

SUPPORTING INFORMATION

THE THIOPYRAN ROUTE TO POLYPROPIONATES: ALDOL DIASTEREOSELECTIVITY OF LINEAR AND TWO- DIRECTIONAL ITERATIVE HOMOLOGATIONS

Dale E. Ward,* Cheng Guo, Pradip K. Sasmal, Chuk C. Man, and Marcelo Sales

Department of Chemistry, University of Saskatchewan,
110 Science Place, Saskatoon, SK S7N 5C9, Canada.

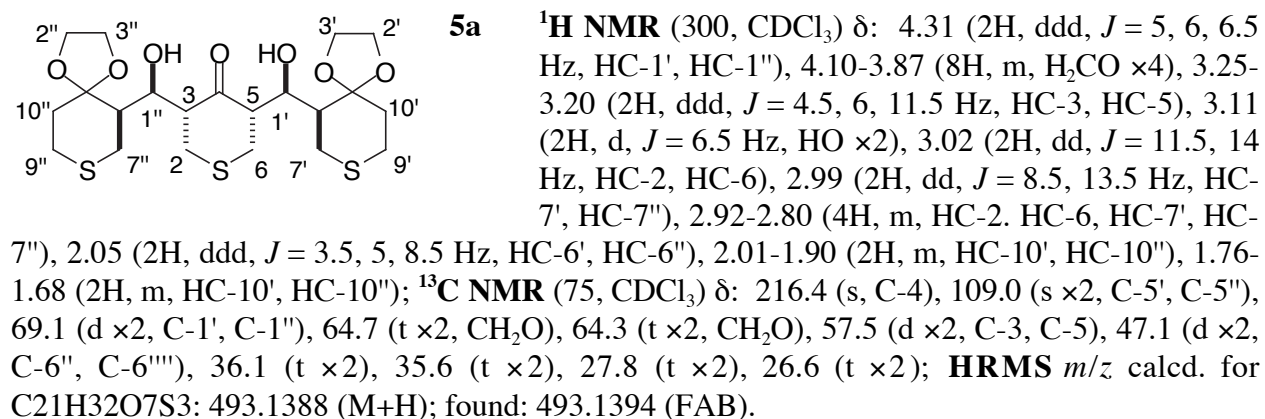
Phone: (306) 966-4656 FAX: (306) 966-4730 e-mail: dale.ward@usask.ca

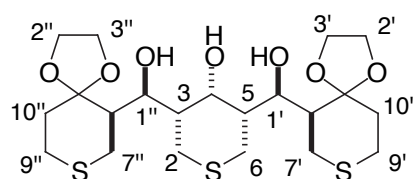
General Procedure for Aldol Reaction: TiCl_4 (1.1) was added dropwise via syringe to a stirred solution of the ketone (**3**, **4**, **11**, or **12**) in dry dichloromethane (ca 0.03 M) at -78°C under Ar. After 2 min, N,N-diisopropylethylamine (2.4 equiv. for **3** and **4**, 1.2 equiv. for **11** and **12**) was added dropwise via syringe and, after stirring 2 h at -78°C , a solution of the aldehyde (1.2-2.0 equiv.) in dry dichloromethane was added dropwise via syringe. After 2.5 h, sat. NH_4Cl was added and the aqueous layer was extracted with ethyl acetate (3×5 mL) [NOTE: the workup must be done quickly while the aqueous layer is still cold]. The combined organic layers were dried over Na_2SO_4 , concentrated, and fractionated by FCC (35-50% EtOAc in hexanes) to give recovered starting material and product aldols.

General Procedure for DIBAL-H Reduction: DIBAL (1.5 M in toluene; 2-3 equiv) was added dropwise via syringe to a stirred solution of the aldol in THF (ca. 0.05 M) at -78°C under argon. After 5 h, excess DIBAL was quenched by dropwise addition of MeOH. The mixture was diluted with 5% HCl and extracted with EtOAc ($\times 3$) and the combined organic layers were washed with brine, dried over Na_2SO_4 , concentrated, and fractionated by FCC (gradient elution, 75-100% EtOAc in hexane) to give the corresponding alcohols (>80% yields).

General Procedure for Acetonide Formation: A solution of the triol, 2,2-dimethoxypropane (ca. 100 equiv.) and p-toluenesulfonic acid monohydrate (catalytic amount) in dichloromethane (ca. 0.01 M in triol) was stirred at room temperature for 2.5-14 h. The reaction mixture was diluted with dichloromethane, washed with NaHCO_3 and with brine, dried over Na_2SO_4 , concentrated, and fractionated by FCC (gradient elution, 20-35% EtOAc in hexanes) to give the acetonide(s) (>80 yields).

General Procedure for Carbonate Formation: A solution of the triol or diol (11 mg, 0.019 mmol) and 1,1'-carbonyldiimidazole (3-5 equiv.) in benzene (ca. 0.01 M in triol) was heated under reflux for 24 h. The cooled (rt) reaction mixture was diluted with EtOAc, washed with water ($2 \times$), dried over Na_2SO_4 , concentrated, and fractionated by FCC (gradient elution, 75-100% EtOAc in hexanes) to give the carbonate(s) (50-85%).

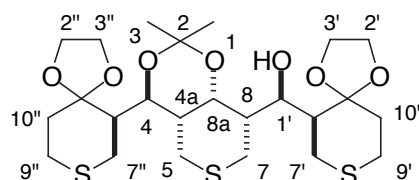




Triol from 5a

$^1\text{H NMR}$ (300, C_6D_6) δ : 5.10 (1H, br s, HC-4), 4.32 (1H, br d, $J = 3, 7$ Hz, HC-1', HC-1''), 3.50-3.18 (15H, m, HO $\times 3$, $\text{H}_2\text{CO} \times 4$, $\text{H}_2\text{C}-3$, $\text{H}_2\text{C}-5$), 3.12 (2H, dd, $J = 10, 14$ Hz, HC-7', HC-7''), 2.84 (2H, br d, $J = 14$ Hz, HC-7', HC-7''), 2.58 (2H, ddd, $J = 3, 11, 14$ Hz, HC-9', HC-9''), 2.32 (2H, br d, $J = 14$ Hz, HC-9', HC-9''), 2.20-

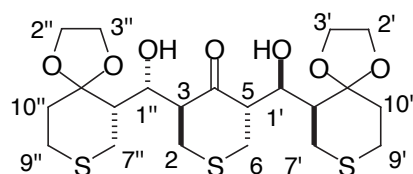
2.00 (4H, m, HC-3, HC-5, HC-6', HC-6''), 1.71 (2H, ddd, $J = 3, 5.5, 13.5$ Hz, HC-10', HC-10''), 1.58 (2H, ddd, $J = 3.5, 11, 13.5$ Hz, HC-10', HC-10''); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 110.0 (s $\times 2$), 70.5 (d $\times 2$), 64.6 (t $\times 2$), 64.4 (d), 64.2 (t $\times 2$), 47.1 (d $\times 2$), 46.1 (d $\times 2$), 35.8 (t $\times 2$), 26.6 (t $\times 2$), 26.6 (t $\times 2$), 24.7 (t $\times 2$); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_7\text{S}_3$: 494.1467; found: 494.1467 (EI).



6a

$^1\text{H NMR}$ (300, C_6D_6) δ : 4.68 (1H, br s, HC-8a), 4.35 (1H, ddd, $J = 2.5, 3, 8.5$ Hz, HC-1'), 3.93 (1H, dd, $J = 5.5, 5.5$ Hz, HC-4), 3.29 (1H, d, $J = 3$ Hz, HO), 3.41-2.80 (14H, m), 2.74 (1H, br d, $J = 14$ Hz), 2.68-2.51 (3H, m), 2.45 (1H, dd, $J = 4, 13$ Hz), 2.25-2.17 (4H, m), 1.93 (1H, ddd, $J = 3, 5.5, 8.5$ Hz, HC-4a),

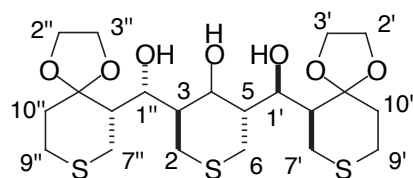
1.80-1.50 (4H, m), 1.49 (3H, s), 1.35 (3H, s); $^{13}\text{C NMR}$ (75, C_6D_6) δ : 110.9 (s), 109.3 (s), 101.6 (s), 72.1 (d), 69.6 (d), 64.9 (t $\times 2$), 64.5 (t), 64.4 (t), 63.9 (d), 50.4 (d), 47.3 (d), 44.9 (d), 44.6 (d), 37.0 (t), 36.7 (t), 29.0 (t), 28.6 (t), 27.4 (t), 27.0 (t), 26.9 (q), 26.8 (t), 25.5 (t), 24.1 (q); **HRMS** m/z calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_7\text{S}_3$: 534.1780; found: 534.1783 (EI).



5b

$^1\text{H NMR}$ (300, CDCl_3) δ : 4.65 (2H, br d, $J = 8$ Hz, H-1'), 4.15-3.90 (8H, m, $\text{H}_2\text{CO} \times 4$), 3.13 (2H, br s, HO $\times 2$), 3.11-2.48 (14H, m), 2.13 (2H, ddd, $J = 3, 5, 13.5$ Hz, HC-10', HC-10''), 2.03 (2H, ddd, $J = 3, 3, 11$ Hz, HC-6', HC-6''), 1.73 (2H, ddd, $J = 3.5, 12, 13.5$ Hz, HC-10', HC-10''); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 212.7 (s),

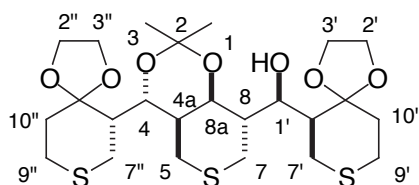
109.8 (s $\times 2$), 68.5 (d $\times 2$), 64.7 (t $\times 2$), 64.4 (t $\times 2$), 54.8 (d $\times 2$), 46.9 (d $\times 2$), 36.2 (t $\times 2$), 33.7 (t $\times 2$), 26.6 (t $\times 2$), 26.5 (t $\times 2$); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{S}_3$: 492.1310; found: 492.1307 (EI).



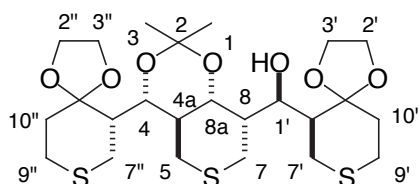
Triol from 5b

$^1\text{H NMR}$ (500, CDCl_3) δ : 4.57 (1H, d, $J = 9$ Hz, H-4), 4.35 (1H, br d, $J = 3$ Hz, H-1' or H-1''), 4.32 (1H, d, $J = 7.5$ Hz, H-1'' or H-1'), 4.10-3.94 (8H, m, H-2'', H-3'', H-2''', H-3'''), 3.39 (3H, br s, HO $\times 3$), 3.07-2.99 (3H, m), 2.89 (1H, dd, $J = 10, 13$ Hz), 2.86-2.77 (2H, m), 2.74 (1H, ddd, $J = 2.5, 3, 14$ Hz), 2.61 (1H, ddd,

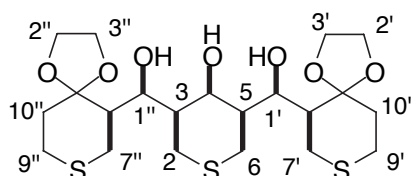
$J = 2.5, 3, 14$ Hz), 2.55-2.49 (2H, m), 2.24 (1H, dd, $J = 3, 13$ Hz), 2.18-2.09 (5H, m), 2.04-2.01 (2H, m), 1.76-1.70 (2H, m); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 110.2 (s), 110.1 (s), 70.7 (d), 68.6 (d), 68.5 (d), 64.8 (t), 64.7 (t), 64.2 (t $\times 2$), 47.4 (d), 46.8 (d), 42.2 (d), 40.5 (d), 36.5 (t), 36.1 (t), 26.6 (t), 26.3 (t), 25.7 (t), 25.6 (t); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{S}_3$: 494.1467; found: 494.1467.



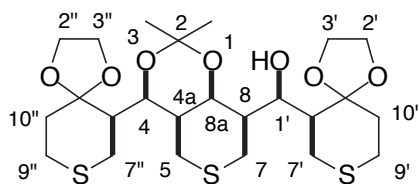
8a $^1\text{H NMR}$ (500, CDCl_3) δ : 4.55 (1H, d, $J = 9.5$ Hz, HC-1'), 4.21 (1H, dd, $J = 3, 3.5$ Hz, HC-4), 4.12-3.99 (3H, m), 3.97-3.91 (5H, m), 3.74 (1H, dd, $J = 3, 6$ Hz, HC-8a), 3.14 (1H, s, HO), 3.05-2.75 (6H, m), 2.72 (1H, br d, $J = 14$ Hz), 2.58-2.47 (3H, m), 2.30 (1H, dd, $J = 3.5, 13$ Hz), 2.21-2.15 (2H, m, HC-10', HC-10''), 2.10 (1H, dddd, $J = 3.5, 4, 6, 12$ Hz, HC-4a), 2.06-1.97 (2H, m), 1.97-1.89 (2H, m, HC-6'', HC-8), 1.78-1.68 (2H, m, HC-10', HC-10''), 1.32 (3H, s, H_3C), 1.31 (3H, s, H_3C); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 110.4 (s), 108.9 (s), 101.0 (s), 70.6 (d), 67.8 (d), 65.0 (t), 64.8 (t $\times 2$), 64.3 (t), 64.2 (d), 51.2 (d), 46.3 (d), 40.4 (d), 39.9 (d), 37.4 (t), 36.4 (t), 27.4 (t), 27.0 (t), 26.8 (t $\times 2$), 26.2 (q), 25.7 (t), 25.4 (t), 23.8 (q); **HRMS** m/z calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_7\text{S}_3$: 534.1780; found: 534.1776 (EI).



10a $^1\text{H NMR}$ (500, CDCl_3) δ : 4.84 (1H, br dd, $J = 2.5, 9.5$ Hz, HC-1'), 4.26 (1H, d, $J = 2.5$ Hz, HO), 4.22-4.17 (1H, m), 4.13-4.09 (1H, m), 4.03-3.85 (6H, m), 3.93 (1H, dd, $J = 1.5, 10.5$ Hz, HC-4), 3.89 (1H, dd, $J = 4.5, 11$ Hz, HC-8a), 3.14 (1H, dd, $J = 12, 14$ Hz), 3.00 (1H, dd, $J = 12, 14$ Hz), 2.98-2.83 (3H, m), 2.65 (1H, ddd, $J = 2.5, 2.5, 14$ Hz), 2.55-2.43 (1H, m), 2.33 (1H, dd, $J = 11.5, 14$ Hz), 2.05-2.07 (2H, dddd, $J = 2.5, 10.5, 11, 11$ Hz, HC-4a), 1.84 (1H, dd, $J = 3, 3.5, 13.5$ Hz, HC-10' or HC-10''), 2.08-2.01 (3H, m, HC-6'', HC-8, HC-10' or HC-10''), 1.86 (1H, dd, $J = 3, 11.5$ Hz, HC-6'), 1.76 (1H, ddd, $J = 3.5, 13, 13.5$ Hz, HC-10' or HC-10''), 1.72 (1H, ddd, $J = 4, 13, 13.5$ Hz, HC-10' or HC-10''), 1.39 (3H, s, H_3C), 1.33 (3H, s, H_3C); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 110.5 (s), 110.3 (s), 102.8 (s), 68.7 (d), 68.6 (d), 67.4 (d), 65.4 (t), 65.1 (t), 65.0 (t), 64.4 (t), 50.4 (d), 47.6 (d), 40.9 (d), 38.4 (t), 38.2 (t), 37.9 (d), 31.3 (t), 30.2 (q), 29.3 (t), 27.1 (t), 27.0 (t), 26.8 (t), 26.7 (t), 18.8 (q); **HRMS** m/z calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_7\text{S}_3$: 534.1780; found: 534.1779 (EI).

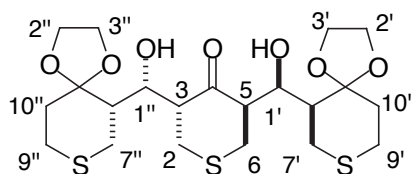


Triol from 5d $^1\text{H NMR}$ (300, CDCl_3) δ : 4.24 (2H, dd, $J = 3, 5.5$ Hz, HC-1', HC-1''), 4.07 (1H, br s, HC-4), 4.05-3.95 (8H, m, $\text{H}_2\text{CO} \times 4$), 3.03 (2H, dd, $J = 13, 13.5$ Hz, HC-2, HC-6), 2.96 (2H, dd, $J = 9.5, 14$ Hz, HC-7', HC-7''), 2.82-2.58 (6H, m), 2.47 (2H, dd, $J = 2.5, 13.5$ Hz, HC-2, HC-6), 2.09-2.19 (4H, m, HC-6', HC-6'', HC-10', HC-10''), 1.88-1.92 (2H, dddd, $J = 2, 2.5, 5.5, 13$ Hz, HC-3, HC-5), 1.79 (2H, ddd, $J = 3.5, 10, 13.5$ Hz, HC-10', HC-10''); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 109.0 (s), 72.3 (d $\times 2$), 72.0 (d), 64.8 (t $\times 2$), 64.6 (t $\times 2$), 48.0 (d $\times 2$), 46.4 (d $\times 2$), 35.5 (t $\times 2$), 27.5 (t $\times 2$), 26.8 (t $\times 2$), 22.6 (t $\times 2$); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_7\text{S}_3$: 494.1467; found: 494.1470 (EI).



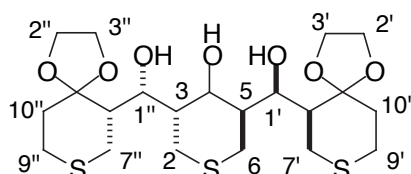
7a $^1\text{H NMR}$ (300, C_6D_6) δ : 4.55 (1H, d, $J = 9.5$ Hz, HC-4), 4.43 (1H, dd, $J = 2.5, 6$ Hz, HC-1'), 4.22 (1H, br s, HC-8a), 3.39 (1H, dd, $J = 13, 13.5$ Hz), 3.33-3.05 (13H, m), 2.96 (1H, br dd, $J = 5.5, 13$ Hz, HC-7''), 2.78-2.52 (4H, m), 2.23-2.31 (4H, m), 2.01 (1H, ddd, $J = 4, 5.5, 9.5$ Hz, HC-6''), 1.71 (1H, ddd, $J = 3, 5, 13.5$ Hz), 1.62-1.54 (1H, m), 1.50-1.36 (2H, m), 1.48 (3H, s), 1.40 (3H, s); $^{13}\text{C NMR}$ (75, C_6D_6) δ : 110.6 (s), 109.1 (s), 100.1 (s), 72.1 (d), 70.7 (d), 70.6 (d), 65.1 (t), 64.6 (t), 64.4 (t), 63.9 (t), 46.7

(d), 46.4 (d), 44.5 (d), 41.5 (d), 36.9 (t), 34.5 (t), 30.4 (q), 29.8 (t), 27.3 (t), 27.2 (t), 27.1 (t), 25.2 (t), 23.0 (t), 19.7 (q); **HRMS** m/z calcd. for C₂₄H₃₈O₇S₃: 534.1780; found: 534.1775 (EI).



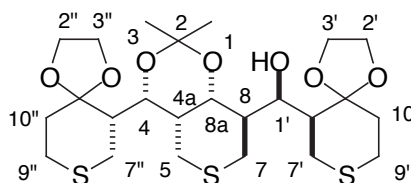
5e ¹H NMR (300, CDCl₃) δ: 4.79 (2H, d, J = 9.5 Hz, HC-1', HC-1''), 3.92-4.14 (8H, m, H₂CO ×4), 3.22-3.14 (2H, m, HC-3, HC-5), 3.05 (2H, br s, HO ×2), 3.01-2.88 (6H, m), 2.77 (2H, ddd, J = 2.5, 13, 13 Hz), 2.69 (2H, ddd, J = 2.5, 3, 14 Hz), 2.49 (2H, br d, J = 13.5 Hz), 2.13 (2H, ddd, J = 3, 4, 14 Hz, H-10', H-10''),

1.75-1.84 (4H, m, H-6', H-6'', H-10', H-10''); ¹³C NMR (75, CDCl₃) δ: 211.2 (s), 110.2 (s ×2), 66.0 (d ×2), 64.7 (t ×2), 64.2 (t ×2), 55.2 (d ×2), 46.9 (d ×2), 35.8 (t ×2), 34.2 (t ×2), 26.5 (t ×2), 25.5 (t ×2); **HRMS** m/z calcd. for C₂₁H₃₂O₇S₃: 492.1310; found: 492.1307 (EI).



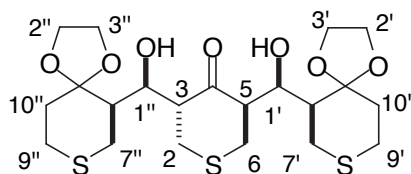
Triol from 5e ¹H NMR (300, CDCl₃) δ: 4.79 (1H, d, J = 10.5 Hz, H-4), 4.15-3.94 (9H, m, H-1' or H-1'', H₂CO ×4'), 3.87 (1H, br d, H-1' or H-1''), 3.22 (1H, dd, J = 3.5, 13.5 Hz), 3.09 (1H, dd, J = 12, 14 Hz), 3.04-2.88 (2H, m), 2.84-2.69 (4H, m), 2.65-2.59 (2H, m), 2.54-2.48 (2H, m), 2.16-2.10 (3H, m),

2.02-1.92 (3H, m), 1.83-1.70 (2H, m); ¹³C NMR (75, CDCl₃) δ: 110.3 (s), 109.9 (s), 71.1 (d), 67.8 (d), 65.0 (d), 64.9 (t), 64.7 (t), 64.4 (t), 64.3 (t), 46.7 (d), 45.9 (d), 42.7 (d), 41.2 (d), 36.5 (t), 35.6 (t), 26.6 (t ×2), 26.5 (t), 25.8 (t), 23.4 (t), 22.7 (t); **HRMS** m/z calcd. for C₂₁H₃₄O₇S₃: 494.1467; found: 494.1467 (EI).



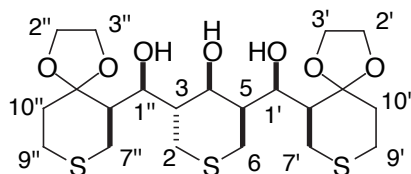
9a ¹H NMR (300, C₆D₆) δ: 5.01 (1H, d, J = 10 Hz, HC-1'), 4.23 (1H, d, J = 9.5 Hz, HC-4), 4.06 (1H, br s, HC-8a), 3.67-3.58 (1H, m), 3.40-3.50 (6H, m), 3.33-3.24 (1H, m), 3.25-3.16 (3H, m), 3.11-2.99 (3H, m), 2.88 (1H, br dd, J = 8, 13.5 Hz, HC-5), 2.71-2.50 (5H, m), 2.26-2.15 (5H, m), 1.81-1.66 (2H, m), 1.64-1.44 (2H,

m), 1.42 (3H, s), 1.30 (3H, s); ¹³C NMR (75, C₆D₆) δ: 111.0 (s), 109.6 (s), 100.0 (s), 72.7 (d), 69.8 (d), 66.3 (d), 65.2 (t), 65.1 (t), 64.4 (t), 64.0 (t), 48.3 (d), 45.2 (d), 42.5 (d), 37.4 (t), 37.2 (d), 36.1 (t), 30.4 (q), 30.0 (t), 27.1 (t ×2), 26.9 (t), 24.6 (t), 22.3 (t), 19.7 (q); **HRMS** m/z calcd. for C₂₄H₃₈O₇S₃: 534.1780; found: 534.1775.



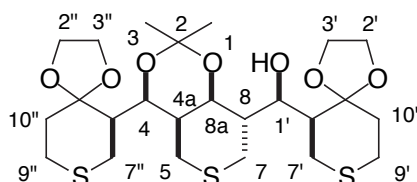
5f ¹H NMR (300, CDCl₃) δ: 4.88 (1H, br d, J = 9 Hz), 4.62 (1H, dd, J = 2, 8.5 Hz), 4.15-3.92 (8H, m), 3.03-2.58 (16H, m), 2.57-2.48 (2H, m), 2.20-2.10 (3H, m), 1.97 (1H, br d, J = 11 Hz), 1.80-1.67 (2H, m); ¹³C NMR (75, CDCl₃) δ: 211.7 (s), 110.2 (s), 110.1 (s), 68.3 (d), 67.4 (d), 65.0 (t), 64.8 (t), 64.5 (t), 64.3 (t),

55.5 (d), 54.6 (d), 47.2 (d), 45.6 (d), 36.4 (t), 36.0 (t), 34.3 (t), 34.1 (t), 26.7 (t), 26.6 (t), 26.2 (t), 26.2 (t); **HRMS** m/z calcd. for C₂₁H₃₂O₇S₃: 492.1310; found: 492.1313 (EI).



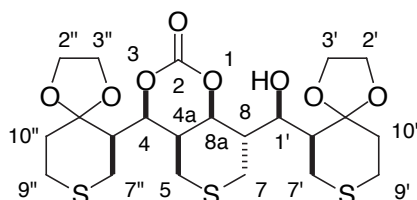
**Triol
from
5f**

$^1\text{H NMR}$ (300, CDCl_3) δ : 4.72 (1H, d, $J = 10$ Hz, HC-1''), 4.23 (1H, br s, HC-1'), 4.18 (1H, dd, $J = 1.5, 8$ Hz, HC-4), 4.14-3.94 (10H, m), 3.13 (1H, dd, $J = 3, 14$ Hz), 3.06-2.93 (3H, m), 2.86-2.75 (3H, m), 2.61-2.49 (4H, m), 2.25 (1H, ddd, $J = 2, 3, 10$ Hz), 2.20-2.12 (4H, m), 1.94-2.06 (2H, m), 1.78-1.68 (2H, m); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 110.6 (s), 110.5 (s), 71.0 (d), 67.8 (d $\times 2$), 65.1 (t), 64.9 (t), 64.4 (t), 64.3 (t), 46.9 (d), 46.1 (d), 42.8 (d), 41.2 (d), 36.5 (t), 36.3 (t), 26.8 (t), 26.7 (t), 26.5 (t), 25.8 (t), 24.4 (t), 24.3 (t); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_7\text{S}_3$: 494.1467; found: 494.1462 (EI).



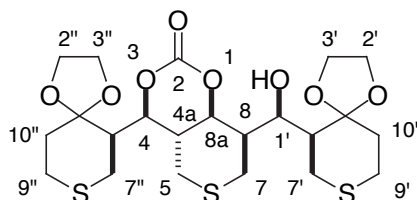
9a'

$^1\text{H NMR}$ (300, CDCl_3) δ : 4.78 (1H, d, $J = 10$ Hz, HC-1'), 4.36 (1H, br s, H-8a), 4.25 (1H, d, $J = 8.5$ Hz, HC-4), 4.14-4.09 (2H, m), 4.04-3.89 (7H, m), 3.21-3.12 (2H, m), 3.06-2.91 (2H, m), 2.82 (1H, dd, $J = 12, 13.5$ Hz), 2.77-2.52 (5H, m), 2.38 (1H, br d, $J = 13.5$ Hz), 2.21-2.11 (2H, m), 2.06-1.97 (3H, m), 1.98-1.88 (2H, m), 1.81-1.69 (2H, m), 1.44 (3H, s), 1.39 (3H, s); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 110.6 (s), 109.1 (s), 99.7 (s), 71.2 (d), 68.2 (d), 66.9 (d), 65.2 (t), 65.1 (t), 64.3 (t), 64.1 (t), 45.9 (d), 45.0 (d), 41.2 (d), 36.4 (t), 36.0 (d), 35.4 (t), 30.1 (q), 29.3 (t), 26.8 (t $\times 2$), 25.6 (t), 24.6 (t), 22.4 (t), 20.1 (q); **HRMS** m/z calcd. for $\text{C}_{24}\text{H}_{38}\text{O}_7\text{S}_3$: 534.1780; found: 534.1782 (EI).



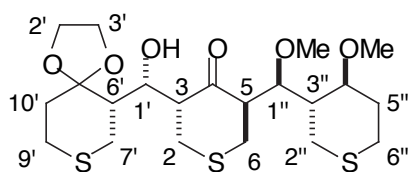
9b

$^1\text{H NMR}$ (500, CDCl_3) δ : 4.96 (1H, br s, HC-8a), 4.87 (1H, br d, $J = 9$ Hz, HC-4), 4.76 (1H, d, $J = 10$ Hz, HC-1'), 4.17-3.86 (8H, m, $\text{H}_2\text{CO} \times 4$), 3.17 (1H, br s, HO), 3.10-3.04 (2H, m), 3.00 (1H, dd, $J = 11.5, 14$ Hz, HC-7'), 2.91 (1H, dd, $J = 7, 14$ Hz, HC-7''), 2.81 (1H, ddd, $J = 2.5, 12, 13.5$ Hz, HC-9'), 2.75-2.50 (7H, m), 2.24 (1H, dddd, $J = 3, 3, 3.5, 10$ Hz, HC-8), 2.22-2.17 (2H, m, HC-6'', HC-10''), 2.14 (1H, br d, $J = 14.5$ Hz, HC-7), 1.99 (1H, dd, $J = 2.5, 11.5$ Hz, HC-6'), 1.90 (1H, ddd, $J = 3, 8, 11.5$ Hz, HC-10''), 1.88-1.71 (2H, m, HC-10', HC-10''); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 149.0 (s), 110.4 (s), 108.3 (s), 80.9 (d), 78.2 (d), 66.7 (d), 65.2 (t), 65.1 (t), 64.4 (t), 64.2 (t), 46.6 (d), 44.8 (d), 39.8 (d), 36.2 (t), 35.0 (t), 33.1 (d), 28.8 (t), 26.7 (t $\times 2$), 25.6 (t), 24.4 (t), 21.3 (t); **HRMS** m/z calcd. for $\text{C}_{22}\text{H}_{32}\text{O}_8\text{S}_3$: 520.1259; found: 520.1257 (EI).



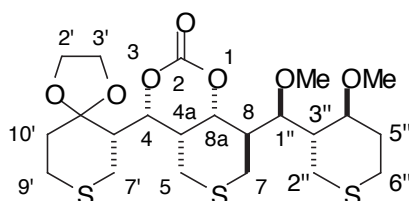
10b

$^1\text{H NMR}$ (500, CDCl_3) δ : 4.89 (1H, br dd, $J = 2.5, 8$ Hz, HC-1'), 4.49 (1H, br d, $J = 9$ Hz, HC-4), 4.24 (1H, dd, $J = 4, 10$ Hz, HC-8a), 4.13-3.92 (8H, m, $\text{H}_2\text{CO} \times 4$), 3.40 (1H, br s, HO), 3.18-3.10 (2H, m), 2.98 (1H, dd, $J = 11, 13.5$ Hz, HC-7'), 2.92 (1H, ddd, $J = 2, 13, 13.5$ Hz), 2.82-2.68 (4H, m), 2.57-2.42 (6H, m), 2.27 (1H, ddd, $J = 2.5, 3, 11$ Hz, HC-6'), 2.14 (1H, br dd, $J = 2, 11$ Hz, HC-6''), 2.13-2.08 (2H, m, HC-10', HC-10''), 1.78-1.69 (2H, m, HC-10', HC-10''); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 147.7 (s), 110.5 (s), 108.0 (s), 82.4 (d), 78.8 (d), 65.9 (d), 65.2 (t), 65.0 (t), 64.9 (t), 64.6 (t), 48.2 (d), 47.5 (d), 39.4 (d), 37.7 (t), 36.1 (t), 34.9 (d), 30.3 (t), 30.1 (t), 26.8 (t), 26.7 (t $\times 2$), 26.2 (t); **HRMS** m/z calcd. for $\text{C}_{22}\text{H}_{32}\text{O}_8\text{S}_3$: 520.1259; found: 520.1257 (EI).



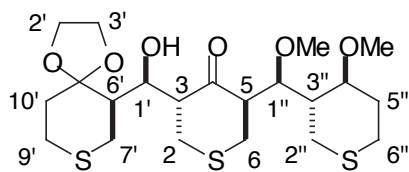
13a $^1\text{H NMR}$ (500, CDCl_3) δ : 4.93 (1H, br d, $J = 9$ Hz, HC-1'), 4.12-3.90 (4H, m, H_2CO ($\times 2$)), 4.06 (1H, dd, $J = 5, 5.5$ Hz, HC-1''), 3.39 (3H, s, H_3CO), 3.28 (3H, s, H_3CO), 3.23 (1H, ddd, $J = 3.5, 8, 8$ Hz, HC-4''), 3.18 (1H, br s, HO), 3.13-3.08 (2H, m), 3.06 (1H, ddd, $J = 5, 5.5, 10$ Hz, HC-5), 2.98-2.83 (5H, m), 2.78-2.66

(3H, m), 2.55-2.40 (3H, m), 2.25 (1H, dddd, $J = 3, 3.5, 7.5, 13.5$ Hz, HC-5''), 2.08 (1H, ddd, $J = 2.5, 4.5, 14$ Hz, HC-10'), 1.99-1.93 (1H, m, HC-3''), 1.84 (1H, ddd, $J = 2, 3.5, 11$ Hz, HC-6'), 1.80-1.65 (2H, m, HC-5'', HC-10') [by difference decoupling: {HC-1'} 2.91 (1H, ddd, $J = <4, <4, 9$ Hz, HC-3)]; $^{13}\text{C NMR}$ (75, CDCl_3) δ : 211.5 (s), 110.3 (s), 79.2 (d), 77.0 (d), 66.4 (d), 64.9 (t), 64.4 (t), 60.7 (q), 55.8 (q or d), 55.7 (d or q), 55.1 (d), 46.3 (d), 44.7 (d), 35.9 (t), 32.8 (t), 32.5 (t), 30.5 (t), 29.1 (t), 26.7 (t), 26.3 (t), 26.0 (t); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_6\text{S}_3$: 478.1518; found: 478.1516 (EI).



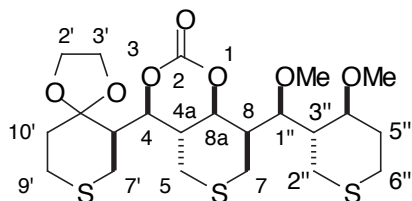
9d $^1\text{H NMR}$ (500, CDCl_3) δ : 4.78 (1H, dd, $J = 2, 10$ Hz, HC-4), 4.72 (1H, br s, HC-8a), 4.03-3.86 (4H, m, H_2CO ($\times 2$)), 3.93 (1H, dd, $J = 1.5, 11$ Hz, HC-1'), 3.50 (3H, s, H_3CO), 3.28 (3H, s, H_3CO), 3.25 (1H, ddd, $J = 4, 10, 10$ Hz, HC-4''), 3.13-3.05 (2H, m, HC-7, HC-7'), 2.89 (1H, dd, $J = 7.5, 13.5$ Hz, HC-7''), 2.81-2.53

(10H, m), 2.52-2.42 (2H, m, HC-4a, HC-5''), 2.20 (1H, ddd, $J = 3, 7.5, 10$ Hz, HC-6'), 1.89 (1H, ddd, $J = 3.5, 8, 13.5$ Hz, HC-10'), 1.84-1.73 (2H, m, HC-3'', HC-10') [by difference decoupling: {HC-4 or HC-8a} 2.44 (1H, dddd, $J = 2, 2, 4.5, 12$ Hz, HC-4a); {HC-1'' or HC-8a} 2.56 (1H, dddd, $J = <4, <4, <4, 11$ Hz, HC-8)]; $^{13}\text{C NMR}$ (75, CDCl_3) δ : 148.8 (s), 108.3 (s), 81.1 (d), 81.0 (d), 78.6 (d), 78.5 (d), 65.2 (t), 64.2 (t), 62.2 (q), 55.8 (q), 46.9 (d), 44.6 (d), 42.4 (d), 34.9 (t), 33.4 (d), 32.7 (t), 31.9 (t), 28.8 (t), 27.7 (t), 26.7 (t), 24.5 (t), 21.4 (t); **HRMS** m/z calcd. for $\text{C}_{22}\text{H}_{34}\text{O}_7\text{S}_3$: 506.1467; found: 506.1469 (EI).

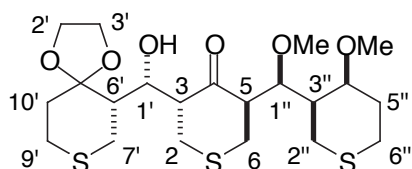


13b $^1\text{H NMR}$ (500, CDCl_3) δ : 4.80 (1H, ddd, $J = 1.5, 3, 9.5$ Hz, HC-1'), 4.13-3.90 (4H, m, H_2CO ($\times 2$)), 4.03 (1H, dd, $J = 3, 7$ Hz, HC-1''), 3.40 (3H, s, H_3CO), 3.31 (1H, ddd, $J = 4.5, 7, 10$ Hz, HC-5), 3.30 (3H, s, H_3CO), 3.18 (1H, ddd, $J = 3.5, 8.5, 8.5$ Hz, HC-4''), 3.10 (1H, d, $J = 3$ Hz, HO), 3.05-2.95 (3H, m), 2.93-2.96 (2H, m),

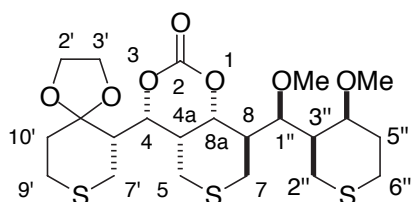
2.85-2.74 (2H, m), 2.74-2.57 (3H, m), 2.57-2.44 (3H, m), 2.32 (1H, dddd, $J = 3, 3.5, 6, 13.5$ Hz, HC-5''), 2.14 (1H, ddd, $J = 2.5, 4.5, 13.5$ Hz, HC-10'), 2.03-1.91 (2H, m, HC-3'', HC-6'), 1.73 (1H, ddd, $J = 3.5, 12.5, 13.5$ Hz, HC-10'), 1.65-1.55 (1H, m, HC-5'') [by difference decoupling: {HC-1'} 2.97 (1H, ddd, $J = 4.5, 5.5, 9.5$ Hz, HC-3)]; $^{13}\text{C NMR}$ (75, CDCl_3) δ : 211.5 (s), 110.0 (s), 79.5 (d), 77.9 (d), 67.9 (d), 65.1 (t), 64.7 (t), 60.4 (q), 55.8 (q), 55.3 (d), 55.1 (d), 47.6 (d), 46.1 (d), 36.7 (t), 33.3 (t $\times 2$), 31.6 (t), 29.5 (t), 26.82 (t), 26.78 (t), 26.3 (t); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_6\text{S}_3$: 478.1518; found: 478.1516 (EI).



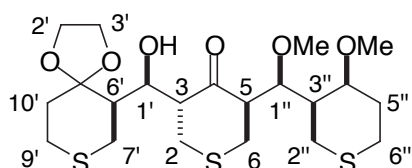
10d $^1\text{H NMR}$ (500, CDCl_3) δ : 4.53 (1H, br d, $J = 9$ Hz, HC-4), 4.27 (1H, dd, $J = 5, 10.5$ Hz, HC-8a), 4.06-3.95 (4H, m, H_2CO ($\times 2$)), 3.93 (1H, dd, $J = 4, 6$ Hz, HC-1''), 3.45 (3H, s, H_3CO), 3.31 (3H, s, H_3CO), 3.28 (1H, ddd, $J = 3.5, 9, 9$ Hz, HC-4''), 3.16 (1H, dd, $J = 12.5, 13$ Hz), 3.03 (1H, br d, $J = 13.5$ Hz), 2.93 (1H, br dd, $J = 12.5, 13$ Hz), 2.84 (1H, br d, $J = 13.5$ Hz), 2.78-2.65 (4H, m), 2.61-2.47 (4H, m), 2.46-2.34 (3H, m), 2.35-2.18 (1H, m, HC-3''), 2.17 (1H, br dd, $J = 3, 11.5$ Hz, HC-6'), 2.12 (1H, ddd, $J = 3, 3.5, 13.5$ Hz, HC-10'), 1.78-1.65 (2H, m, HC-5'', HC-10), [by difference decoupling: {HC-4 or HC-8a} 2.43 (1H, br ddd, $J = 9, 10.5, 12$ Hz, HC-4a), 2.69 (1H, m, $J = \text{all} < 6$ Hz, HC-8)]; $^{13}\text{C NMR}$ (75, CDCl_3) δ : 148.1 (s), 108.0 (s), 82.0 (d), 79.2 (d), 79.0 (d), 77.7 (d), 65.2 (t), 65.0 (t), 60.7 (q), 56.0 (q), 47.8 (d), 47.1 (d), 39.5 (d), 37.7 (t), 35.3 (d), 31.2 (t), 29.9 (t), 29.3 (t), 29.0 (t), 27.2 (t), 26.9 (t), 26.3 (t); **HRMS** m/z calcd. for $\text{C}_{22}\text{H}_{34}\text{O}_7\text{S}_3$: 506.1467; found: 506.1465 (EI).



14a $^1\text{H NMR}$ (500, C_6D_6) δ : 5.01 (1H, dd, $J = 2, 9$ Hz, HC-1'), 3.70 (1H, dd, $J = 4, 7$ Hz, HC-1''), 3.45-3.27 (2H, m), 3.28 (1H, br s, HC-4''), 3.26 (3H, s, H_3CO), 3.24-3.05 (4H, m), 3.04 (1H, br s, HO), 3.03 (3H, s, H_3CO), 3.01 (1H, ddd, $J = 4, 4.5, 9$ Hz, HC-3), 2.98-2.83 (6H,), 2.78 (1H, ddd, $J = 3, 3.5, 12.5$ Hz), 2.63-2.54 (2H, m), 2.21 (1H, br d), 2.02-1.87 (4H, m), 1.77-1.64 (2H, m), 1.51-1.43 (1H, m); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 211.4 (s), 110.2 (s), 80.4 (d), 75.6 (d), 66.1 (d), 64.9 (t), 64.5 (t), 61.1 (q), 56.5 (q), 54.9 (d), 54.8 (d), 46.7 (d), 46.8 (d), 36.0 (t), 31.2 (t), 30.2 (t), 29.5 (t), 26.7 (t), 26.0 (t), 24.5 (t), 22.1 (t); **HRMS** m/z calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_6\text{S}_3$: 479.1596 (M+H); found: 479.1602 (CI).

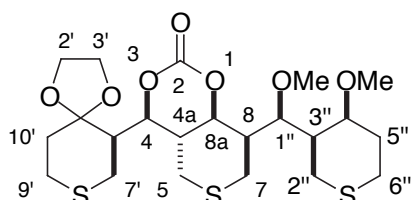


9c $^1\text{H NMR}$ (500, CDCl_3) δ : 4.89 (1H, br d, $J = 10$ Hz, HC-4), 4.85 (1H, br d, $J = 3.5$ Hz, HC-8a), 4.00-3.88 (4H, m, H_2CO ($\times 2$)), 3.62 (1H, dd, $J = 5, 8$ Hz, HC-1''), 3.47 (1H, ddd, $J = 2, 2, 4$ Hz, HC-4''), 3.42 (3H, s, H_3CO), 3.30 (3H, s, H_3CO), 3.10 (1H, ddd, $J = 1, 3, 14$ Hz, HC-7'), 2.96 (1H, ddd, $J = 2.5, 13, 13.5$ Hz, HC-6''), 2.93-2.87 (3H, m), 2.77 (1H, ddd, $J = 3.5, 9, 13$ Hz, HC-9'), 2.68-2.58 (5H, m), 2.39 (1H, dddd, $J = 3, 3.5, 3.5, 14.5$ Hz, HC-5''), 2.29-2.23 (2H, m), 2.22 (1H, dddd, $J = 3, 3.5, 4.5, 8$ Hz, HC-8), 2.18 (1H, ddd, $J = 3, 6.5, 9.5$ Hz, HC-6'), 2.16 (1H, dddd, $J = 2, 3, 5, 12$ Hz, HC-3''), 1.85-1.71 (2H, m, $\text{H}_2\text{C}-10'$), 1.64 (1H, dddd, $J = 2, 3.5, 13.5, 14.5$ Hz, HC-5''); $^{13}\text{C NMR}$ (75, CDCl_3) δ : 148.6 (s), 108.0 (s), 81.2 (d), 79.9 (d), 79.2 (d), 74.6 (d), 65.2 (t), 64.2 (t), 60.4 (q), 56.3 (q), 46.8 (d), 44.2 (d), 42.7 (d), 34.5 (d), 34.4 (t), 29.6 (t), 28.8 (t), 26.7 (t), 25.4 (t), 23.3 (t), 22.4 (t), 20.7 (t); **HRMS** m/z calcd. for $\text{C}_{22}\text{H}_{34}\text{O}_7\text{S}_3$: 506.1467; found: 506.1467 (EI).

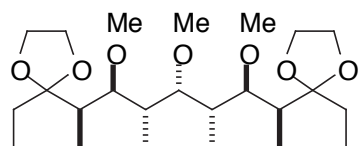


14b $^1\text{H NMR}$ (500, C_6D_6) δ : 5.02 (1H, ddd, $J = 2, 2.5, 9$ Hz, HC-1'), 3.89 (1H, dd, $J = 5, 7$ Hz, HC-1''), 3.50-3.30 (3H, m), 3.32 (3H, s, H_3CO), 3.30-3.05 (6H, m), 3.01 (3H, s, H_3CO), 3.01-2.73 (2H, m), 2.94 (1H, d, $J = 2.5$ Hz, HO), 2.70 (1H, dd, $J = 4.5, 14$ Hz), 2.63-2.49 (3H,), 2.35-2.25 (1H, m), 2.27 (1H, ddd, $J = 2.5, 5, 13.5$ Hz), 2.20 (1H, br d, $J = 13.5$ Hz), 2.05 (1H, dddd, $J = 2.5, 3, 7, 11.5$ Hz, HC-3''), 2.01-

1.93 (1H, m), 1.91 (1H, ddd, $J = 2, 3.5, 11$ Hz, HC-6'), 1.72 (1H, ddd, $J = 3, 5, 13.5$ Hz, HC-5''), 1.57 (1H, ddd, $J = 3.5, 12, 13.5$ Hz, HC-5''), 1.45-1.38 (1H, m) [by difference decoupling: {HC-1''} 3.25 (1H, ddd, $J = 5, 5, 11.5$ Hz, HC-5); {HC-1'} 2.83 (1H, ddd, $J = 5, 5, 9$ Hz, HC-3)]; ^{13}C NMR (75, CDCl_3) δ : 211.1 (s), 110.1 (s), 80.6 (d), 75.7 (d), 68.5 (d), 65.1 (t), 64.5 (t), 60.9 (d), 56.6 (d), 54.7 (q), 54.2 (q), 47.4 (d), 46.7 (d), 36.5 (t), 32.0 (t), 30.5 (t), 29.5 (t), 26.8 (t), 26.2 (t), 24.5 (t), 22.2 (t); HRMS m/z calcd. for $\text{C}_{21}\text{H}_{34}\text{O}_6\text{S}_3$: 485.1678 (M+Li); found: 485.1677 (FAB, LiBr).



10c ^1H NMR (500, CDCl_3) δ : 4.52 (1H, dd, $J = 1, 10$ Hz, HC-4), 4.31 (1H, dd, $J = 5.5, 11$ Hz, HC-8a), 4.06-3.98 (4H, m, H_2CO ($\times 2$)), 3.68 (1H, dd, $J = 5, 7$ Hz, HC-1''), 3.40 (3H, s, H_3CO), 3.30 (3H, s, H_3CO), 3.29 (1H, br s, HC-4''), 3.16 (1H, dd, $J = 11.5, 13.5$ Hz, HC-7'), 2.98-2.86 (4H, m), 2.78-2.71 (2H, m), 2.66 (1H, dddd, $J = 3.5, 10, 11, 11.5$ Hz, HC-4a), 2.54-2.30 (6H, m), 2.22 (1H, br dd, $J = 2, 13.5$ Hz, HC-5''), 2.20-2.14 (1H, m, HC-3''), 2.16 (1H, ddd, $J = 1, 3.5, 11$ Hz, HC-6'), 2.12 (1H, ddd, $J = 3, 4, 13.5$ Hz, HC-10'), 1.73 (1H, ddd, $J = 3.5, 13, 13.5$ Hz, HC-10'), 1.71-1.63 (1H, m, HC-5''); ^{13}C NMR (75, CDCl_3) δ : 148.3 (s), 108.0 (s), 81.7 (d), 80.4 (d), 79.2 (d), 75.6 (d), 65.2 (t), 65.0 (t), 60.8 (q), 56.6 (t), 47.8 (d), 47.5 (d), 39.2 (d), 37.7 (t), 35.1 (d), 29.5 (t), 29.3 (t), 27.9 (t), 26.8 (t), 26.2 (t), 24.5 (t), 22.0 (t); HRMS m/z calcd. for $\text{C}_{22}\text{H}_{34}\text{O}_7\text{S}_3$: 506.1467; found: 506.1467 (EI).



15 ^1H NMR (300, CDCl_3) δ : 4.08-3.87 (8H, m, H_2CO $\times 4$), 3.50 (3H, s, H_3CO), 3.38 (6H, s, H_3CO $\times 2$), 3.37-3.00 (3H, m), 3.32 (1H, br s), 2.03-1.86 (4H, m), 1.83-1.62 (4H, m), 0.97 (6H, d, $J = 7.0$ Hz, H_3C $\times 2$), 0.93 (6H, d, $J = 7.0$ Hz, H_3C $\times 2$), 0.89 (6H, t, $J = 7.0$ Hz, H_3C $\times 2$); ^{13}C NMR (75, CDCl_3) δ : 114.2 (s $\times 2$), 82.5 (d), 80.7 (d $\times 2$), 65.41 (t $\times 2$), 65.38 (t $\times 2$), 61.1 (q), 58.5 (q $\times 2$), 40.9 (d $\times 2$), 40.1 (d $\times 2$), 27.2 (t $\times 2$), 11.3 (q $\times 2$), 9.6 (q $\times 2$), 7.6 (q $\times 2$); HRMS m/z calcd. for $\text{C}_{24}\text{H}_{46}\text{O}_7$: 446.3243 (417.2852 for M-C 2H_5); found: 417.2859 (M - C 2H_5 , EI).