Supporting Information

Enzymatic synthesis of alkyl glucosides by \( \beta \)-glucosidases in a 2-in-1 deep eutectic solvent system

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Figure S1. NMR experiments on the produced glycolipids from the butyl-β-D-glucopyranoside synthesis: (A) $^1$H-NMR. (B) $^1$H-$^{13}$C COSY spectra. (C) $^1$H-$^{13}$C HMBC spectra. (D) $^1$H-$^{13}$C HSQC spectra.
Figure S2. NMR experiments on the produced glycolipids from the hexyl-β-D-glucopyranoside synthesis: (A) $^1$H-NMR. (B) $^1$H- $^{13}$C COSY spectra. (C) $^1$H- $^{13}$C HMBC spectra. (D) Mass spectra of HGP.

The chemical shifts of HGP are given as follows:

$^1$H NMR (300 MHz, DMSO-d$_6$) δ (ppm), 4.72 (d, J = 5.0 Hz, 1H), 4.66 (s, 2H), 3.88 (d, J = 7.8 Hz, 1H), 3.61 – 3.38 (m, 2H), 3.20 (ddt, J = 13.3, 9.4, 4.4, 4.4 Hz, 2H), 3.12 (s, 2H), 2.97 – 2.75 (m, 3H), 2.71 (td, J = 8.7, 8.4, 3.6 Hz, 1H), 1.30 (dq, J = 12.9, 6.8, 6.7, 6.7 Hz, 2H), 1.18 – 0.96 (m, 7H), 0.66 (td, J = 7.1, 6.9, 4.3 Hz, 3H).

$^{13}$C NMR (600 MHz, CDCl$_3$/MeOD 70:30) δ (ppm), 102.9, 76.1, 73.2, 70.6, 69.8, 61.7, 30.9, 30.5, 29.1, 22.0, 20.2, 13.7.

Figure S2 D. shows the mass spectrum of the purified glycolipid fraction from the synthesis of hexyl-β-D-glucopyranoside (HGP) using the β-glucosidase formulation GC 151. The molecular mass of the corresponding compound ($M_{\text{HGP}}$) is 264.15 g/mol. The m/z of 265.16 corresponds to the protonated hexyl-β-D-glucopyranoside [$M_{\text{HGP}}$ + H]$^+$. Other adducts observed were attributed to ([$M_{\text{HGP}}$ + Na]$^-$-H$_2$O) with a 269.14 m/z, [$M_{\text{HGP}}$ + NH$_4$]$^+$ with the peak at 282.19, and [MHGP + Na]$^+$ with a peak at m/z of 287.15. The other signals could not be clearly assigned.
Figure S3. NMR experiments on the produced glycolipids from the octyl-β-D-glucopyranoside synthesis: (A) $^1$H-NMR. (B) $^1$H-$^{13}$C COSY spectra. (C) $^1$H-$^{13}$C HMBC spectra. (D) Mass spectra of OGP.

The chemical shifts of OGP are given as follows:

$^1$H NMR (300 MHz, DMSO-d6) $\delta$ 6.31 – 6.11 (m, 1H), 4.93 (s, 1H), 4.45 (s, 1H), 4.08 (d, $J=7.8$ Hz, 1H), 3.82 – 3.60 (m, 1H), 3.51 – 3.31 (m, 1H), 3.18 – 2.85 (m, 2H), 2.45 (s, 2H), 1.80 (d, $J=5.6$ Hz, 2H), 1.49 (d, $J=5.8$ Hz, 2H), 1.37 – 1.20 (m, 11H), 1.15 (s, 2H), 0.91 – 0.80 (m, 3H).

$^{13}$C NMR (600 MHz, CDCl3/MeOD 70:30) $\delta$ (ppm), 103.1, 76.1, 74.0, 73.6, 70.2, 63.8, 30.5, 30.3, 29.9, 24.4, 23.0, 20.2, 19.4.

Figure S3 D. shows the mass spectrum of the purified glycolipid fraction from the synthesis of octyl-β-D-glucopyranoside (OGP) using the β-glucosidase formulation GC 151. The molecular mass of the corresponding compound (MOGP) is 292.37 g/mol.

The signal at 293.20 corresponds to octyl-β-D-glucopyranoside attached to a proton [MOGP + H]$^+$+. Other identifiable adducts are ([MOGP + Na]$^+$-H$_2$O) with the peak at 297.31, [MOGP + NH$_4$]$^+$ with the peak at 310.22, and ([MOGP + H]$^+$+H$_2$O) with the peak at 311.33.
**Figure S4.** Calibration curve of butyl-β-glucopyranoside and chromatograph from the HPLC-ELSD analysis.

\[ y = 50879x^2 + 54506x - 411.95 \]

\[ R^2 = 0.9997 \]

**Figure S5.** Calibration curve of hexyl-β-glucopyranoside and chromatograph from the HPLC-ELSD analysis.

\[ y = 80571x^2 + 35874x - 453.04 \]

\[ R^2 = 0.9999 \]
Figure S6. Calibration curve of octyl-β-glucopyranoside and chromatograph from the HPLC-ELSD analysis.

\[ y = 40264x^2 + 58529x - 1380.3 \]

\[ R^2 = 0.9964 \]