-4-ol* (**9**). A round bottom flask was charged with copper(I)cyanide (0.19 g, 2.2 mmol), gently heated under vacuum, and then slowly cooled under a flow of N_2, THF (20 ml) was then added and the resulting suspension was cooled to −20°, stirred and vinyl magnesium bromide (1M in THF, 22 ml, 22 mmol) added. A soln. of **8** (1.5 g, 5.5 mmol) in THF (10 ml) was added to the above reagent and the mixture was stirred at −20° for 1 h, and then stirred at r.t. for 2 h. After consumption of the starting material, the mixture was quenched with sat. aq. NH_4Cl. The H_2O layer was extracted with AcOEt, and the combined org. layers were washed with brine, dried (anh. Na_2SO_4) and concentrated. The residue was purified by CC on SiO_2 (5% AcOEt/hexane) to afford **9** (1.40 g, 85%) as a colorless liquid. $[\alpha]_D^{25} = -16.8$ ($c = 0.9$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 5.82–5.78 (*m*, 1 H); 5.19–5.01 (*m*, 2 H); 3.94–3.90 (*m*, 1 H); 3.77–3.73 (*m*, 1 H); 2.90 (br. *s*, 1 H); 2.23 (*t*, $J = 6.0$, 2 H); 1.70–1.41 (*m*, 3 H); 1.39–1.21 (*m*, 5 H); 1.10–0.68 (*m*, 14 H); 0.09 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 134.8; 117.2; 72.9; 70.1; 42.2; 42.0; 37.8; 31.9; 31.8; 25.7; 24.2; 22.5; 17.8; 13.9; −4.1; −4.7. ESI-MS: 301 ($[M+H]^+$). HR-MS: 323.2391 ($[M+Na]^+$, $C_{17}H_{36}NaO_2Si^+$; calc. 323.2382).

*(5*R*,7*S*)-2,2,3,3,9,9,10,10-Octamethyl-5-pentyl-7-(prop-2-en-1-yl)-4,8-dioxa-3,9-disilaundecane* (**10**). To a stirred soln. of allylalcohol **9** (1.0 g, 3.3 mmol) and imidazole (0.448 g, 6.6 mmol) in dry CH_2Cl_2 (30 ml) was added TBS-Cl (0.99 g, 6.6 mmol) slowly at 0°. The mixture was kept at r.t. for 6 h, and then

quenched with H_2O. The CH_2Cl_2 layer was separated, and the aq. layer was extracted with CH_2Cl_2. The combined org. portion was washed with H_2O, brine, and dried (anh. Na_2SO_4). The solvent was removed *in vacuo*, and the residue was purified by CC on SiO_2 (3% AcOEt/hexane) to form the TBS-protected allyl alcohol **10** (1.21 g, 88%) as a colorless liquid. $[\alpha]_D^{25} = +5.58$ ($c = 0.9$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 5.90–5.73 (*m*, 1 H); 5.11–5.02 (*m*, 2 H); 3.86–3.82 (*m*, 1 H); 3.79–3.75 (*m*, 1 H); 2.34–2.12 (*m*, 2 H); 1.63–1.57 (*m*, 1 H); 1.51–1.22 (*m*, 9 H); 1.03–0.80 (*m*, 21 H); 0.07 (*s*, 6 H); 0.04 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 135.1; 116.8; 69.6; 69.3; 44.6; 41.9; 37.4; 32.2; 25.9; 25.7; 24.8; 22.7; 18.19; 18.14; 14.1; −4.2; −4.3; −4.4. ESI-MS: 415 ($[M+H]^+$).

(*3*R,*5*R)-*3,5-Bis{[*tert-*butyl(dimethyl)silyl]oxy}decanoic Acid* (**11**). A mixture of CCl_4 (2 ml), MeCN (2 ml), and H_2O (3 ml) was taken in a flask. The alkene **10** (1 g, 2.4 mmol), sodium metaperiodate (2.05 g, 9.6 mmol), and subsequently ruthenium trichloride hydrate 11 mg (2.2 mol-%) were added to this biphasic mixture. The mixture was stirred for 3 h at r.t. Then CH_2Cl_2 (20 ml) was added, and the phases were separated. The upper aq. phase was extracted three times with CH_2Cl_2. The combined org. extracts were dried (anh. Na_2SO_4) and concentrated. The resulting residue was diluted with Et_2O, filtered through a *Celite* pad, and concentrated. The residue was purified by CC on SiO_2 (20% AcOEt/hexane) to form acid **11** (0.777 g, 75%) as colorless semisolid. $[\alpha]_D^{25} = -5.60$ ($c = 0.4$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.26–4.22 (*m*, 1 H); 3.73–3.67 (*m*, 1 H); 2.59 (*dd*, $J = 15.0, 5.0$, 1 H); 2.45 (*dd*, $J = 15.0, 6.8$, 1 H); 1.78–1.55 (*m*, 2 H); 1.45–1.12 (*m*, 8 H); 0.98–0.72 (*m*, 21 H); 0.07 (*s*, 6 H); 0.04 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 176.9; 69.3; 66.8; 44.4; 42.1; 37.3; 32.1; 29.8; 25.8; 25.7; 24.6; 22.6; 17.9; 17.8; 14.0; −4.2; −4.5; −4.8. ESI-MS: 433 ($[M+H]^+$). HR-MS: 455.2994 ($[M+Na]^+$, $C_{22}H_{48}NaO_4Si_2^+$; calc. 455.2988).

*(3*R,*5*R*)-3,5-Dihydroxydecanoic Acid* (**12**). To a ice-cooled soln. of **11** (0.70 g, 1.6 mmol) in THF (10 ml) was added TBAF (1M THF, 4.86 ml, 4.86 mmol). After 15 min of stirring, the mixture was brought to r.t. and stirred for another 5 h. After completion of the reaction, the mixture was concentrated, and purified by CC on SiO_2 to afford dihydroxy acid **12** (0.247 g, 76%) as a colorless semisolid. The compound **12** was utilized immediately for *Yamaguchi*'s macrolactonization [4][6] to obtain **1** in 45% yield as a colorless oil. $[\alpha]_D^{25} = +9.1$ ($c = 0.3$, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 200 MHz): 4.99–4.91 (*m*, 2 H); 4.10–4.04 (*m*, 2 H); 3.75 (br. *s*, 2 OH); 2.71 (*d*, $J = 3.0$, 4 H); 2.04 (*ddd*, $J = 15.0, 10.0, 3.0$, 2 H); 1.98 (*td*, $J = 4.0, 15.0$, 2 H); 1.65–1.41 (*m*, 4 H); 1.38–1.19 (*m*, 12 H); 0.85 (*t*, $J = 6.0$, 6 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 173.0; 72.5; 64.9; 39.3; 38.2; 31.8; 31.5; 25.5; 22.5; 14.0. ESI-MS: 395 ($[M+Na]^+$). Along with **1**, monomeric lactone **2** was also obtained in 25% yield.

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