Supporting Information for

Lipase-Catalyzed Regioselective Acylation of Sugar in Microreactors

Li-Hua Du[1*], Xi-Ping Luo[2]

[1]*College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou, 310014, China*

[2]*Department of Environmental Science and Technology, Zhejiang A&F University, Hangzhou, 311300, China*

* Corresponding author: Li-Hua Du, Tel./fax: +86 571 88320903; e-mail: orgdlh@yahoo.com.cn; orgdlh@zjut.edu.cn.

Materials

Unless otherwise stated, all chemicals were obtained from commercial sources and used without further purification. Lipozyme TLIM from *Thermomyces lanuginosus* was purchased from Novo Nordisk. Vinyl palmitate and vinyl laurate were purchased from Aldrich. Harvard Apparatus PHD2000 syringe pumps were purchased from Harvard.

Purification of the Products

When the conversion of sugar to sugar monoesters reached the maximum value (determined by TLC and HPLC), the *tert*-amyl alcohol solvent was evaporated under reduced pressure. The products were eluted with a gradient of chloroform/methanol (10:1). The purification was monitored by TLC. The fractions containing the main

products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR.

Thin-Layer Chromatography

Analytical TLC was performed on silica gel 60 plates (Merck) using chloroform/methanol 4:1 (v/v) as eluent. Spots were detected by immersion in a solution of H_2SO_4/CH_3OH 1:1 (v/v), drying, and heating at 120 °C for 5 min.

High Performance Liquid Chromatography (HPLC)

Analyses were carried out by reverse-phase high performance liquid chromatography (HPLC) using a system equipped with a Spectra-Physics pump, a Hypersil ODS C18 column (250 × 4.6 mm) and a refraction index detector (Spectra-Physics). For the analysis of sugar esters of lauric acid, methanol/water 90:10 (v/v) was used as mobile phase (flow rate 1.1 mL/min), and for esters of palmitic acid methanol/water 95:5 (v/v) was used (flow rate, 1.1 mL/min). In both cases, the temperature of the column was kept constant at 40°C. Calibration analyses were performed using mono- and di-esters obtained and isolated as described above.

Experimental setup

The equipment configuration that was used for the enzymatic synthesis of sugar esters reactions starting from sugars and vinyl carboxylate is described in Figure 1. Harvard Apparatus PHD2000 syringe pumps were used to deliver reagents from syringes to the reactor. On the syringe pump, a 10 mL syringe with the sugar solution and a 10 mL syringe with vinyl carboxylate in 2-methyl -2-butanol were mounted. Lipozyme TL IM were filled in silica gel tubing (inner diameter ID= 2.0mm, length = 1m). The temperature of this reaction was controlled by water bath, just immersed the

tubing in water and control the temperature of water. Streams Ⅰ and Ⅱ were mixed together at a flow rate of 10.4 μL min^{-1} in a Y-mixer at 52 °C and the resulting stream (20.8μL min^{-1}) was connected to a sample vial which was used to collect the final mixture.

General Procedure for Sugar-6-acetate Synthesis in Continuous Flow Microreactors

Method D: 0.4 mmol of the sugar was dissolved in 10 mL 2-methyl -2-butanol/DMSO=4:1 (feed Ⅰ, ~0.04 M) and 7.2 mmol vinyl acetate were dissolved in 10 mL 2-methyl -2-butanol (feed Ⅱ; ~0.72 M). Lipozyme TL IM (0.87 g) were filled in silica gel tubing (inner diameter ID= 2.0 mm, length = 1m). Streams Ⅰ and Ⅱ were mixed together at a flow rate of 10.4 μL min^{-1} in a Y-mixer at 52 °C and the resulting stream (20.8μL min^{-1}) was connected to a sample vial which was used to collect the final mixture. The final mixture was then evaporated, and the oily residue was submitted to column chromatography on silica gel (200–300 mesh). The products were eluted with a gradient of chloroform/methanol (6:1). The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR.

General Procedure for 6-O-lauroylsugars Synthesis in Continuous Flow Microreactors

Method C: 0.4 mmol of the sugar was dissolved in 10 mL 2-methyl -2-butanol/DMSO=4:1 (feed Ⅰ, ~0.04 M) and 4.4 mmol vinyl laurate were dissolved in 10 mL 2-methyl -2-butanol (feed Ⅱ; ~0.44 M). Lipozyme TL IM (0.87 g) were filled in silica gel tubing (inner diameter ID= 2.0 mm, length = 1m). Streams Ⅰ and Ⅱ were mixed together at a flow rate of 10.4 μL min^{-1} in a Y-mixer at 55 °C and the

resulting stream (20.8μL min^{-1}) was connected to a sample vial which was used to collect the final mixture. The final mixture was then evaporated, and the oily residue was submitted to column chromatography on silica gel (200–300 mesh). The products were eluted with a gradient of chloroform/methanol (6:1). The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR.

General Procedure for 6-O-palmitoylsugars Synthesis in Continuous Flow Microreactors

Method B: 0.4 mmol of the sugar was dissolved in 10 mL 2-methyl -2-butanol/DMSO=4:1 (feed Ⅰ, ~0.04 M) and 2.0 mmol vinyl palmitate were dissolved in 10 mL 2-methyl -2-butanol (feed Ⅱ; ~0.20 M). Lipozyme TL IM (0.87 g) were filled in silica gel tubing (inner diameter ID= 2.0 mm, length = 1m). Streams Ⅰ and Ⅱ were mixed together at a flow rate of 10.4 μL min^{-1} in a Y-mixer at 52 °C and the resulting stream (20.8μL min^{-1}) was connected to a sample vial which was used to collect the final mixture. The final mixture was then evaporated, and the oily residue was submitted to column chromatography on silica gel (200–300 mesh). The products were eluted with a gradient of chloroform/methanol (6:1). The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by ^{1}H NMR.

In order to examine the reproducibility of the method, we repeated the reaction five times, the result are illustrate in Figure S1.

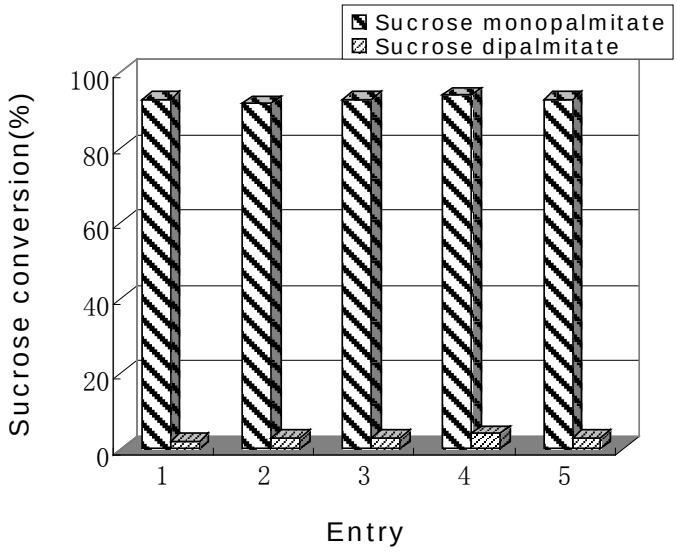


Figure S1. The reproducibility of the reaction on the conversion of 6-O-palmitoylsucrose catalysed by Lipozyme TL IM in a flow microreactor..

General Procedure for Sugar esters Synthesis under Shaker Conditions (Method A).

6-O-palmitoylsucrose Synthesis: Sucrose (0.1 mmol) was added to 4 mL of solvent (2-methyl-2-butanol/DMSO=4:1). The biocatalyst (45 mg/mL，0.18 g) was then added and the suspension maintained at 50 °C for 30 min with magnetic stirring. Vinyl palmitate (0.8 mmol，0.23 g) was then added. The reactions were performed in the presence of molecular sieves. Aliquots were withdrawn at different times, analyzed by TLC and HPLC. When the conversion of sucrose to sucrose monopalmitate reached the maximum value (determined by TLC and HPLC), the mixture was cooled and filtered. The tert-amyl alcohol was evaporated under reduced pressure. The residual vinyl palmitate was eliminated by extraction with hexane. The remaining dimethyl sulfoxide (containing the reaction substances) was mixed with one volume of water. The sucrose esters were extracted with 2 vol of cyclohexane/butanol 1:2 for palmitate esters. The organic phase was then evaporated, and the oily residue was submitted to column chromatography on silica gel (200–300 mesh). The products were eluted with a gradient of chloroform/methanol (10:1). The purification was monitored by TLC. The fractions containing the main products were pooled, the solvent evaporated, and the residue analyzed by H NMR.

Reaction Optimization Studies. We optimized the synthesis of 6-O-palmitoylsucrose varying several parameters. First, the effect of the percentage of DMSO in the reaction mixture was analyzed. Figure S2 illustrates the function of the percentage of the DMSO (v/v) to the formation of sucrose monopalmitate and sucrose dipalmitate. The conversion of sucrose 6-monoesters reaches a maximum in 24 h at 20% DMSO and diesters reaches a maximum at 10% DMSO.

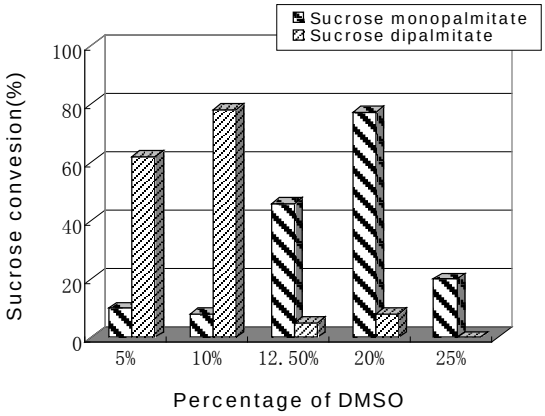


Figure S2. The influence of the percentage of DMSO on the conversion of 6-O-palmitoylsucrose.

Furthermore, the influence of the amount of biocatalyst was also studied. In these experiments, three molecular sieves (3 Å) were added to 4 mL cosolvent (2-methyl-2-butanol/DMSO 4:1 v/v). The amount of biocatalyst was varied between 30 mg/mL and 55 mg/mL. The highest conversion of 6-O-palmitoylsucrose can be obtained when 45 mg/mL (0.18 g) Lipozyme TL IM were added (Figure S3).

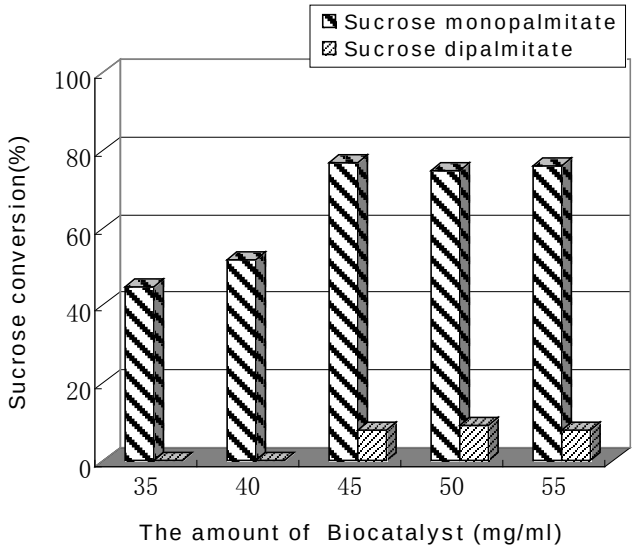


Figure S3. The influence of the amount of Lipozyme TL IM (mg/mL) on the conversion of 6-O-palmitoylsucrose.

Finally, the influence of the molar ratio of sucrose/vinyl palmitate on the conversion of 6-O-palmitoylsucrose was investigated (Figure S4). The highest conversion and regioselectivity of 6-O-palmitoylsucrose can be obtained when vinyl palmitate/sucrose=8:1.

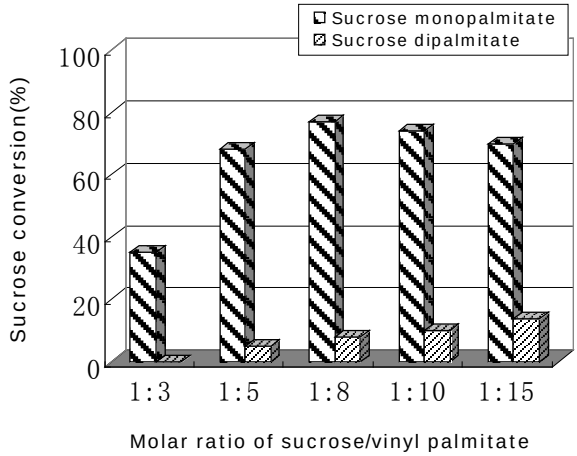
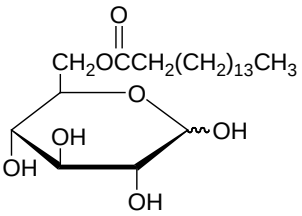
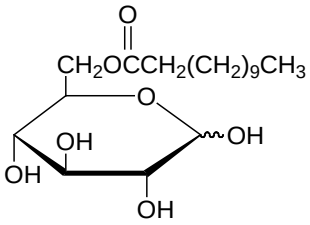


Figure S4. The influence of sucrose/vinyl palmitate on the conversion of 6-O-palmitoylsucrose catalysed by Lipozyme TL IM in shaker reactor.

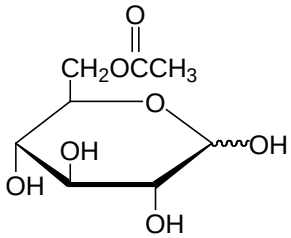
Experimental Procedures for Examples Described in Table 1



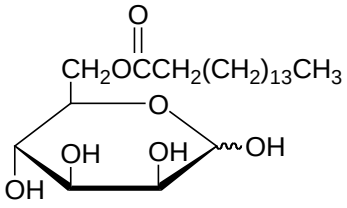
6-O-palmiate-α-D-glucose (**3a**) : m. p.129-132°C, lit [S2]; ^{1}H-NMR (DMSO-d6,δ, ppm)：6.36 (d, 1H, *J* = 4.0 Hz, l-OH of α -D-glucose), 5.06 (d, 1H, *J* = 5.5 Hz, H-l of α-D-glucose), 4.89 (d, 1H, *J* = 5.5 Hz, 4-OH of α-D-glucose), 4.77 (d, 1H, *J* = 4.5 Hz, 3-OH of α -D-glucose), 4.55 (d, 1H, *J* = 7.0 Hz, 2-OH of α-D-glucose), 4.27 (d, 1H, *J* = 2.0 Hz, H-6 of α -D-glucose), 3.99 (1H，dd，*J* = 6.3 Hz, *J* = 11.6 Hz, H-6' of α -D-glucose), 3.76 (m, 1H, H-5 of α -D-glucose), 3.43 (m, 1H, H-3 of α-D-glucose), 3.13 (m, 1H, H-2 of α -D-glucose), 3.04 (m, 1H, H-4 of α -D-glucose), 2.28-2.25 (m, 2H, a-CH_2), 1.52-1.50 (t, 2H, *J* = 7.0 Hz, β-CH_2), 1.25 (m, 24H, *n*-CH_2), 0.86 (t, 3H, *J* = 7.0 Hz, CH_3).



6-O-laurate--α-D-glucose (**3b**): m. p.126-132°C, lit [S2]; ^{1}H-NMR (DMSO-d6, δ, ppm): 6.36 (d, 1H, *J* = 4.0 Hz, l-OH of α -D-glucose), 5.06 (d, 1H, *J* = 5.5 Hz, H-l of α -D-glucose), 4.89 (d, 1H, *J* = 5.5 Hz, 4-OH of α -D-glucose), 4.77 (d, 1H, *J* = 4.5 Hz, 3-OH of α -D-glucose), 4.55 (d, 1H, *J* = 7.0 Hz, 2-OH of α -D-glucose), 4.27 (d, 1H, *J* = 2.0 Hz, H-6 of α -D-glucose), 3.99 (1H，dd，*J* = 6.3 Hz, *J* = 11.6 Hz, H-6' of α -D-glucose), 3.76 (m, 1H, H-5 of α -D-glucose), 3.43 (m, 1H, H-3 of α -D-glucose), 3.13 (m, 1H, H-2 of α -D-glucose), 3.04 (m, 1H, H-4 of α -D-glucose), 2.27-2.25 (m, 2H, a-CH_2), 1.52-1.50 (t, 2H, *J* = 7.0 Hz, β-CH_2), 1.24 (m, 16H, n-CH_2), 0.85 (t, 3H, *J* = 7.0 Hz, CH_3).

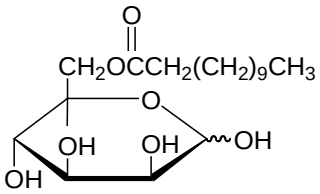


6-O-acetate-D-glucose (**3c**): yellow oil liquid, lit [S1]; ^{1}H-NMR (DMSO-d6, δ, ppm): 6.71 (d, 0.5H, *J* = 6.5 Hz, 1-OH of β-D-glucose), 6.36 (d, 0.5H, *J* = 4.5 Hz, 1-OH of α-D-glucose), 5.15 -4.57 (br m, other OH of D-glucose), 4.32 (m, 1.5H, H-6 (1H) and βH-1 (0.5H) of D-glucose), 4.0 (m, 1H, H-6' of D-glucose), 3.77 (m, 0.5H, α H-5 of D-glucose), 3.39-3.30, 3.13, 3.03 (br m, other α or β H of D-glucose), 2.90 (0.5 H, m, βH-2 of D-glucose), 2.00 (3H, s, CH_3).

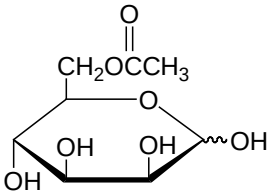


6-O-palmiate-α-D-mannose (**3d**) : yellow oil solid, lit [S3]; ^{1}H-NMR (DMSO-d6, δ,

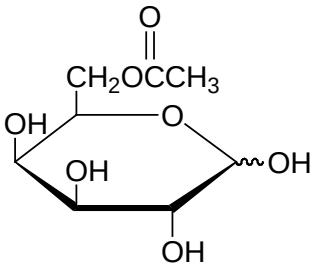
ppm)：6.39 (d, 1H, *J* = 4.5 Hz, l-OH of α-D-mannose), 4.91- 4.86 (m, 2H, H-l of α-D-mannose and 4-OH of α -D- mannose), 4.64 (d, 1H, *J* = 4.0 Hz, 3-OH of α -D-mannose), 4.56 (d, 1H, *J* = 6.0 Hz, 2-OH of α -D- mannose), 4.29 (d, 1H, *J* = 1.5 Hz, H-6 of α -D- mannose), 3.99 (m, 1H, H-6' of α-D-mannose), 3.72 (m, 1H, H-5 of α -D-mannose), 3.53 (m, 2H, H-3, H-2 of α-D-mannose), 3.29 (m, 1H, H-4 of α-D-mannose), 2.26 (m, 1H, a-CH_2), 2.18 (m, 1H, a-CH_2), 1.50 (m, 2H, β-CH_2), 1.24 (m, 24H, *n*-CH_2), 0.85 (t, 3H, *J* = 7.0 Hz, CH_3).



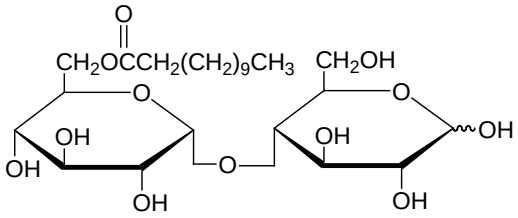
6-O-lauroate-α-D-mannose (**3e**) : yellow oil solid, lit [S3] ; ^{1}H-NMR (DMSO-d6, δ, ppm)：6.37 (d, 1H, *J* = 4.5 Hz, l-OH of α-D-mannose), 4.91- 4.86 (m, 2H, H-l of α-D-mannose and 4-OH of α -D- mannose), 4.64 (d, 1H, *J* = 4.0 Hz, 3-OH of α-D-mannose), 4.56 (d, 1H, *J* = 6.0 Hz, 2-OH of α -D- mannose), 4.29 (d, 1H, *J* = 1.5 Hz, H-6 of α -D- mannose), 3.99 (m, 1H, H-6′ of α-D-mannose), 3.72 (m, 1H, H-5 of α -D-mannose), 3.53 (m, 2H, H-3, H-2 of α-D-mannose), 3.29 (m, 1H, H-4 of α-D-mannose), 2.27 (m, 1H, a-CH_2), 2.18 (m, 1H, a-CH_2), 1.51 (m, 2H, β-CH_2), 1.24 (m, 16H, *n*-CH_2), 0.85 (t, 3H, *J* = 7.0 Hz, CH_3).



6-O-acetate-α-D-mannose (**3f**): yellow oil liquid, lit [S1]; ^{1}H-NMR (DMSO-d6,δ, ppm)：6.38 (d, 1H, *J* = 4.5 Hz, l-OH of α-D-mannose), 4.90- 4.86 (m, 2H, H-l of α-D-mannose and 4-OH of α -D- mannose), 4.64 (d, 1H, *J* = 4.0 Hz, 3-OH of α-D-mannose), 4.56 (d, 1H, *J* = 6.0 Hz, 2-OH of α -D- mannose), 4.27 (d, 1H, *J* = 1.5 Hz, H-6 of α -D- mannose), 3.99 (m, 1H, H-6′ of α-D-mannose), 3.72 (m, 1H, H-5 of α -D-mannose), 3.53 (m, 2H, H-3, H-2 of α-D-mannose), 3.29 (m, 1H, H-4 of α-D-mannose), 2.00 (s, 3H, CH_3).

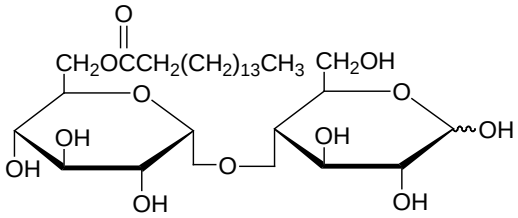


6-O-acetate-D-galactose (**3g**): yellow oil liquid, lit [S1]; ^{1}H-NMR (DMSO-d6,δ, ppm)：6.62 (d, 0.25H, *J* = 6.5 Hz, 1-OH of β-D-galactose), 6.27 (d, 0.75H, *J* = 4.5 Hz, 1-OH of α-D- galactose), 4.94 (s, 1H, H-1 of α-D-galactose), 4.54 (m, 2H, 3-OH and 4-OH of α-D-galactose), 4.33 (d, 1H, *J* = 6.0 Hz, 2-OH of α -D- galactose), 4.08 (m, 2H, H-6 and H-6′ of α-D-galactose), 3.99 (t, 1H, H-5 of α -D- galactose), 3.66 (s, 1H, H-4 of α-D-galactose), 3.54 (m, 1H, H-3 of α -D- galactose), 3.50 (m, 1H, H-2 of α -D-galactose), 2.01 (s, 3H, CH_3).

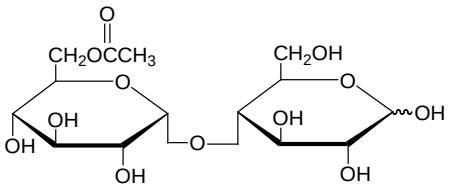


6'-O-lauroate-D-maltose (**3h**) : yellow oil solid, lit [S4] ^{1}H-NMR (DMSO-d6, δ, ppm)：6.70 (d, 0.63H, *J* = 6.5 Hz, 1β-OH of D-maltose), 6.37 (d, 0.37 H, *J* = 4.5 Hz, 1α-OH of D-maltose), 5.57 (d, 1H, *J* = 4.5, 2'β-OH and 2'α-OH of D-maltose), 5.50 (0.5H, d, *J* = 3.0 Hz, 3β-OH of D-maltose), 5.35 (0.5H, d, *J* = 3.0 Hz, 3α-OH of D-maltose), 5.20-5.18 (t, 1H, *J* = 5.5 Hz, 4'β-OH and 4'α-OH of D-maltose), 5.04 (d, 1H, *J* = 5.0 Hz, 3'β-OH and 3'α-OH of D-maltose), 5.00 (m, 1H, H-1'α and H-1'β of D-maltose), 4.97 (d, 0.5H, *J* = 3.0 Hz, H-1α of D-maltose), 4.91 (d, 0.5H, *J* = 4.0 Hz, 2β-OH of D-maltose), 4.64 (0.5H, d, *J* = 6.5, 2α-OH of D-maltose), 4.51 (t, 0.5H, *J* = 6.0 Hz, 6β-OH of D-maltose), 4.41 (t, 0.5H, *J* = 6.0 Hz, 6α-OH of D-maltose), 4.30-4.27 (m, 1.5H, H_a-6'α, H_a-6'β and H-1β of D-maltose), 4.02 (m, 1H, H_b-6'α and H_b-6'β of D-maltose), 3.74-3.62 (m, 3H, H_a-6β, H-5'α, H-5'β, H-5α, H_a-6α and H_b-6α of D-maltose), 3.56-3.40 (m, 1.5H, H-3'α, H-3'β and H-3β of D-maltose), 3.36-3.26 (m, 3H, H-4α, H-4β, H-2'α, H-2'β, H-2α and H-5β of D-maltose), 3.22-3.18 (m, 1H, H-4'α and H-4'β of D-maltose), 2.96 (m, 0.5H, H-2β of D-maltose), 2.30 (t, 2H, *J* = 7.5 Hz,

a-CH_2), 1.51 (t, 2H, *J* = 7.0 Hz, β-CH_2), 1.26 (m, 16H, *n*-CH_2), 0.85 (t, 3H, *J* = 7.0 Hz, CH_3).

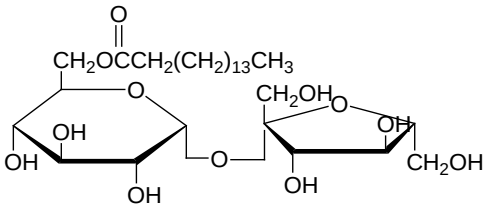


6'-O-palmiate-D-maltose (**3i**) :white solid, ^{1}H-NMR (DMSO-d6, δ, ppm)：6.69 (d, 0.45H, *J* = 6.0 Hz, 1β-OH of D-maltose), 6.36 (d, 0.55H, *J* = 4.5 Hz, 1α-OH of D-maltose), 5.55 (d, 1H, *J* = 4.5, 2'β-OH and 2'α-OH of D-maltose), 5.50 (0.5H, d, *J* = 3.0 Hz, 3β-OH of D-maltose), 5.34 (0.5H, d, *J* = 3.0 Hz, 3α-OH of D-maltose), 5.17 (t, 1H, *J* = 5.5 Hz, 4'β-OH and 4'α-OH of D-maltose), 5.04 (d, 1H, *J* = 5.0 Hz, 3'β-OH and 3'α-OH of D-maltose), 5.00 (m, 1H, H-1'α and H-1'β of D-maltose), 4.97 (d, 0.5H, *J* = 3.0 Hz, H-1α of D-maltose), 4.91 (d, 0.5H, *J* = 4.0 Hz, 2β-OH of D-maltose), 4.64 (0.5H, d, *J* = 6.5, 2α-OH of D-maltose), 4.50 (t, 0.5H, *J* = 6.0 Hz, 6β-OH of D-maltose), 4.40 (t, 0.5H, *J* = 6.0 Hz, 6α-OH of D-maltose), 4.30-4.27 (m, 1.5H, H_a-6'α, H_a-6'β and H-1β of D-maltose), 4.02 (m, 1H, H_b-6'α and H_b-6'β of D-maltose), 3.74-3.62 (m, 3H, H_a-6β, H-5'α, H-5'β, H-5α, H_a-6α and H_b-6α of D-maltose), 3.56-3.40 (m, 1.5H, H-3'α, H-3'β and H-3β of D-maltose), 3.36-3.26 (m, 3H, H-4α, H-4β, H-2'α, H-2'β, H-2α and H-5β of D-maltose), 3.22-3.18 (m, 1H, H-4'α and H-4'β of D-maltose), 2.96 (m, 0.5H, H-2β of D-maltose), 2.32-2.29 (m, 1H, a-CH_2), 2.19-2.16 (m, 1H, a-CH_2), 1.51 (m, 2H, β-CH_2), 1.24 (m, 24H, *n*-CH_2), 0.85 (t, 3H, *J* = 7.0 Hz, CH_3).

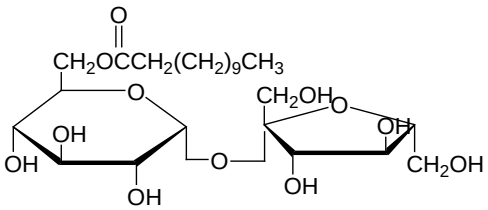


6'-O-acetate-D-maltose (**3j**): yellow oil liquid, lit [S1]; ^{1}H-NMR (DMSO-d6,δ, ppm)：6.70 (d, 0.50H, *J* = 6.5 Hz, 1β-OH of D-maltose), 6.37 (d, 0.50H, *J* = 4.5 Hz, 1α-OH of D-maltose), 5.57 (d, 1H, *J* = 4.5 Hz, 2'β-OH and 2'α-OH of D-maltose), 5.50 (d, 0.5H, *J* = 3.0 Hz, 3β-OH of D-maltose), 5.35 (d, 0.5H, *J* = 3.0 Hz, 3α-OH of

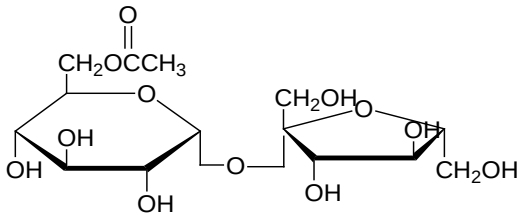
D-maltose), 5.18 (t, 1H, *J* = 5.5 Hz, 4'β-OH and 4'α-OH of D-maltose), 5.04 (d, 1H, *J* = 5.0 Hz, 3'β-OH and 3'α-OH of D-maltose), 5.00 (m, 1H, H-1'α and H-1'β of D-maltose), 4.97 (d, 0.5H, *J* = 3.0 Hz, H-1α of D-maltose), 4.91 (d, 0.5H, *J* = 4.0 Hz, 2β-OH of D-maltose), 4.64 (d, 0.5H, *J* = 6.5 Hz, 2α-OH of D-maltose), 4.51 (t, 0.5H, *J* = 6.0 Hz, 6β-OH of D-maltose), 4.41 (t, 0.5H, *J* = 6.0 Hz, 6α-OH of D-maltose), 4.30-4.27 (m, 1.5H, $H_α$-6'α, $H_α$-6'β and H-1β of D-maltose), 4.02 (m, 1H, H_b-6'α and H_b-6'β of D-maltose), 3.74-3.62 (m, 3H, $H_α$-6β, H-5'α, H-5'β, H-5α, $H_α$-6α and H_b-6α of D-maltose), 3.56-3.40 (m, 1.5H, H-3'α, H-3'β and H-3β of D-maltose), 3.36-3.26 (m, 3H, H-4α, H-4β, H-2'α, H-2'β, H-2α and H-5β of D-maltose), 3.22-3.18 (m, 1H, H-4'α and H-4'β of D-maltose), 2.96 (m, 0.5H, H-2β of D-maltose), 2.02 (s, 3H, CH_3).



6-O-palmiate-D- sucrose (**3k**): lit [S5]; ^{1}H-NMR (DMSO-d6,δ, ppm)：5.18-5.14 (m, 3H, 2β-OH of sucrose, 3α-OH of sucrose and 4β-OH of sucrose), 5.03 (d, 1H, *J* = 5.5 Hz, 3'β-OH of sucrose), 4.90 (s, 1H, 4'α-OH of sucrose), 4.83-4.80 (t, 1H, *J* = 6.5 Hz, 5'β-OH of sucrose), 4.58 (d, 1H, *J* = 8.0 Hz, 1'β-OH of sucrose), 4.41-4.39 (t, 1H, *J* = 5.0 Hz, $H_α$-6α of sucrose), 4.24 (d, 1H, *J* = 10.5 Hz, H_b-6α of sucrose), 4.04-3.99 (m, 1H, H-5β of sucrose), 3.92-3.86 (m, 2H, H-5'α and $H_α$-1'α of sucrose), 3.73 (d, 1H, *J* = 6.0 Hz, H_b-1'α of sucrose), 3.60-3.47 (m, 4H, H-3'α, H-4'β, H_a-6'β and H_b-6'βof sucrose), 3.35 (m, 1H, H-3β of sucrose), 3.22-3.19 (m, 1H, H-2β of sucrose), 3.09-3.04 (m, 1H, H-4β of sucrose), 2.31-2.29 (m, 2H, a-CH_2), 1.52-1.50 (t, 2H, *J* = 7.0 Hz, β-CH_2), 1.25 (m, 24H, *n*-CH_2), 0.86 (t, 3H, *J* = 7.0 Hz, CH_3).



6-O-lauroylsucrose: (**3l**) : lit [S5]; ^{1}H-NMR (DMSO-d6, δ, ppm)：5.18-5.14 (m, 3H, 2β-OH of sucrose, 3α-OH of sucrose and 4β-OH of sucrose), 5.03 (d, 1H, *J* = 5.5 Hz, 3'β-OH of sucrose), 4.90 (s, 1H, 4'α-OH of sucrose), 4.83-4.80 (t, 1H, *J* = 6.5 Hz, 5'β-OH of sucrose), 4.58 (d, 1H, *J* = 8.0 Hz, 1'β-OH of sucrose), 4.41-4.39 (t, 1H, *J* = 5.0 Hz, $H_α$-6α of sucrose), 4.24 (d, 1H, *J* = 10.5 Hz, H_b-6α of sucrose), 4.04-3.99 (m, 1H, H-5β of sucrose), 3.92-3.86 (m, 2H, H-5'α and $H_α$-1'α of sucrose), 3.73 (d, 1H, *J* = 6.0 Hz, H_b-1'α of sucrose), 3.60-3.47 (m, 4H, H-3'α, H-4'β, H_a-6'β and H_b-6'βof sucrose), 3.35 (m, 1H, H-3β of sucrose), 3.22-3.19 (m, 1H, H-2β of sucrose), 3.09-3.04 (m, 1H, H-4β of sucrose), 2.31-2.29 (m, 2H, a-CH_2), 1.52-1.50 (t, 2H, *J* = 7.0 Hz, β-CH_2), 1.25 (m, 16H, *n*-CH_2), 0.86 (t, 3H, *J* = 7.0 Hz, CH_3).



6-O-acetate-sucrose: (**3m**) : lit [S6]; ^{1}H-NMR (DMSO-d6, δ, ppm)：5.18-5.14 (m, 3H, 2β-OH of sucrose, 3α-OH of sucrose and 4β-OH of sucrose), 5.03 (d, 1H, *J* = 5.5 Hz, 3'β-OH of sucrose), 4.90 (s, 1H, 4'α-OH of sucrose), 4.83-4.80 (t, 1H, *J* = 6.5 Hz, 5'β-OH of sucrose), 4.58 (d, 1H, *J* = 8.0 Hz, 1'β-OH of sucrose), 4.41-4.39 (t, 1H, *J* = 5.0 Hz, $H_α$-6α of sucrose), 4.24 (d, 1H, *J* = 10.5 Hz, H_b-6α of sucrose), 4.04-3.99 (m, 1H, H-5β of sucrose), 3.92-3.86 (m, 2H, H-5'α and $H_α$-1'α of sucrose), 3.73 (d, 1H, *J* = 6.0 Hz, H_b-1'α of sucrose), 3.60-3.47 (m, 4H, H-3'α, H-4'β, H_a-6'β and H_b-6'βof sucrose), 3.35 (m, 1H, H-3β of sucrose), 3.22-3.19 (m, 1H, H-2β of sucrose), 3.09-3.04 (m, 1H, H-4β of sucrose), 2.02 (s, 3H, CH_3).

References

[1] S. Park, R. J. Kazlauskas, *J. Org. Chem*. **2001**, *66*, 8395-8401.

[2] P. Degn, L. H. Pedersen, J. Duus, W. Zimmermann, *Biotechnology Letters* **21:** 275–280, 1999.

[3] W. Tsuzuki, Y. Kitamura, T. Suzuki, S. Kobayashi, *Biotechnol Bioeng*. **1999**, *64*, 267-271.

[4] Q. Liu, C. Jia, J. M. Kim, P. Jiang, X. Zhang, B. Feng, S. Xu, *Biotechnol Lett*.

2008 *30*, 497–502.

[5] M. Ferrer, M. A. Cruces, M. Bernabe´, A. Ballesteros, F. J. Plou, *Biotechnol Bioeng*. **1999,** *65*, 10-16.

[6] M. Verhaegen, P.Leonard, **EU Patent**: 1, 905, 838, A1, 2008-02-04.