Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

The direct and one-pot transformation of xylan into the biodegradable surfactants, alkyl xylosides, is aided by an ionic liquid

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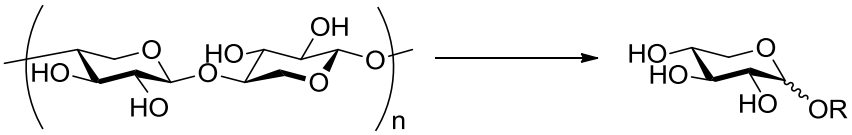
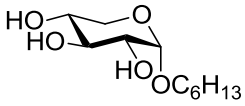
General experimental methods

Melting points were determined on a micro hot-stage (Yanako MP-S3). Optical rotations were measured on a JASCO P-2200 polarimeter. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECA-500 (500 MHz and 125 MHz) spectrometer. ^{1}H NMR data are reported as follows; chemical shift in parts par million (ppm) downfield or upfield, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet and m = multiplet) and coupling constants (Hz). ^{13}C chemical shifts are reported in ppm downfield or upfield from CD_3OD (δ 49.00). Silica gel TLC and column chromatography were performed on Merck TLC 60F-254 (0.25 mm) and Silica Gel 60 N (spherical, neutral, 40-50 μm) (Kanto Chemical Co., Inc.), respectively.

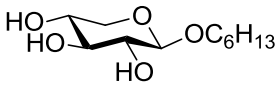
General procedure for the glycosylations in Tables 1-3



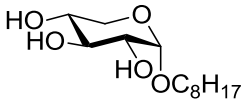
A suspension of xylan (20.0 mg) in ionic liquid (400 mg) was heated with stirring at 90 ˚C until a clear solution formed. To the resulting solution were added a fatty alcohol and an acid catalyst. After the mixture was stirred at indicated temperature for indicated reaction time, the reaction was quenched by addition of H_2O (0.5 mL). The resulting mixture was extracted with EtOAc (1 mL x 5) and the combined extracts were concentrated in *vacuo*. Purification of the residue by flash column chromatography ($CHCl_3$/MeOH = 9/1) gave the corresponding alkyl xyloside.



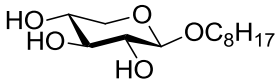
Hexyl α-D-xylopyranoside[1]: White solid; R_f 0.39 (9/1 $CHCl_3$/MeOH); $[\alpha]^{24}_{D}$ +132.2 (*c* 1.0, MeOH); mp 73-74 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 4.70 (d, 1H, *J* = 3.5 Hz), 3.70-3.64 (m, 1H), 3.59-3.40 (m, 5H), 3.35 (dd, 1H, *J* = 3.5, 9.5 Hz), 1.69-1.56 (m, 2H), 1.47-1.27 (m, 6H), 0.91 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 100.3, 75.2, 73.6, 71.6, 69.3, 63.0, 32.9, 30.6, 27.0, 23.7, 14.4.



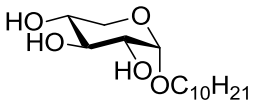
Hexyl β-D-xylopyranoside[1]: White solid; R_f 0.43 (9/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ −48.9 (*c* 1.0, MeOH); mp 71-72 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 4.18 (d, 1H, *J* = 7.5 Hz), 3.85-3.77 (m, 2H), 3.54-3.44 (m, 2H), 3.34-3.27 (m, 1H), 3.20-3.13 (m, 2H), 1.63-1.57 (m, 2H), 1.41-1.29 (m, 6H), 0.90 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 105.0, 77.9, 74.9, 71.2, 70.9, 66.9, 32.8, 30.8, 26.8, 23.7, 14.4.



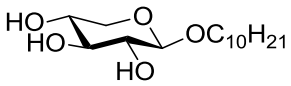
Octyl α-D-xylopyranoside[2]: White solid; R_f 0.38 (9/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ +115.0 (*c* 1.0, MeOH); mp 75-76 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 4.70 (d, 1H, *J* = 3.5 Hz), 3.69-3.64 (m, 1H), 3.59-3.40 (m, 5H), 3.35 (dd, 1H, *J* = 3.5, 9.5 Hz), 1.67-1.60 (m, 2H), 1.42-1.30 (m, 10H), 0.90 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 100.3, 75.2, 73.6, 71.6, 69.2, 63.0, 33.0, 30.7, 30.6, 30.4, 27.4, 23.7, 14.4.



Octyl β-D-xylopyranoside[2]: White solid; R_f 0.40 (9/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ −31.3 (*c* 1.0, MeOH); mp 74-75 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 4.18 (d, 1H, *J* = 7.5 Hz), 3.85-3.77 (m, 2H), 3.54-3.44 (m, 2H), 3.35-3.27 (m, 1H), 3.20-3.13 (m, 2H), 1.63-1.58 (m, 2H), 1.38-1.30 (m, 10H), 0.90 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 105.1, 77.9, 74.9, 71.2, 70.9, 66.9, 33.0, 30.8, 30.5, 30.4, 27.1, 23.7, 14.4.



Decanyl α-D-xylopyranoside[3]: White solid; R_f 0.40 (9/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ +101.5 (*c* 1.0, MeOH); mp 66-67 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 4.70 (d, 1H, *J* = 3.5 Hz), 3.69-3.64 (m, 1H), 3.59-3.41 (m, 5H), 3.35 (dd, 1H, *J* = 3.5, 9.5 Hz), 1.68-1.58 (m, 2H), 1.44-1.30 (m, 14H), 0.90 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 100.3, 75.2, 73.6, 71.6, 69.2, 63.0, 33.1, 30.8, 30.7, 30.6, 30.5, 27.4, 23.7, 14.4.



Decanyl β-D-xylopyranoside[3]: White solid; R_f 0.44 (9/1 $CHCl_3$/MeOH); $[\alpha]^{24}_D$ −36.5 (*c* 1.0, MeOH); mp 69-70 °C; ^{1}H NMR (500 MHz, CD_3OD) δ 4.18 (d, 1H, *J* = 7.5 Hz), 3.85-3.77 (m, 2H), 3.54-3.44 (m, 2H), 3.32-3.27 (m, 1H), 3.20-3.13 (m, 2H), 1.63-1.57 (m, 2H), 1.38-1.29 (m, 14H), 0.90 (t, 3H, *J* = 7.0 Hz); ^{13}C NMR (125 MHz, CD_3OD) δ 105.1, 77.9, 74.9, 71.2, 70.9, 66.9, 33.1, 30.8, 30.7×2, 30.6, 30.5, 27.1, 23.7, 14.4.

References

[1] N. Villandier and A. Corma, *Chem. Commun.* 2010, **46**, 4408.

[2] W. Xu, G. Osei-Prempeh, C. Lema, E. D. Oldham, R. J. Aguilera, S. Parkin, S. E. Rankin, B. L. Knutson and H.-J. Lehmler, *Carbohydr. Res*., 2012, **349**, 12.

[3] F. Bouxin, S. Marinkovic, J. L. Bras and B. Estrine, *Carbohydr. Res*., 2010, **345**, 2469.

^{1}H and ^{13}C NMR spectra

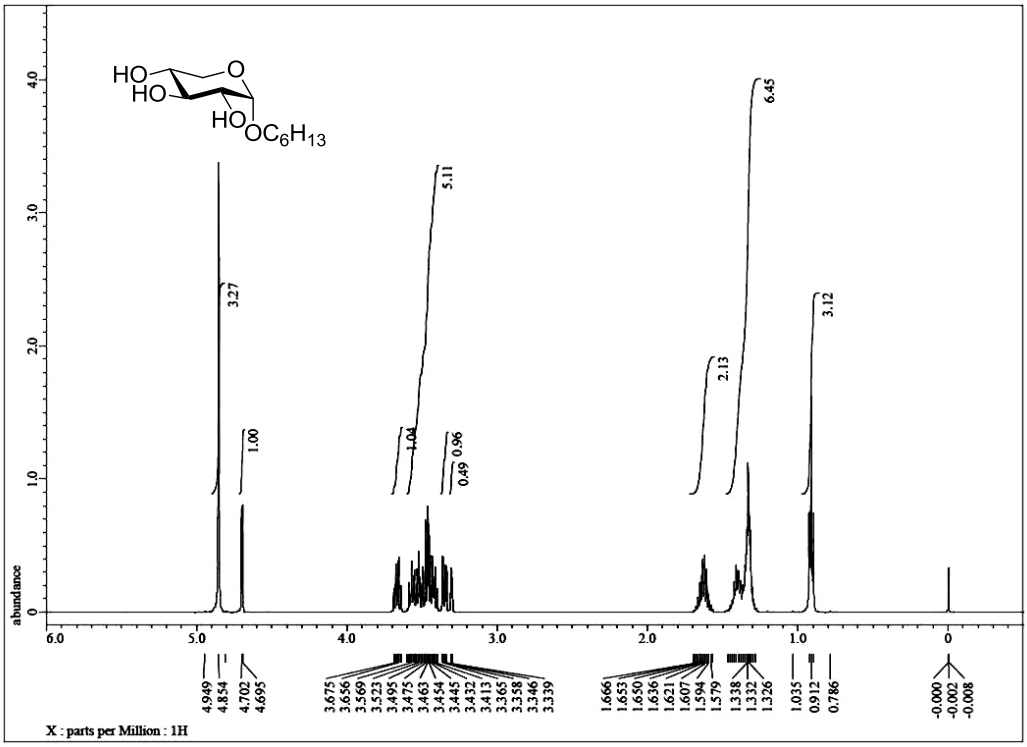


Figure 1. ^{1}H NMR spectrum of hexyl α-D-xylopyranoside

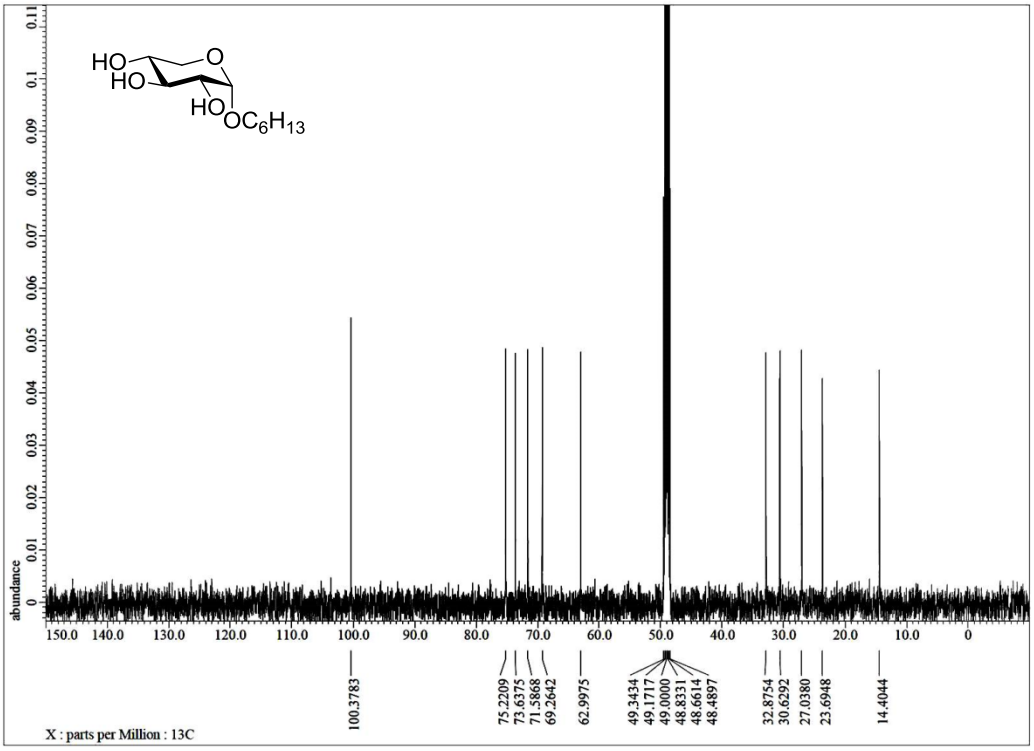


Figure 2. ^{13}C NMR spectrum of hexyl α-D-xylopyranoside

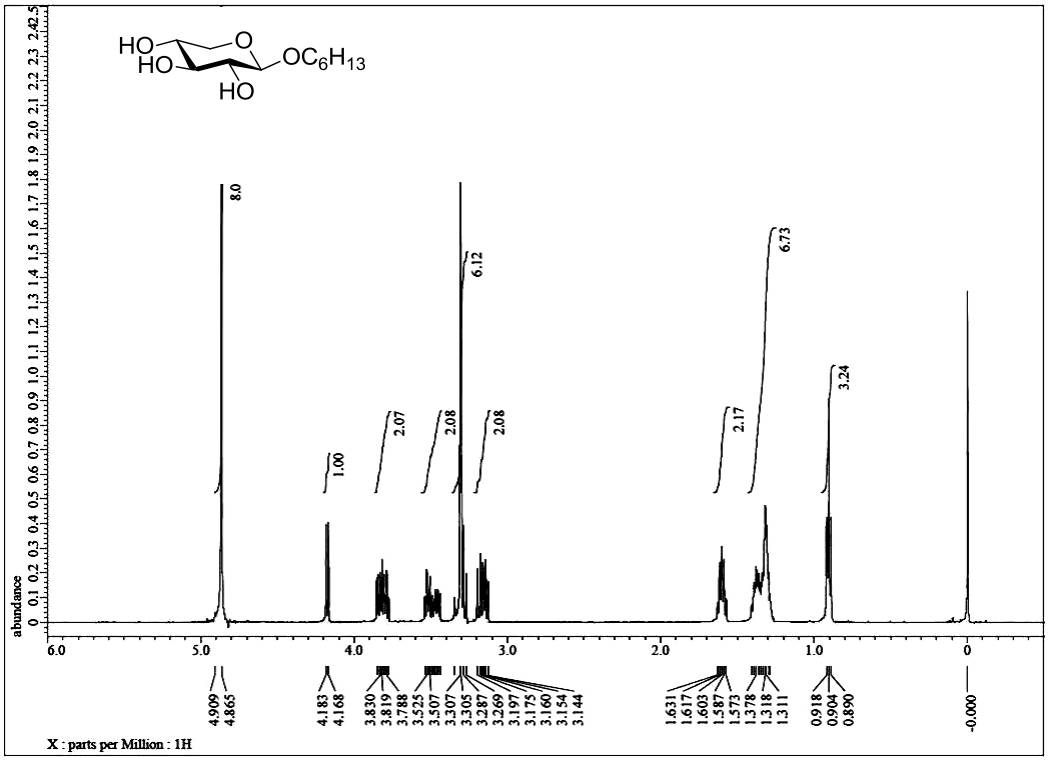


Figure 3. ^{1}H NMR spectrum of hexyl β-D-xylopyranoside

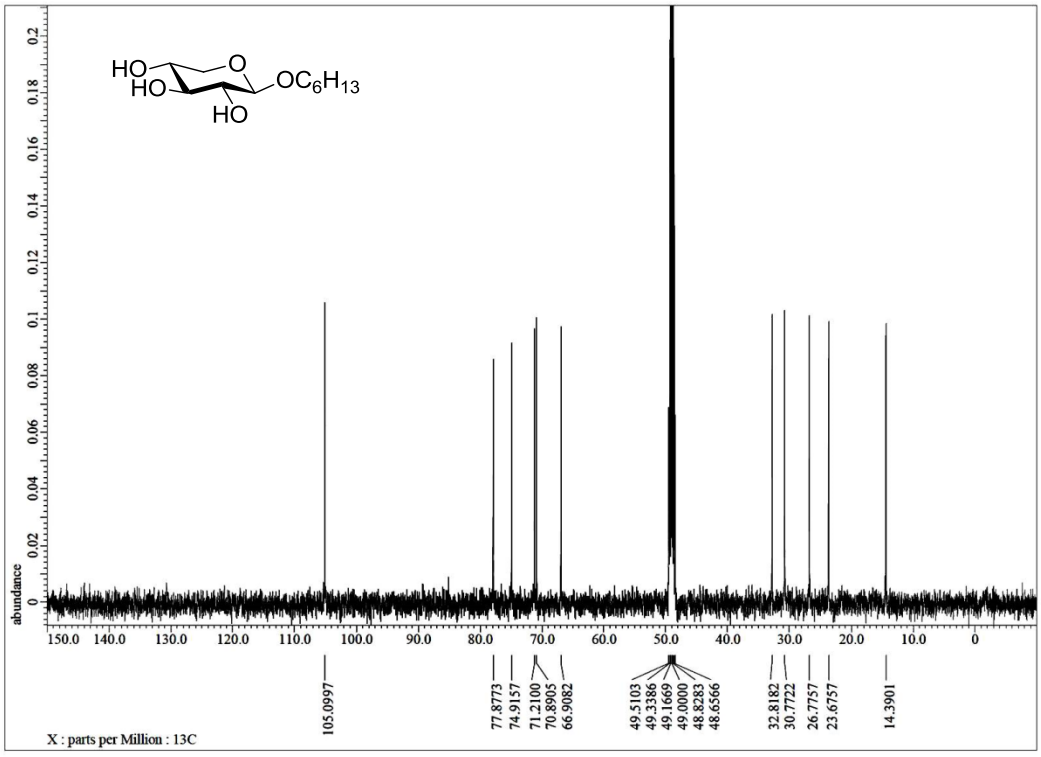


Figure 4. ^{13}C NMR spectrum of hexyl β-D-xylopyranoside

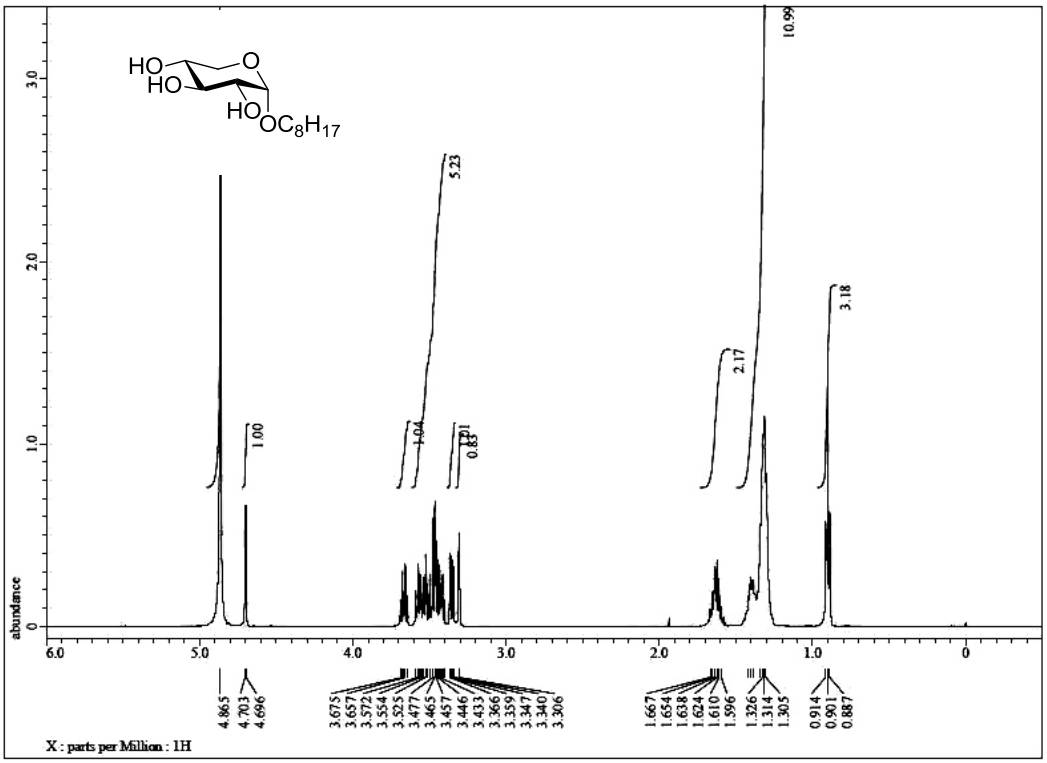


Figure 5. ^{1}H NMR spectrum of octyl α-D-xylopyranoside

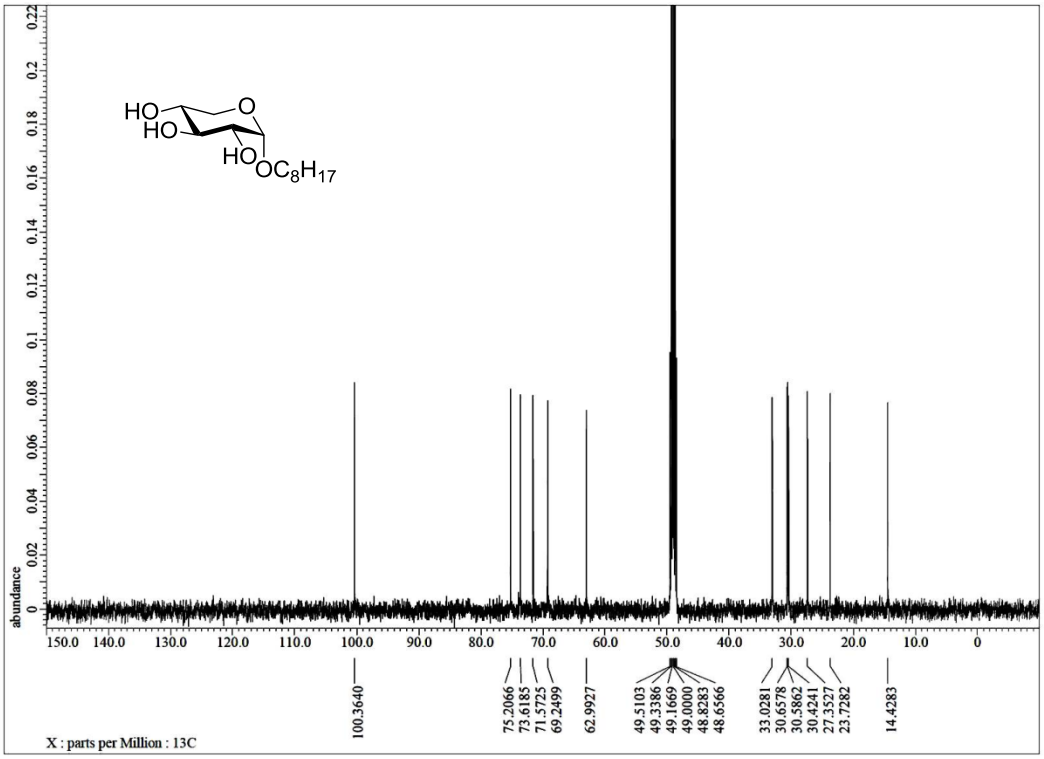


Figure 6. ^{13}C NMR spectrum of octyl α-D-xylopyranoside

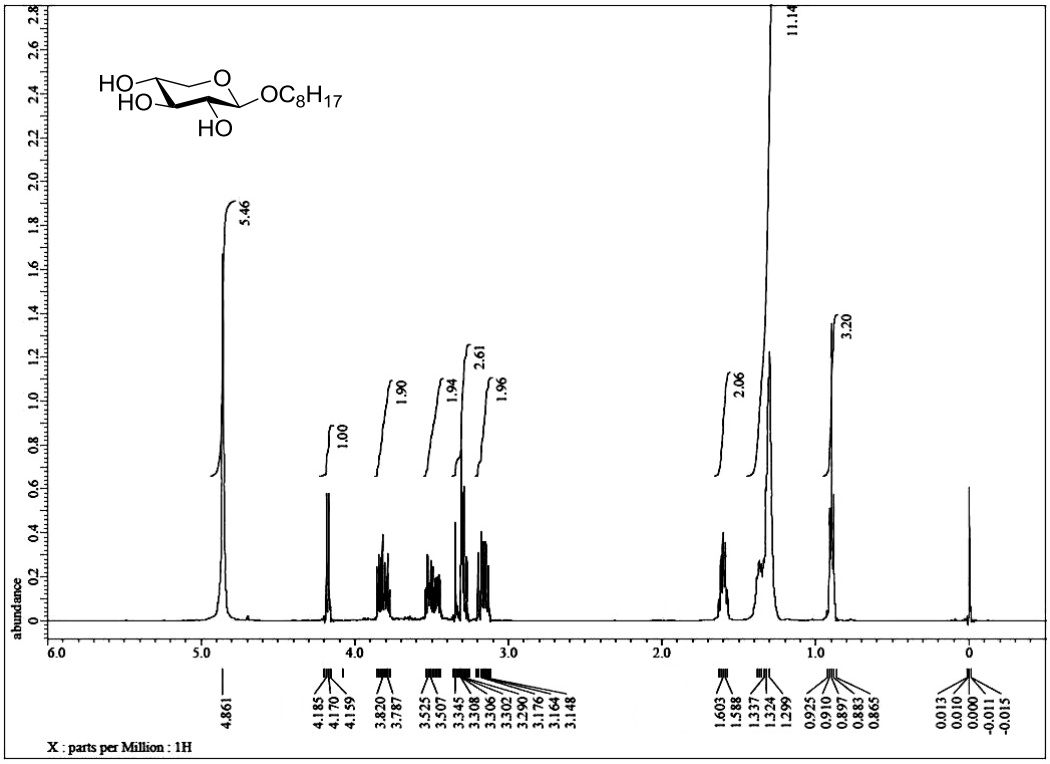


Figure 7. ^{1}H NMR spectrum of octyl β-D-xylopyranoside

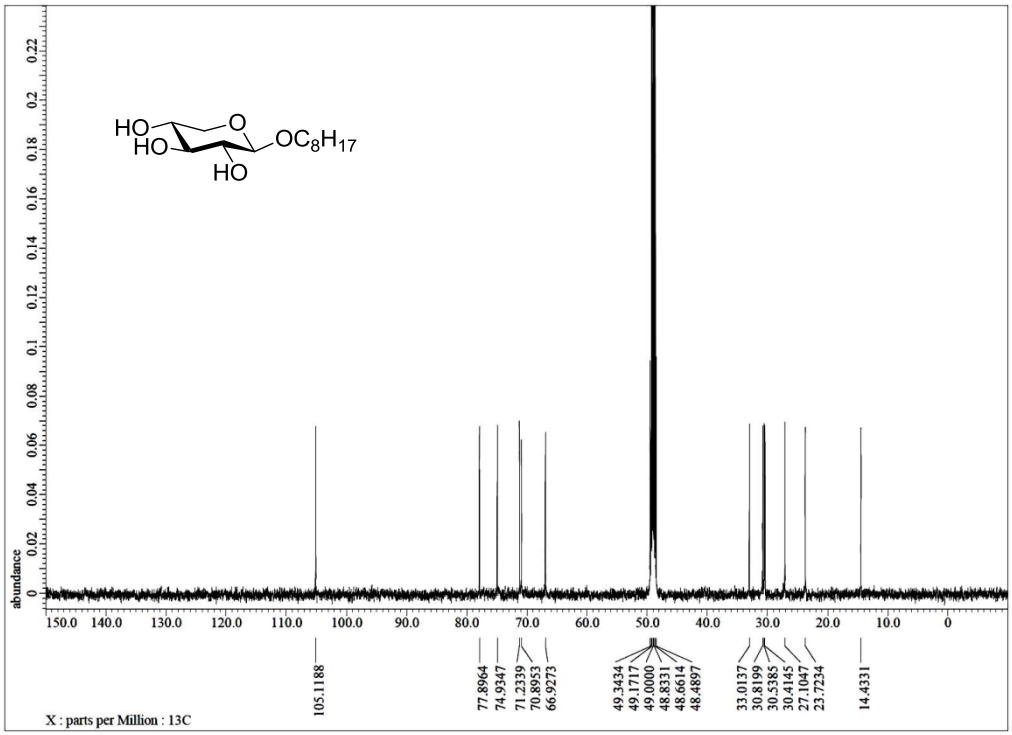


Figure 8. ^{13}C NMR spectrum of octyl β-D-xylopyranoside

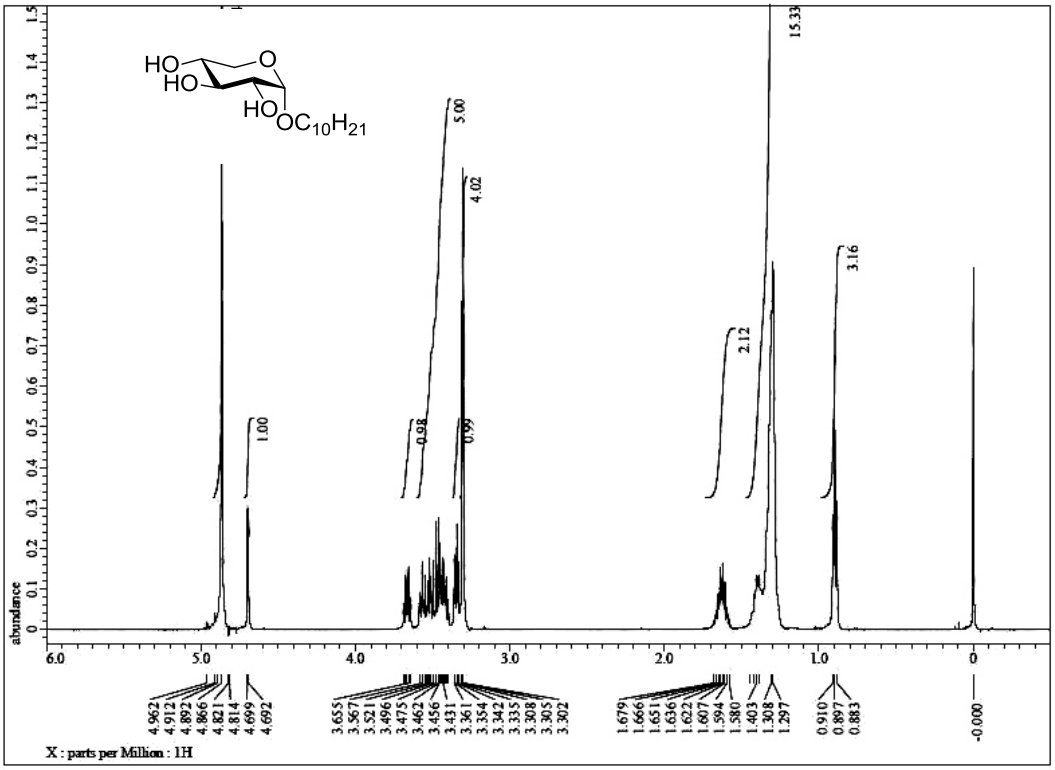


Figure 9. ^{1}H NMR spectrum of decanyl α-D-xylopyranoside

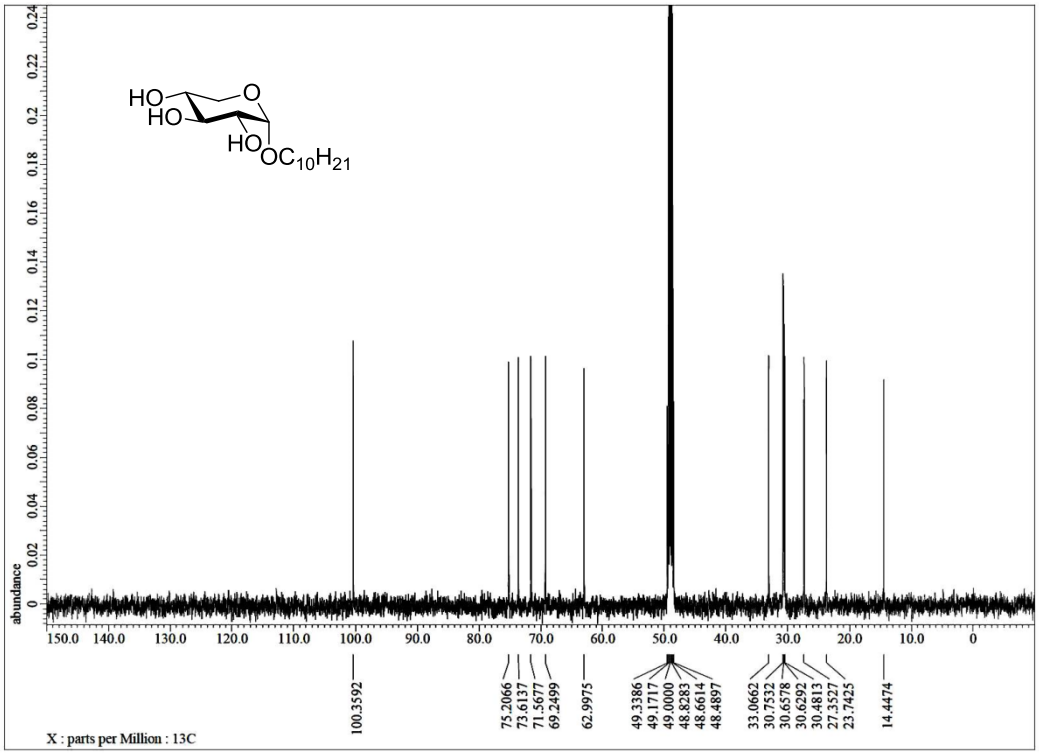


Figure 10. ^{13}C NMR spectrum of decanyl α-D-xylopyranoside

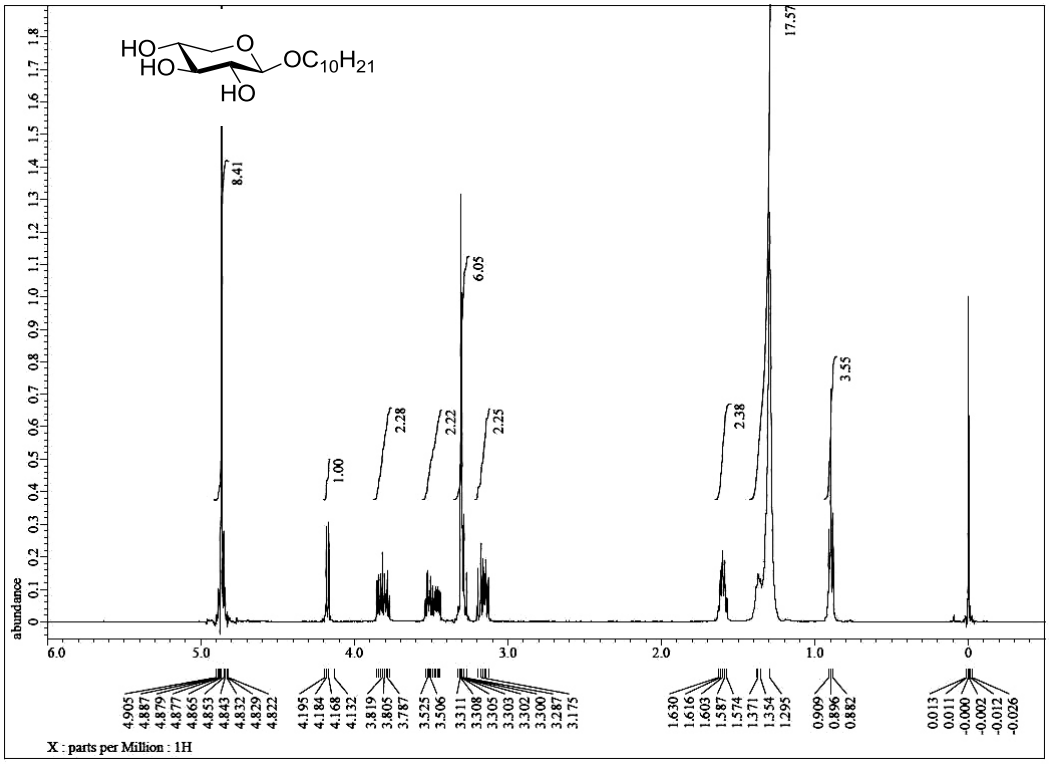


Figure 11. ^{1}H NMR spectrum of decanyl β-D-xylopyranoside

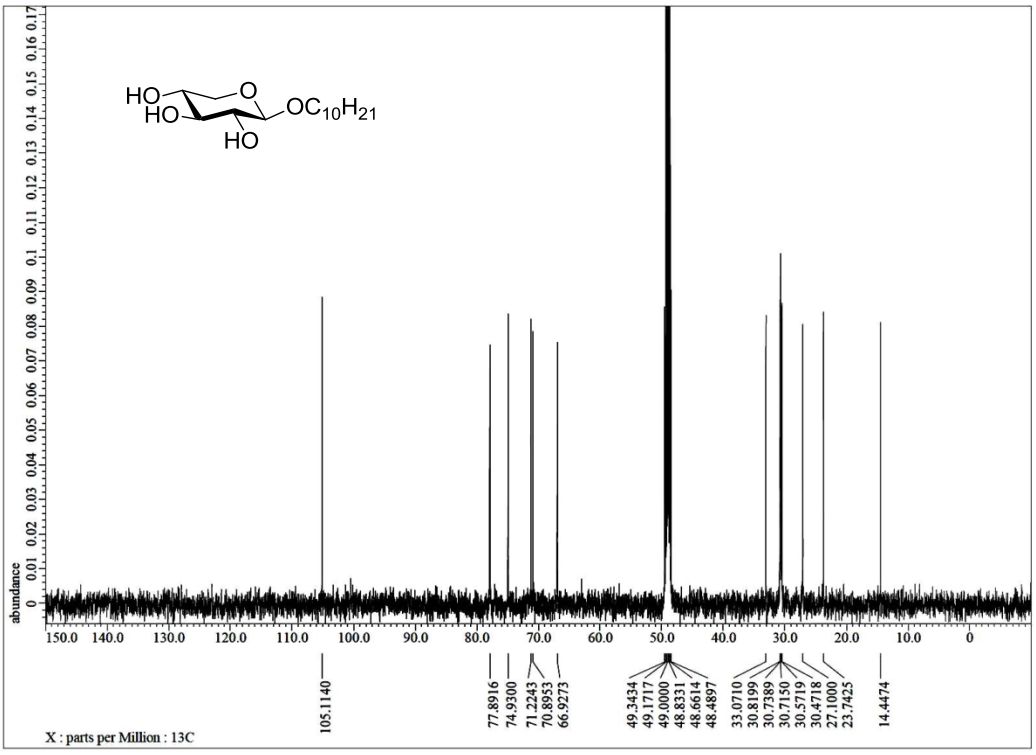


Figure 12. ^{13}C NMR spectrum of decanyl β-D-xylopyranoside