SUPPORTING INFORMATION FOR:

Solvent-Free Synthesis of High-Purity Sucrose Fatty Acid Mono-Esters and a Comparison of their Properties with those of their Commercial Counterparts

Meng-Fei Xie†‡, Lorenzo V. White§, Martin G. Banwell†, Yong Wang*†‡, and Ping Lan*†‡

†Guangdong Saskatchewan Oil Seed Joint Laboratory, Department of Food Science and Engineering, Jinan University, Guangzhou 510632, Guangdong, China

‡Institute for Advanced and Applied Chemical Synthesis, Jinan University, Guangzhou/Zhuhai, 510632/519070, Guangdong, China

*Corresponding authors (Y. W., Email: twyong@jnu.edu.cn, Tel.: +86-20-85226326; P. L., E-mail: ping.lan@jnu.edu.cn, Tel: +86-20-85221367)

CONTENTS

Synthesis of standard samples 6-O-stearoylsucrose (1) and 6,6‘-O-stearoylsucrose (2) 2

1H- and 13C-NMR Spectra of Compounds 1-2 4

The analytical plot (A) and calibration (B) curve of compounds 1, 2, and sucrose as well as methyl stearate 8
Synthesis of standard samples 6-O-stearoylsucrose (1) and 6,6′-O-stearoylsucrose (2)

**6-O-stearoylsucrose, 1.** A solution of sucrose (3.0 g, 8.7 mmol) in anhydrous THF/pyridine (50 mL, 1:1, v/v) was treated with lipzyme TLIM (3.0 g, 100% w/w loading) and vinyl stearate (13.5 g, 5.0 eq., 43.5 mmol). The ensuing mixture was stirred magnetically at 50 °C for 48 h then cooled and the residual enzyme removed by filtration and the solid thus retained washed with dichloromethane (2 × 30 mL) then methanol (2 × 30 mL). The combined filtrates were dried (Na₂SO₄), filtered then concentrated under reduced pressure to afford a yellow oil that was subjected to flash chromatography on silica and eluting with methanol/dichloromethane (1:9, v/v). Concentration of the relevant fractions (Rf = 0.2) then afforded compound 1 (2.5 g, 47%) as an amorphous, white solid. ¹H NMR (600 MHz, methanol-d₄) δ 5.38 (d, J = 3.8 Hz, 1H, H-1), 4.40 (dd, J = 12.0, 2.1 Hz, 1H, H-6a), 4.17 (dd, J = 12.0, 5.4 Hz, 1H, H-5), 4.09 (d, J = 8.4 Hz, 1H, H-6b), 4.05 – 3.95 (m, 2H, H-3’, H-1’a), 3.84 – 3.75 (m, 2H, H-6’a, H-6’b), 3.76 – 3.68 (m, 2H, H-6’a, H-6’b), 3.76 – 3.68 (m, 2H, H-6’a, H-6’b), 3.62 (d, J = 12.3 Hz, 1H, 6’-OH), 3.58 (d, J = 12.3 Hz, 1H,1-OH), 3.42 (dd, J = 9.8, 3.8 Hz, 1H, H-3), 3.31 – 3.26 (m, 1H, H-4), 2.37 (t, J = 7.5 Hz, 2H, -CH₂-CO-), 1.62 (p, J = 7.3 Hz, 2H, -CH₂-C₂H₂-CO-), 1.37 – 1.29 (m, 9H, -CH₂-), 1.29 (s, 20H, -CH₃-), 0.90 (t, J = 7.0 Hz, 3H, -CH₃). ¹³C NMR (151 MHz, methanol-d₄) δ 175.39 (C=O), 150.10 (C2’), 93.27 (C1), 83.77 (C5’), 79.11 (C3’), 75.80 (C4’), 74.36 (C3), 73.03 (C2), 71.84 (C5), 71.52 (C4), 64.55 (C6), 63.99 (C1’), 63.81 (C6’), 34.80 (-CH₂-CO-), 32.94, 30.65 (∗6), 30.62 (∗2), 30.51, 30.33 (∗2), 30.10, 25.88, 23.59 (-CH₂-CH₃), 14.30 (-CH₃). MS (ESI, +ve): m/z 626 [M+NH₄⁺]⁺

**6,6′-O-stearoylsucrose, 2.** A solution of mono-ester 1 (2.0 g, 3.3 mmol) in
anhydrous acetone (80 mL) was treated with Novozym 435 (2.0 g, 100% w/w loading) and vinyl stearate (5.1 g, 5.0 eq., 16.5 mmol). The ensuing mixture was stirred magnetically at 45 °C for 24 h then cooled and the residual enzyme removed by filtration and the solid thus retained washed with dichloromethane (2 × 30 mL) then methanol (2 × 30 mL). The combined filtrates were dried (Na₂SO₄), filtered then concentrated under reduced pressure to afford a yellow oil that was subjected to flash chromatography on silica and eluting with methanol/dichloromethane (1:9, v/v). Concentration of the relevant fractions (Rf = 0.4) then afforded compound 2 (1.8 g, 63%) as an amorphous, white solid. ¹H NMR (600 MHz, DMSO-d₆) δ 5.37 (d, J = 5.8 Hz, 1H), 5.10 (dd, J = 6.9, 4.8 Hz, 2H), 5.04 (d, J = 5.6 Hz, 1H), 4.88 (d, J = 4.9 Hz, 1H), 4.83 (t, J = 6.4 Hz, 1H), 4.73 (d, J = 7.8 Hz, 1H), 4.33 – 4.26 (m, 2H), 4.15 (dd, J = 11.7, 8.4 Hz, 1H), 3.94 – 3.86 (m, 3H), 3.79 (td, J = 8.3, 5.8 Hz, 1H), 3.73 (td, J = 8.3, 2.7 Hz, 1H), 3.48 (td, J = 9.2, 4.5 Hz, 1H), 3.41 – 3.34 (m, 2H), 3.20 (ddd, J = 9.7, 6.0, 3.7 Hz, 1H), 3.00 (td, J = 9.2, 5.3 Hz, 1H), 2.29 (dt, J = 18.4, 7.5 Hz, 4H), 1.50 (q, J = 6.8 Hz, 4H), 1.29 – 1.21 (m, 56H), 0.85 (t, J = 6.9 Hz, 6H). ¹³C NMR (151 MHz, DMSO-d₆) δ 172.59, 103.90, 91.27, 78.98, 74.63, 72.39, 71.27, 70.27, 69.94, 65.54, 64.00, 61.73, 33.14, 33.06, 31.16, 28.95, 28.93, 28.87, 28.85, 28.80, 28.66, 28.62, 28.58, 28.38, 28.34, 24.27, 21.96, 13.79. MS (ESI, +ve): m/z 892 [M+NH₄]⁺
600 MHz $^1$H NMR Spectrum of Compound 1 (Recorded in Methanol-$d_4$)
150 MHz $^{13}$C NMR Spectrum of Compound 1 (Recorded in Methanol-$d_4$)
600 MHz $^1$H NMR Spectrum of Compound 2 (Recorded in DMSO-$d_6$)
150 MHz $^{13}$C NMR Spectrum of Compound 2 (Recorded in DMSO-$d_6$)
The analytical plot (A) and calibration curve of sucrose stearic acid mono-ester (B) (0.01-0.16 mg/mL)
The analytical plot (A) and calibration curve of sucrose stearic acid di-ester (B) (0.01–0.16 mg/mL)
The analytical plot (A) and calibration curve of sucrose (0.01–0.16 mg/mL) (B)
The analytical plot (A) and calibration curve of sucrose stearate (B) (0.01–0.16 mg/mL)