Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Research 342 (2007) 154–162
Carbohydrate RESEARCH

Alkenyl and alkenoyl amphiphilic derivatives of D-xylose and their surfactant properties

Céline Damez,[a] Sandrine Bouquillon,[a,*] Dominique Harakat,[a] Françoise Hénin,[a] Jacques Muzart,[a] Isabelle Pezron[b] and Ljepsa Komunjer[b]

[a]*Unité Mixte de Recherche 'Réactions Sélectives et Applications', CNRS—Université de Reims Champagne-Ardenne, Boîte no. 44, BP 1039, F-51687 Reims, France*
[b]*Unité Mixte de Recherche 'Génie des Procédés Industriels', CNRS—Université de Technologie de Compiègne, BP 20529, F-60205 Compiègne, France*

Received 10 March 2006; received in revised form 7 November 2006; accepted 7 November 2006
Available online 17 November 2006

Abstract—Unsaturated fatty alkyl xylosides and the corresponding 1-*O*-acyl esters were prepared. Critical micellar concentrations, surface tension areas per molecule and foaming value of some of these new amphiphilic compounds have been determined.

Keywords: Xylose; Esterification; Glycosylation; Surfactants

1. Introduction

For several years, we have been concerned with the synthesis of surfactants from renewable sources.[1,2] We already obtained pentosides having an octadienyl chain, with a double bond in terminal position, from the Pd-catalyzed telomerization of butadiene with pentoses.[1] We have now prepared xylosides containing only the terminal double bond. Alkenyl glucosides have been reported in the literature during recent years: C_3–C_9 alkenyl 2,3-unsaturated-glucosides from glucose and alkenols by using Ferrier reaction;[3a] terminal unsaturated C_3–C_{11} alkenyl glucopyranosides;[3b] galactopyranosides through cross-metathesis reaction of allyl galactopyranosides and olefins;[3c] C_4–C_{22} alk(en)yl glucosides in admixtures[3d] and undecenyl glucopyranosides for the preparation of monolayers on silica surface.[3e] But to our knowledge, no pure pentosides with an unsaturated terminal chain together with their surfactant properties are yet described. Since fatty esters are of great importance in cosmetics because of large skin and eye tolerance,[4] we have also prepared a fatty ester of D-xylose in anomeric position. Here, we describe the preparation of these amphiphilic compounds and, for three of them, their surfactant properties.

2. Results and discussion

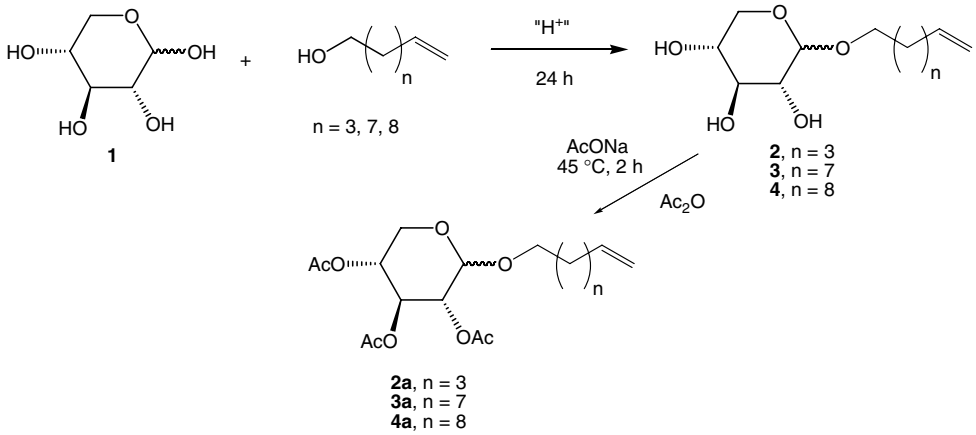
2.1. Glycosylations

Glycosylation of D-xylose (**1**) has been performed with hex-5-enol, dec-9-enol and undec-10-enol using three different acidic catalysts: Amberlite IR 120® (H^+) resin,[5] *p*-toluenesulfonic acid (PTSA)[6] and acetyl chloride[7] (Scheme 1 and Table 1).

Reactions were initially performed with hex-5-enol (Table 1) and the yield and anomeric ratio of the glycosides were evaluated by GC after acetylation (Scheme 1) of a sample of the crude mixture. The use of 2 equiv of hex-5-enol and 1 equiv (weight) of Amberlite IR 120® in THF at 80 °C led to 65% conversion of **1** (entry 1). When a large excess of hex-5-enol was employed, this one playing the role of both reagent and solvent, the conversion increased slightly and **2** was isolated in

* Corresponding author. Tel.: +33 3 26 91 81 96; fax: +33 3 26 91 31 66; e-mail: sandrine.bouquillon@univ-reims.fr

0008-6215/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carres.2006.11.013



Scheme 1. Synthesis of alkenyl D-xylopyranosides and their acetylated derivatives.

Table 1. Glycosylation of D-xylose with hex-5-enol[a]

Entry	'H$^+$' (equiv)	Hex-5-enol (equiv)	Solvent	T (°C)	**1**, conversion[b] (%)	**2**, yield[c] (%) (α/β)[b]
1	Resin[d] (1)	2	THF	80	65	n.d.[e]
2	Resin[d] (1)	6.5	—	80	77	70 (13:12)
3	PTSA (0.4)	2	THF	80	60	n.d.[e]
4	PTSA (0.6)	2	THF	80	75	72 (11:14)
5	AcCl (0.25)	6.5	—	45	60	n.d.[e]
6	AcCl (0.5)	6.5	—	45	80	71 (3:1)

[a] Conditions: D-xylose (100 mg, 0.667 mmol), 24 h.
[b] Determined by GC after acetylation of an aliquot of the crude mixture.
[c] Isolated yield.
[d] Resin = Amberlite IR 120® (equiv wt).
[e] n.d.: Not determined.

70% yield (entry 2). The transformation was also efficient with substoechiometric amounts of PTSA and AcCl instead of Amberlite IR 120®. Proper conversions and yields were observed in the presence of 0.6 equiv of PTSA (entries 3 and 4) or 0.5 equiv of AcCl (entry 6).

The main results of xylose glycosylation with dec-9-enol and undec-10-enol are collected in Table 2. The poor to moderate yields of **3** and **4** obtained with Amberlite IR 120® (entries 1 and 2) were strongly increased using PTSA (entries 3 and 4) or AcCl (entries 4 and 5) as catalysts.

Considering industrial processes of glycosylation of hexoses using PTSA as the acidic source,[8] we explored another workup procedure. After heating **1** (1 g) at 80 °C for 24 h with 0.6 equiv of PTSA using undec-10-enol as solvent, the crude reaction mixture was distilled at 130 °C under diminished pressure to remove the alcohol. The residue was taken up with 1:50 EtOAc–water to separate residual **1** and PTSA from **4**. Evaporation of the EtOAc phase afforded **4** (70%).

From the results collected in Tables 1 and 2, it appears that the anomeric ratio depends on the acidic source. The α-xyloside is preferentially formed in the presence of Amberlite IR 120® and acetyl chloride while the β-xyloside is preponderant with PTSA. Nevertheless, these experiments have been carried out at different temperatures as the reaction temperature could also influence the α/β ratios.[9] Comparison of the ^{13}C NMR shifts of

Table 2. Glycosylation of D-xylose with dec-9-enol and undec-10-enol[a]

Entry	'H$^+$' (equiv)	Alcohol (equiv)	Solvent	T (°C)	**1**, conversion[b] (%)	**3** or **4**, yield[c] (%) (α/β ratio)[b]
1	Resin[d] (1)	Dec-9-enol (6.5)	—	80	74	**3**, 45 (3:2)
2	Resin[d] (1)	Undec-9-enol (6.5)	—	80	76	**4**, 18 (7:3)
3	PTSA (0.6)	Dec-9-enol (2)	THF	80	85	**3**, 81 (43:57)
4	PTSA (0.6)	Undec-9-enol (2)	THF	80	77	**4**, 65 (21:29)
5	AcCl (0.5)	Dec-9-enol (6.5)	—	45	84	**3**, 71 (7:3)
6	AcCl (0.5)	Undec-9-enol (6.5)	—	45	90	**4**, 75 (13:7)

[a] Conditions: D-xylose (100 mg, 0.667 mmol), 24 h.
[b] Determined by GC after acetylation of an aliquot of the crude mixture.
[c] Isolated yield.
[d] Resin = Amberlite IR 120® (equiv wt).

anomeric carbons of the different xylosides with literature[10] shows that only pyranose forms were isolated. The separation of the anomers was tedious for **2**, **3** and **4** but relatively easy for **2a**, **3a** and **4a**. Therefore, α and β anomers of **2**, **3** and **4** have been obtained in pure forms by O-deacetylation of the corresponding acetylated α- and β-xylosides.

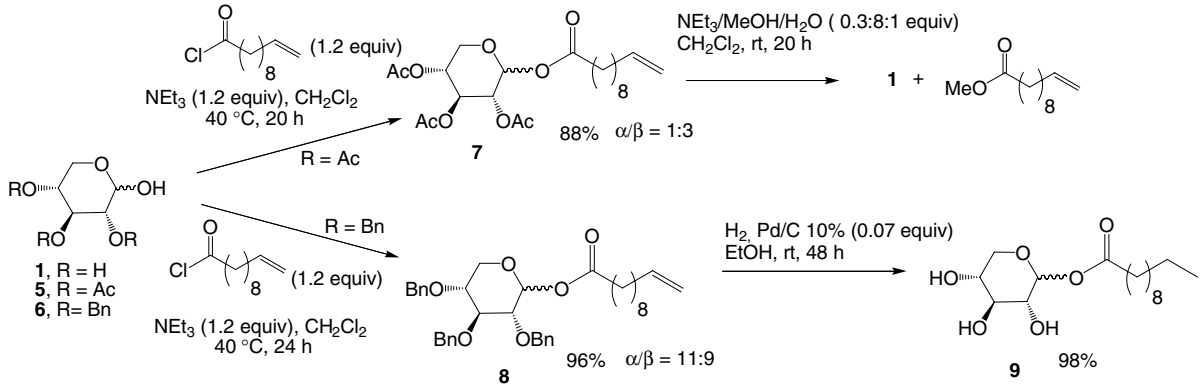
2.2. Esterifications

Esterification of (2,3,4-tri-*O*-acetyl)-D-xylopyranose[11] (**5**) and 2,3,4-tri-*O*-benzyl-D-xylopyranose[12] (**6**) was performed with undecenoyl chloride in the presence of triethylamine in refluxing CH_2Cl_2 (Scheme 2); **6** led to a yield slightly better than **5** (96% instead of 88%). Deprotection of the acetylated ester **7** using various conditions led unfortunately to **1** and methyl undecenoate, even when using triethylamine in water.[13] In contrast, deprotection of benzylated ester **8** by Pd-catalyzed hydrogenolysis was very efficient and involved simultaneously the double bond hydrogenation. We did not succeed to separate the anomeric forms of **8** and **9** by silica gel chromatography.

2.3. Surface-active properties

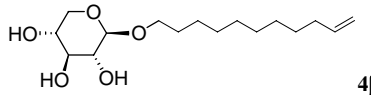
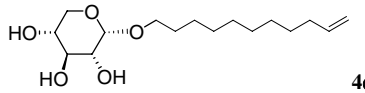
The surface tension characteristics of xylosides **4β** and **4α** and the 1-*O*-ester **9** are reported, respectively, in Tables 3 and 4 and the corresponding curves in Figure 1. Surface tension variations of **2** revealed its surfactant properties but no CMC or γ_{CMC} could be determined, the solution becoming turbid at 0.18 mmol/L. No tensiometry study of **3** was performed, its structure being close to the structure of **4**. Surface tension variations for **4α** are slightly shifted towards the lower concentrations compared to **4β**, revealing that α derivatives are less hydrophilic than β derivatives. This effect is usually attributed to differences in head group hydratation but is low compared to the effect observed from alkyl glucosides.[14] CMC values of **4α**, **4β** and **9** are similar, but the surface tension decrease at the CMC of **9** is at least 10 mN/m less (36.5 and 39 compared to 25 mN/m). The calculated areas per molecule are higher for **4α** and **4β** than for **9** (45 and 42 compared to 32 $Å^2$/molecule). Consequently, the critical packing parameters of **4α** and **4β** will be in the range 0.46–0.5, allowing to predict their packing as rods rather than as bilayers.

1-Undecanoyl-D-xylopyranose (**9**) exhibits excellent surfactant properties characterized by a surface tension of 25 mN/m for a critical micellar concentration (CMC) of 58 mg/L (0.18 mmol/L). The surface tension variation as a function of concentration is shown in Figure 1 and compared with the results obtained for the corresponding undecenyl xylopyranosides. The area per molecule, calculated from the slope of the surface tension curve below the CMC, is 32 $Å^2$.



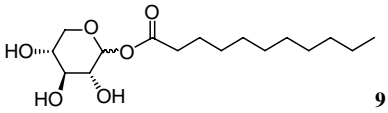
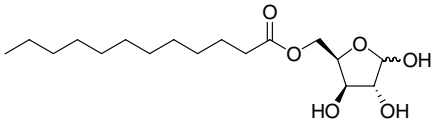
Scheme 2. Synthesis of 1-*O*-undecanoyl-D-xylopyranose.

Table 3. Surface tension characteristics of xylosides

Entry	Compound	CMC (mmol/L)[a]	γ_{CMC} (mN/m)[a]	a ($Å^2$)[a]
1	 **4β**	0.18	39	42
2	 **4α**	0.16	36.5	45

[a] CMC = critical micellar concentration, γ_{CMC} = surface tension at CMC, a = area of polar head per molecule.

Table 4. Surface tension characteristics of esters

Entry	Compound	CMC (mmol/L)[a]	γ_{CMC} (mN/m)[a]	a (Å^2)[a]
1	 **9**	0.18	25	32
2		0.041[14]	28.9[14]	34[14]

[a] CMC = Critical micellar concentration, γ_{CMC} = surface tension at CMC, a = area of polar head per molecule.

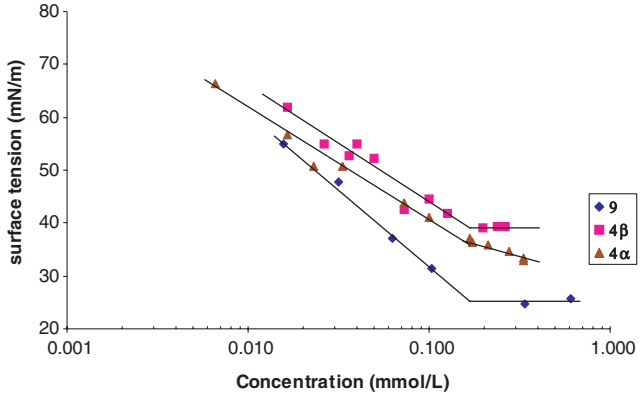


Figure 1. Surface tension of **9**, **4α** and **4β** as a function of concentration.

The surface tension data obtained for the 1-*O*-ester have been compared to those reported for 5-*O*-lauroyl-xylofuranose[15] (Table 4). The latter one, characterized by a lower CMC value (Table 4, entry 2), appears more hydrophobic than 1-undecanoyl-D-xylopyranose (**9**), which is however a more efficient surfactant since its decrease in surface tension at the CMC is larger (Table 4, entry 1). The areas per molecule of the two esters are similar. They are characterized by a critical packing parameter, which is around 0.62 showing, from simple geometric considerations that these molecules will have a tendency to pack as vesicles or bilayers.[15]

The foaming value of **9** was also evaluated using a method adapted from the Ross–Miles[16] procedure. As commonly described in the literature,[17] the foaming value of a compound must be measured at its CMC as it often displays maximum foaming ability at this concentration. Consequently, measures were firstly conducted at the CMC of **9** that is, 58 mg/L (0.18 mmol/L) and compared to the values obtained for SDS[16] and Oramix CG110®[18] (reference and commercially available foaming surfactants, Chart 1) at the same concentration (Fig. 2): ester **9** and Oramix CG 110® behaved in a similar way at this concentration and produced a persistent foam while SDS showed the less foam ability and the less stable foam.

Next, in order to consider surfactant concentrations closer to the CMC values of SDS and Oramix CG 110 (respectively, 2.33 and 4.2 g/L) the foaming value of **9** was evaluated at 528 mg/L (1.66 mmol/L), which represents the limit of the aqueous solubility of this ester

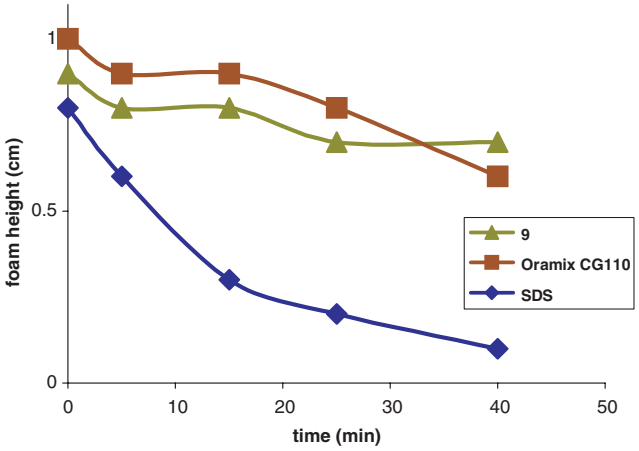


Figure 2. Comparative foaming powers at 58 mg/L.

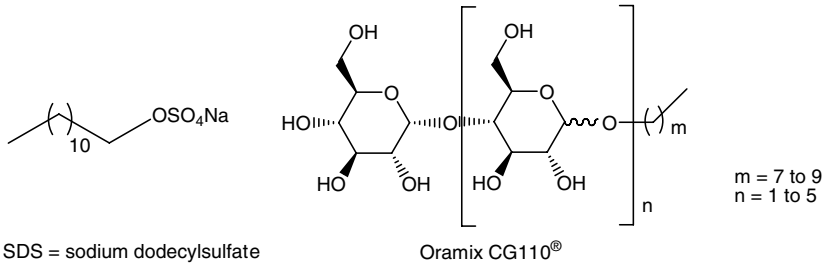


Chart 1. SDS and Oramix CG 110.

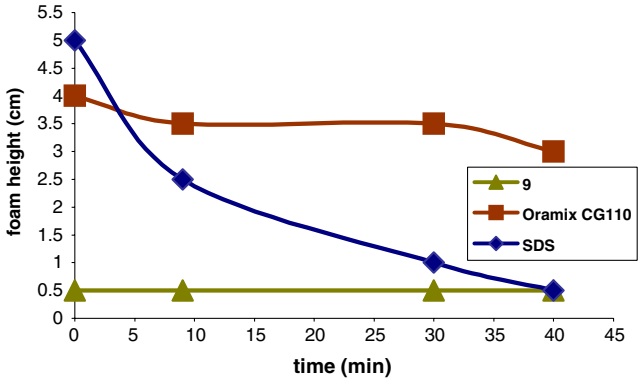


Figure 3. Comparative foaming values at 528 mg/L.

(Fig. 3). Despite its small initial foam height, **9** led to a very stable and persistent foam. Here again, we observed the instability of the foam produced with SDS while Oramix CG 110 displayed the best foaming ability.

From these results, it appears that 1-undecanoyl-D-xylopyranose exhibits an interesting foaming ability similar to the foaming ability of Oramix CG 110 at low concentrations and could find applications in cosmetics or personal care products as a shampoo or foaming bath.

3. Conclusion

1-*O*-Alkenoyl-D-xylose and alkenyl D-xylosides are easily prepared and exhibit interesting surface-active properties. The ester derivative is characterized by a decrease in surface tension, which is lower than the surface tension generally obtained with sugar esters and displays interesting foaming properties at low concentrations. These compounds can be considered as new environmentally favourable nonionic surfactants, which could be included in personal care or cosmetic formulations.

4. Experimental

4.1. General methods

All reagents used were commercially available and used as received. Solvents were dried and distilled under argon before use (CH_2Cl_2 over $CaCl_2$ and diethyl ether, THF over sodium/benzophenone) and kept over molecular sieves. ^1H and ^{13}C NMR spectra were recorded on an AC 250 Bruker in $CDCl_3$, MeOD or acetone-d_6 with TMS as reference for ^1H spectra and $CDCl_3$ (δ 77.0), MeOD (δ 49.9) or acetone-d_6 (δ 30.6) for ^{13}C spectra. The infrared spectra were recorded with Spectrafile IR™ Plus MIDAC. C, H and N analyses were performed on a Perkin Elmer 2400 CHN equipment. GC was recorded on a Hewlett–Packard HP-6890 gas chromatograph, fitted with DB-1 capillary column (25 m, 0.32 mm), a flame ionization detector and HP-3395 integrator; chromatography was carried out on SDS Silica 60 (40–63 μm), Art 2050044 (flash-chromatography) or Silica 60 F_{254} (TLC plates).

All experiments (MS and HRMS) were obtained on a hybrid tandem quadrupole/time-of-flight (Q-TOF) instrument, equipped with a pneumatically assisted electrospray (Z-spray) ion source (Micromass, Manchester, UK) operated in positive mode. The electrospray potential was set to 3 kV in positive ion mode (flow of injection 5 μL/min.) and the extraction cone voltage was usually varied between 30 and 90 V).

Surface tension was measured by the Wilhelmy plate method. Aqueous solns were prepared by dissolving the samples in ultra-pure deionized water (18 $m\Omega\,cm^{-1}$) and diluting to the desired concentration. All measurements were performed at 25 °C with an automatic tensiometer (Krüss K100). Each surface tension measurement was repeated three times. The time required for equilibrium was fixed to 30 min. The foaming value was measured with a method adapted from Ross and Miles procedure[15] but using less vol of samples. A standard vol (100 mL) of surfactant soln falls from a fixed height onto a fixed vol (50 mL) of the same soln placed into a cylindrical vessel. The height of the foam produced after all the soln has been dropped is measured as a function of time.

4.2. Xylosides

4.2.1. General procedure of glycosylation using Amberlite IR120®. The alcohol (4.3 mmol, 6.5 equiv) and Amberlite IR120® (100 mg) were stirred at 80 °C for 15 min. D-Xylose (100 mg, 0.666 mmol, 1 equiv) was added. After 24 h, a 0.5 M soln of NaOMe (0.1 mL) was added to neutralize the medium. After filtration on a fritted glass (porosity 4), the resulting filtrate was purified by preparative TLC (9:1 MeOH–CH_2Cl_2).

4.2.2. General procedure of glycosylation using PTSA. PTSA (77.1 mg, 0.4 mmol, 0.6 equiv) was added at 80 °C in three parts over 3 h (25.7 mg every h) to a soln of D-xylose (100 mg, 0.666 mmol, 1 equiv) and alcohol (1.3 mmol, 2 equiv) in THF (5 mL). After 24 h, a 0.5 M soln of NaOMe (0.7 mL) was added to neutralize the medium and purification was carried out by preparative TLC (9:1 MeOH–CH_2Cl_2).

4.2.3. General procedure of glycosylation using acetyl chloride. The alcohol (6.5 equiv) and acetyl chloride (24 μL, 0.33 mmol, 0.5 equiv) were heated at 45 °C for 15 min. D-Xylose (100 mg, 0.667 mmol, 1 equiv) was then added. After 24 h, a 0.5 M soln of NaOMe (0.6 mL) was used to neutralize the medium. Purifica-

tion was carried out by preparative TLC (9:1 MeOH–CH_2Cl_2).

4.2.4. General procedure of acetylation of xylosides. To calculate the xylose conversion and the proportion of anomers, the crude mixtures were acetylated by adding Ac_2O (2 mL, 2.13 mmol, 3.2 equiv) and NaOAc (52 mg, 0.634 mmol, 0.95 equiv). The resulting mixture was stirred for 2 h at 45 °C. Diethylether (20 mL) was added and the organic phase was washed with saturated Na_2CO_3 (5 × 50 mL). After drying over $MgSO_4$ and concentration under diminished pressure, α- and β-xylosides were purified by chromatography on silica gel (9:1 petroleum ether–EtOAc).

4.2.5. General procedure for deprotection of acetylated xylosides. The acetylated compound was dissolved in 1:1 MeOH–CH_2Cl_2, and a 0.5 M soln of NaOMe (1.5 equiv) was then added. After stirring for 24 h at room temperature, the mixture was neutralized with Amberlite IR120® and filtered to liberate almost quantitatively the unprotected corresponding compound.

4.2.6. Hex-5′-enyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (2aβ). Colourless oil; $[\alpha]_D^{20}$ −36 (*c* 4.0, $CHCl_3$). IR (film): 2939 (F), 2865 (m), 1756 (s), 1434 (w), 1370 (m), 1223 (s), 1074–1047 (s); ^{1}H NMR ($CDCl_3$): 5.79 (1H, ddt, *J* 3.5 Hz, *J* 6.7 Hz, *J* 10.3 Hz, H-5′), 5.16 (1H, t, *J* 8.6 Hz, H-3), 4.90–5.00 (4H, H-2, H-4, H-6′), 4.12 (1H, dd, *J* 5.1 Hz, *J* 11.8 Hz, H-5e), 4.50 (1H, d, *J* 6.8 Hz, H-1), 3.82 (1H, dt, *J* 3.3 Hz, *J* 9.6 Hz, H-1′), 3.46 (1H, dt, *J* 3.2 Hz, *J* 9.6 Hz, H-1′), 3.36 (1H, dd, *J* 8.8 Hz, *J* 11.8 Hz, H-5a), 1.97–2.13 (11H, H-4′, $3CH_3$), 1.51–1.68 (2H, H-2′), 1.38–1.49 (2H, H-3′); ^{13}C NMR ($CDCl_3$): 169.4–169.9–170.1 (3C=O), 138.6 (C-5′), 114.8 (C-6′), 100.7 (C-1), 71.6 (C-2), 70.9 (C-3), 69.5 (C-1′), 69.0 (C-4), 62.1 (C-5), 33.4 (C-4′), 28.9 (C-2′), 25.3 (C-3′), 20.8 ($3CH_3$); HRMS: calcd for $[M+Na]^+$ 381.1525, found 381.1522. Anal. Calcd for $C_{17}H_{26}O_8$: C, 56.97; H, 7.31. Found: C, 57.04; H, 7.45.

4.2.7. Hex-5′-enyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (2aα). Colourless oil; $[\alpha]_D^{20}$ +98 (*c* 7.6, $CHCl_3$). IR (film): 2935 (s), 2860 (m), 1755 (s), 1434 (w), 1372 (m), 1222 (s), 1045 (m); ^{1}H NMR ($CDCl_3$): δ 5.72 (1H, m, H-5′), 5.40 (1H, dd, *J* 9.7 Hz, *J* 9.7 Hz, H-3), 4.84–4.97 (4H, H-1, H-4, H-6′), 4.70 (1H, dd, *J* 3.3 Hz, *J* 9.6 Hz, H-2), 3.71 (1H, m, H-5e), 3.62 (1H, m, H-1′b), 3.53 (1H, m, H-5a), 3.32 (1H, m, H-1′a), 1.92–2.06 (11H, H-4′, $3CH_3$), 1.50–1.61 (2H, H-2′), 1.35–1.44 (2H, H-3′); ^{13}C NMR ($CDCl_3$): δ 169.9, 170.1, 171.0 (3C=O), 138.5 (C-5′), 114.7 (C-6′), 95.6 (C-1), 71.1 (C-2), 69.6 (C-3), 69.4 (C-4), 68.2 (C-1′), 58.2 (C-5), 33.4 (C-4′), 28.7 (C-2′), 25.3 (C-3′), 20.7 ($3CH_3$); HRMS: calcd for $[M+Na]^+$ 381.1525, found 381.1542. Anal. Calcd for $C_{17}H_{26}O_8$: C, 56.97; H, 7.31. Found: C, 56.89; H, 7.53.

4.2.8. Dec-9′-enyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (3aβ). Colourless oil; $[\alpha]_D^{20}$ −16 (*c* 2.0, $CHCl_3$). IR (film): 2928 (F), 2856 (m), 1756 (s), 1435 (w), 1370 (m), 1224 (s), 1049 (s), 906 (w); ^{1}H NMR ($CDCl_3$): 5.79 (1H, ddt, *J* 3.5 Hz, *J* 6.7 Hz, *J* 10.3 Hz, H-9′), 5.14 (1H, t, *J* 8.6 Hz, H-3), 4.83–5.07 (4H, H-2, H-4, H-10′), 4.45 (1H, d, *J* 6.8 Hz, H-1), 4.11 (1H, dd, *J* 5.1 Hz, *J* 11.8 Hz, H-5e), 3.80 (1H, dt, *J* 3.3 Hz, *J* 9.6 Hz, H-1′), 3.45 (1H, dt, *J* 3.2 Hz, *J* 9.6 Hz, H-1′), 3.34 (1H, dd, *J* 8.8 Hz, *J* 11.8 Hz, H-5a), 1.93–2.10 (11H, H-8′, $3CH_3$), 1.43–1.61 (2H, H-2′), 1.15–1.41 (10H, H-3′, H-4′, H-5′, H-6′, H-7′); ^{13}C NMR ($CDCl_3$): 169.6–170.0–170.3 (3C=O), 139.3 (C-9′), 114.3 (C-10′), 100.8 (C-1), 71.7 (C-3), 71.0 (C-2), 69.8 (C-4), 69.1 (C-1′), 62.2 (C-5), 33.9 (C-8′), 29.0–29.2–29.4–29.5 (C-2′, C-4′, C-5′, C-6′, C-7′), 26.0 (C-3′), 20.9 ($3CH_3$); HRMS: calcd for $[M+Na]^+$ 437.2151, found 437.2141. Anal. Calcd for $C_{21}H_{34}O_8$: C, 60.85; H, 8.27. Found: C, 60.83; H, 8.66.

4.2.9. Dec-9′-enyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (3aα). Colourless oil; $[\alpha]_D^{20}$ +88 (*c* 2.1, $CHCl_3$). IR (film): 2928 (s), 2856 (m), 1755 (s), 1435 (w), 1368 (m), 1228 (s), 1049 (s), 941–909 (w); ^{1}H NMR ($CDCl_3$): 5.81 (1H, ddt, *J* 6.6 Hz, *J* 10.2 Hz, *J* 17.0 Hz, H-9′), 5.48 (1H, dd, *J* 9.7 Hz, *J* 9.8 Hz, H-3), 4.87–4.97 (4H, H-1, H-4, H-10′), 4.79 (1H, dd, *J* 3.6 Hz, *J* 9.8 Hz, H-2), 3.77 (1H, dd, *J* 6.0 Hz, *J* 10.8 Hz, H-5e), 3.54–3.72 (2H, m, H-1′b, H-5a), 3.37 (1H, dt, *J* 6.6 Hz, *J* 9.7 Hz, H-1′a), 2.01–2.12 (11H, H-8′, $3CH_3$), 1.51–1.72 (2H, H-2′), 1.24–1.43 (10H, H-3′, H-4′, H-5′, H-6′, H-7′); ^{13}C NMR ($CDCl_3$): 170.1–170.2–170.4 (3C=O), 139.3 (C-9′), 114.3 (C-10′), 95.7 (C-1), 71.3 (C-3), 69.8 (C-2), 69.7 (C-4), 68.6 (C-1′), 58.4 (C-5), 33.9 (C-8′), 29.6–29.7–29.8–29.9–30.0 (C-2′, C-4′, C-5′, C-6′, C-7′), 26.2 (C-3′), 20.9–21.0–21.1 ($3CH_3$); HRMS: calcd for $[M+Na]^+$ 437.2151, found 437.2146. Anal. Calcd for $C_{21}H_{34}O_8$: C, 60.86; H, 8.27. Found: C, 61.04; H, 8.65.

4.2.10. Undec-9′-enyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (4aβ). Colourless oil; $[\alpha]_D^{20}$ −30 (*c* 1.9, $CHCl_3$). IR (film): 2927 (s), 2855 (m), 1758 (s), 1434 (w), 1370 (m), 1224 (s), 1048 (s), 757 (m); ^{1}H NMR ($CDCl_3$): 5.79 (1H, ddt, *J* 3.5 Hz, *J* 6.7 Hz, *J* 10.3 Hz, H-11′), 5.13 (1H, t, *J* 8.6 Hz, H-3), 4.81–4.98 (4H, H-2, H-4, H-10′), 4.45 (1H, d, *J* 6.9 Hz, H-1), 4.09 (1H, dd, *J* 5.1 Hz, *J* 11.8 Hz, H-5e), 3.81 (1H, dt, *J* 3.3 Hz, *J* 9.6 Hz, H-1′), 3.43 (1H, dt, *J* 3.2 Hz, *J* 9.6 Hz, H-1′), 3.32 (1H, dd, *J* 8.8 Hz, *J* 11.8 Hz, H-5a), 1.94–2.10 (11H, H-9′, $3CH_3$), 1.47–1.67 (2H, H-2′), 1.21–1.43 (12H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′); ^{13}C NMR ($CDCl_3$): 169.6–170.0–170.3 (3C=O), 139.4 (C-10′), 114.3 (C-11′), 100.8 (C-1), 71.7 (C-3), 71.0 (C-2), 69.9

(C-4), 69.1 (C-1′), 62.2 (C-5), 33.9 (C-9′), 29.0–29.1–29.3–29.4–29.5–29.6 (C-2′, C-4′, C-5′, C-6′, C-7′, C-8′), 26.0 (C-3′), 20.9 ($3CH_3$); HRMS: calcd for $[M+Na]^+$ 451.2308, found 451.2310. Anal. Calcd for $C_{22}H_{36}O_8$: C, 61.66; H, 8.47. Found: C, 61.83; H, 8.88.

4.2.11. Undec-9′-enyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (4aα). Colourless oil; $[\alpha]_D^{20}$ +99 (*c* 2.3, $CHCl_3$). IR (film): 2927 (s), 2855 (m), 1756 (s), 1436 (w), 1368 (m), 1225 (s), 1050 (s), 939 (w); ^1H NMR ($CDCl_3$): 5.79 (1H, ddt, *J* 6.6 Hz, *J* 10.2 Hz, *J* 17.0 Hz, H-10′), 5.46 (1H, dd, *J* 9.7 Hz, *J* 9.8 Hz, H-3), 4.84–4.98 (4H, H-1, H-4, H-11′), 4.74 (1H, dd, *J* 3.6 Hz, *J* 9.8 Hz, H-2), 3.73 (1H, dd, *J* 6.0 Hz, *J* 10.8 Hz, H-5e), 3.54–3.68 (2H, H-1′b, H-5a), 3.37 (1H, dt, *J* 6.6 Hz, *J* 9.7 Hz, H-1′a), 1.96–2.13 (11H, H-9′, $3CH_3$), 1.49–1.67 (2H, H-2′), 1.17–1.41 (12H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′); ^{13}C NMR ($CDCl_3$): 170.1–170.2–170.4 (3C=O), 139.3 (C-10′), 114.3 (C-11′), 95.7 (C-1), 71.3 (C-3), 69.8 (C-2), 69.7 (C-4), 68.6 (C-1′), 58.4 (C-5), 33.9 (C-9′), 29.5–29.6–29.7–29.8–29.9–30.1 (C-2′, C-4′, C-5′, C-6′, C-7′, C-8′), 26.2 (C-3′), 20.9 ($3CH_3$); HRMS: calcd for $[M+Na]^+$ 451.2308, found 451.2311. Anal. Calcd for $C_{22}H_{36}O_8$: C, 61.66; H, 8.47. Found: C, 61.74; H, 8.48.

4.2.12. Hex-5′-enyl β-D-xylopyranoside (2β). From hex-5′-enyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (450 mg) in MeOH–CH_2Cl_2 (6 mL) and methanolic NaOMe (3.8 mL); 282 mg (97%); yellow oil; $[\alpha]_D^{20}$ −12 (*c* 1.2, MeOH). IR (film): 3373 (s), 2919 (m), 2849 (m), 1591 (s), 1465 (w), 1351 (m), 1048 (s), 970 (w); ^1H NMR (MeOD): 5.19 (1H, m, H-5), 4.75–4.82 (5H, H-6′, 3OH), 3.98 (1H, d, *J* 7.3 Hz, H-1), 3.50–3.71 (2H, H-1′, H-5), 3.20–3.40 (2H, H-1′, H-4), 3.01–3.19 (1H, m, H-3), 2.85–3.00 (2H, H-2, H-5a), 1.87–2.05 (2H, H-4′), 1.44–1.62 (2H, H-2′), 1.28–1.42 (2H, H-3′); ^{13}C NMR (MeOD): 138.5 (C-5′), 114.7 (C-6′), 105.4 (C-1), 78.2 (C-3), 75.3 (C-2), 71.6 (C-4), 71.1 (C-1′), 67.3 (C-5), 33.8 (C-4′), 30.7 (C-2′), 27.5 (C-3′); HRMS: calcd for $[M+Na]^+$ 255.1208, found 255.1212.

4.2.13. Hex-5′-enyl α-D-xylopyranoside (2α). From hex-5′-enyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (378 mg) in MeOH–CH_2Cl_2 (6 mL) and methanolic NaOMe (3.2 mL); 240 mg (98%); clear yellow oil; $[\alpha]_D^{20}$ +76.5 (*c* 3.4, MeOH). IR (film): 3383 (s), 2933 (s), 1567 (m), 1414 (m), 1150 (s), 1044 (s), 943–910 (m); ^1H NMR (MeOD): δ 5.72 (1H, m, H-5′), 4.82–4.97 (8H, H-6′, 6OH), 4.67 (1H, d, *J* 3.4 Hz, H-1), 3.23–3.76 (7H, H-1′, H-2, H-3, H-4, H-5a, H-5e), 1.87–2.05 (2H, H-4′), 1.44–1.62 (2H, H-2′), 1.28–1.42 (2H, H-3′); ^{13}C NMR (MeOD): 138.5 (C-5′), 114.7 (C-6′), 100.7 (C-1), 75.6 (C-3), 74.0 (C-2), 72.0 (C-4), 69.5 (C-1′), 63.4 (C-5), 33.8 (C-4′), 30.5 (C-2′), 27.7 (C-3′). HRMS: calcd for $[M+Na]^+$ 255.1208, found 255.1207.

4.2.14. Dec-9′-enyl β-D-xylopyranoside (3β). From dec-9′-enyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (517 mg) in MeOH–CH_2Cl_2 (8 mL) and methanolic NaOMe (3.8 mL); 345 mg (96%); yellow paste; $[\alpha]_D^{20}$ −22 (*c* 1.2, MeOH); IR (film): 3383 (s), 2918 (s), 2852 (w), 1589 (s), 1434 (w), 1351 (m), 1049 (s), 980 (w); ^1H NMR (MeOD): 5.72 (1H, m, H-9′), 4.80 (5H, H-10′, 3OH), 4.09 (1H, d, *J* 7.4 Hz, H-1), 3.59–3.80 (2H, H-1′, H-5e), 3.32–3.49 (2H, H-1′, H-4), 3.16–3.28 (1H, m, H-3), 3.01–3.15 (2H, H-2, H-5a), 1.81–1.99 (2H, H-8′), 1.41–1.58 (2H, H-2′), 1.12–1.38 (10H, H-3′, H-4′, H-5′, H-6′, H-7′); ^{13}C NMR (MeOD): 138.5 (C-5′), 114.7 (C-6′), 105.5 (C-1), 78.2 (C-3), 75.2 (C-2), 71.6 (C-4), 71.3 (C-1′), 67.3 (C-5), 34.0 (C-8′), 30.7, 30.9, 31.0, 31.1 (C-2′, C-4′, C-5′, C-6′, C-7′), 27.5 (C-3′); HRMS: calcd for $[M+Na]^+$ 311.1834, found 311.1832.

4.2.15. Dec-9′-enyl α-D-xylopyranoside (3α). From dec-9′-enyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (325 mg) in MeOH–CH_2Cl_2 (5 mL) and methanolic NaOMe (2.4 mL); 216 mg (96%); white paste; $[\alpha]_D^{20}$ +78 (*c* 0.82, MeOH); IR (film): 3385 (s), 2920 (m), 2852 (w), 1592 (m), 1468 (w), 1144 (w), 1043 (m). ^1H NMR (MeOD): 5.69 (1H, ddt, *J* 6.7 Hz, *J* 9.9 Hz, *J* 13.3 Hz, H-9′), 4.70–4.91 (5H, H-10′, 3OH), 4.59 (1H, d, *J* 3.5 Hz, H-1), 3.15–3.63 (7H, H-1′, H-2, H-3, H-4, H-5a, H-5e), 1.71–1.90 (2H, H-8′), 1.44–1.53 (2H, H-2′), 1.11–1.29 (12H, H-3′, H-4′, H-5′, H-6′, H-7′); ^{13}C NMR (MeOD): 140.9 (C-9′), 115.6 (C-10′), 101.2 (C-1), 76.0 (C-3), 74.4 (C-2), 72.4 (C-4), 70.1 (C-1′), 63.9 (C-5), 35.7 (C-8′), 30.9, 31.0, 31.4, 31.5, 31.6 (C-2′, C-4′, C-5′, C-6′, C-7′), 28.2 (C-3′); HRMS: calcd for $[M+Na]^+$ 311.1834, found 311.1838.

4.2.16. Undec-10′-enyl β-D-xylopyranoside (4β). From undec-9′-enyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (388 mg) in MeOH–CH_2Cl_2 (5 mL) and methanolic NaOMe (2.8 mL); 268 mg (98%); beige paste; $[\alpha]_D^{20}$ −30 (*c* 0.60, MeOH). IR (film): 3366 (s), 2922 (s), 2853 (m), 1595 (s), 1465 (w), 1377–1352 (m), 1049 (m); ^1H NMR (D_2O): 5.71 (1H, ddt, *J* 3.3 Hz, *J* 6.8 Hz, *J* 10.0 Hz, H-10′), 4.74–4.94 (5H, H-11′, 3OH), 4.09 (1H, d, *J* 7.5 Hz, H-1), 3.61–3.80 (2H, H-1′, H-5e), 3.32–3.49 (2H, H-1′, H-4′), 3.18–3.27 (1H, H-3), 3.02–3.16 (2H, H-2, H-5a), 1.83–2.01 (2H, H-9′), 1.33–1.61 (2H, H-2′), 1.01–1.32 (12H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′); ^{13}C NMR (D_2O): 140.5 (C-10′), 115.3 (C-11′), 105.4 (C-1), 78.2 (C-3), 75.2 (C-2), 71.6 (C-4′), 71.3 (C-1′), 67.3 (C-5), 35.3 (C-9′), 30.5, 30.6, 31.0, 31.1, 31.2 (C-2′, C-4′, C-5′, C-6′, C-7′, C-8′), 27.6 (C-3′); HRMS: calcd for $[M+Na]^+$ 325.1991, found 325.1992.

4.2.17. Undec-10′-enyl α-D-xylopyranoside (4α). From undec-9′-enyl 2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (224 mg) in MeOH–CH_2Cl_2 (5 mL) and methanolic NaOMe (1.6 mL); 152 mg (96%); beige paste; $[\alpha]_D^{20}$

+70.6 (*c* 0.68, MeOH). IR (film): 3385 (s), 2920 (m), 2852 (w), 1592 (m), 1468 (w), 1144 (w), 1043 (m); ^{1}H NMR (MeOD): 5.69 (1H, ddt, *J* 6.7 Hz, *J* 9.9 Hz, *J* 13.3 Hz, H-10′), 4.70–4.91 (5H, H-11′, 3OH), 4.59 (1H, d, *J* 3.5 Hz, H-1), 3.15–3.63 (7H, H-1′, H-2′, H-3′, H-4′, H-5a, H-5e), 1.71–1.90 (2H, H-9′), 1.44–1.53 (2H, H-2′), 1.11–1.29 (12H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′); ^{13}C NMR (MeOD): 140.9 (C-10′), 115.6 (C-11′), 101.2 (C-1), 76.0 (C-3), 74.4 (C-2), 72.4 (C-4), 70.1 (C-1′), 63.9 (C-5), 35.7 (C-9′), 30.9, 31.0, 31.4, 31.5, 31.6 (C-2′, C-4′, C-5′, C-6′, C-7′, C-8′), 28.2 (C-3′); HRMS: calcd for $[M+Na]^+$ 325.1991, found 325.1993.

4.3. 1-*O*-Acyl derivatives of D-xylose

Et_3N (63 μL, 0.45 mmol, 1.2 equiv) was added to a soln of 2,3,4-tri-*O*-acetyl-D-xylopyranose (100 mg, 0.36 mmol) in CH_2Cl_2 (2 mL). After slow addition of undec-10-enoyl chloride (96 μL, 0.45 mmol, 1.2 equiv), the mixture was refluxed for 20 h. After evaporation of the solvent, chromatography (7:3 petroleum ether–EtOAc) afforded 2,3,4,6-tri-*O*-acetyl-1-*O*-undec-10′-enoyl-α-D-xylopyranose (41 mg, 62%) and undec-10′-enoyl-2,3,4-tri-*O*-acetyl-α-D-xylopyranoside (41 mg, 26%) as white solids.

4.3.1. 2,3,4-Tri-*O*-acetyl-1-*O*-undec-10′-enoyl-β-D-xylopyranose (7β). Mp: 57–59 °C; $[\alpha]_D^{20}$ −14 (*c* 2.08, $CHCl_3$). IR (film): 2920 (m), 2852 (w), 1752 (s), 1377 (w), 1233(s) 1089 (m); ^{1}H NMR ($CDCl_3$): 5.85 (1H, m, H-10′), 5.72 (1H, d, *J* 6.9 Hz, H-1), 5.20 (1H, t, *J* 8.1 Hz, H-3), 4.89–5.09 (4H, H-2, H-4, H-11′a, H-11′b), 4.11 (1H, dd, *J* 5.1 Hz, *J* 11.8 Hz, H-5e), 3.52 (1H, dd, *J* 8.8 Hz, *J* 11.8 Hz, H-5a), 2.31 (2H, t, *J* 7.5 Hz, H-2′), 1.96–2.07 (11H, H-9′, $3CH_3$), 1.18–1.40 (12H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′); ^{13}C NMR ($CDCl_3$): 172.3 (C-1′), 169.7–170.2–170.3 (3C=O), 139.6 (C-10′), 114.6 (C-11′), 92.3 (C-1), 71.4 (C-2), 69.9 (C-3), 68.7 (C-4), 63.2 (C-5), 34.5 (C-2′), 34.2 (C-9′), 29.2–29.3–29.4–29.5–29.6 (C-4′, C-5′, C-6′, C-7′, C-8′), 25.1 (C-3′), 21.0–21.1–21.2 ($3CH_3$). Anal. Calcd for $C_{22}H_{34}O_9$: C, 59.71; H, 7.74. Found: C, 59.94; H, 7.92.

4.3.2. 2,3,4-Tri-*O*-acetyl-1-*O*-undec-10′-enoyl-α-D-xylopyranose (7α). Mp: 50–53 °C; $[\alpha]_D^{20}$ +39.3 (*c* 1.22, $CHCl_3$). IR (film), cm^{-1}: 2926 (m), 2855 (w), 1759 (s), 1463 (w), 1368 (w), 1221 (s) 1045 (m); ^{1}H NMR ($CDCl_3$): 6.28 (1H, d, *J* 3.6 Hz, H-1), 5.82 (1H, ddt, *J* 3.5 Hz, *J* 6.7 Hz, *J* 10.3 Hz, H-10′), 5.48 (1H, t, *J* 9.8 Hz, H-3), 4.88–5.09 (4H, H-2, H-4, H-11′), 3.94 (1H, dd, *J* 5.9 Hz, *J* 11.1 Hz, H-5e), 3.70 (1H, dd, *J* 10.6 Hz, *J* 11.1 Hz, H-5a), 2.41 (2H, t, *J* 7.3 Hz, H-2′), 1.96–2.07 (11H, H-9′, $3CH_3$), 1.59–1.72 (2H, H-2′), 1.18–1.40 (12H, H-3′, H-4′, H-5′, H-6′, H-7′, H-8′); ^{13}C NMR ($CDCl_3$): 172.3 (C-1′), 170.5, 170.2, 170.1 (3C=O), 139.6 (C-10′), 114.6 (C-11′), 89.4 (C-1), 69.9 (C-2), 69.8 (C-3), 69.1 (C-4), 61.1 (C-5), 34.6 (C-2′), 34.2 (C-9′), 29.3, 29.4, 29.5, 29.6, 29.7 (C-4′, C-5′, C-6′, C-7′, C-8′), 25.2 (C-3′), 20.9–21.1–21.2 ($3CH_3$). Anal. Calcd for $C_{22}H_{34}O_9$: C, 59.71; H, 7.74. Found: C, 60.06; H, 7.54.

4.4. 2,3,4-Tri-*O*-benzyl-1-*O*-undec-10′-enoyl-D-xylopyranose (8)

A similar procedure as above with Et_3N (80 μL, 0.57 mmol, 1.2 equiv), 2,3,4-tri-*O*-benzyl-D-xylopyranose (200 mg, 0.47 mmol, 1 equiv), CH_2Cl_2 (2 mL) and undec-10-enoyl chloride (123 μL, 0.57 mmol, 1.2 equiv) led to **8** (258 mg, 96%) as a clear yellow oil; IR (film): 3065–3031 (w), 2926 (s), 2855 (m), 1738 (s), 1497 (w), 1455 (m), 1274 (m), 1075 (s), 736 (m); ^{1}H NMR ($CDCl_3$): 7.03–7.38 (30H, H arom), 6.21 (1H, d, *J* 3.6 Hz, H-1α), 5.71 (2H, ddt, *J* 6.6 Hz, *J* 10.2 Hz, *J* 17.0 Hz, H-10′), 5.51 (1H, d, *J* 7.7 Hz, H-1β), 4.51–5.02 (16H, CH_2, H-11′), 3.19–3.92 (10H, H-2, H-3, H-4, H-5), 2.32 (2H, dt, *J* 7.4 Hz, *J* 11.7 Hz, H-2′b), 2.28 (2H, dt, *J* 3.8 Hz, *J* 11.7 Hz, H-2′a), 1.79–1.99 (4H, H-9′), 1.41–1.68 (4H, H-3′), 1.09–1.41 (20H, H-4′, H-5′, H-6′, H-7′, H-8′); ^{13}C NMR ($CDCl_3$): 172.9 ($C=O_\alpha$), 172.6 ($C=O_\beta$), 139.6 (C-10′), 138.1–138.2–138.3–138.4–138.5–138.8 (Cq arom), 128.1–128.2–128.3–128.4–128.8–128.9 (CH arom), 114.6 (C-11′), 94.9 (C-1β), 90.2 (C-1α), 84.1 (C-2β), 81.6 (C-3β), 80.9 (C-2α), 79.1 (C-3α), 77.6 (C-4β), 77.5 (C-4α), 74.2–75.4–76.9 ($CH_2\beta$), 73.7–76.0–76.2 ($CH_2\alpha$), 64.9 (C-5β), 62.6 (C-5α), 34.2–34.6–34.7 (C-2′, C-9′), 25.0–25.3 (C-3′), 29.3–29.4–29.6–29.7–30.1 (C-4′, C-5′, C-6′, C-7′, C-8′); HRMS: calcd for $[M+Na]^+$ 609.3195, found 609.3194. Anal. Calcd for $C_{37}H_{46}O_6$: C, 75.74; H, 7.90. Found: C, 75.64; H, 8.05.

4.5. 1-*O*-Undecenoyl-D-xylopyranose (9)

Compound **8** (1.62 g, 2.76 mmol) and Pd/C 10% Janssen (20.6 mg, 0.07 equiv) were suspended in abs EtOH (27 mL). After stirring at room temperature for 48 h under a hydrogen atmosphere and filtration over Celite, evaporation of the solvent led to the title derivative (861 mg, 98%) as a white paste; IR (film): 3358 (s), 2924 (s), 2853 (m), 1758 (m), 1737 (m), 1701 (m), 1467 (w), 1377 (w), 1247 (w), 1074 (s), 721 (w); ^{1}H NMR (acetone-d_6, 500 MHz): 6.04 (1H, d, *J* 3.4 Hz, H-1α), 5.44 (1H, d, *J* 7.6 Hz, H-1β), 3.83 (1H, dd, *J* 5.0 Hz, *J* 12.4 Hz, H-5β), 3.49–3.68 (6H, H-2α, H-2β, H-3α, H-4α, H-5α), 3.46 (1H, t, *J* 8.1 Hz, H-4β), 3.36 (1H, dd, *J* 10.0 Hz, *J* 11.2 Hz, H-3β), 3.30 (1H, t, *J* 12.4 Hz, H-5), 2.40 (1H, dd, *J* 1.3 Hz, *J* 7.1 Hz, H-2′α), 2.35 (2H, dd, *J* .0 Hz, *J* 7.4 Hz, H-2′β), 2.26 (1H, H-2′α), 1.54–1.67 (2H, H-3′), 2.03–2.08 (3H, OH), 1.22–1.42 (14H,

H-4′, H-5′, H-6′, H-7′, H-8′, H-9′, H-10′), 0.87 (3H, t, *J* 6.7 Hz, H-11′); ^{13}C NMR (acetone-d_6): 172.7 (C-1′α), 172.6 (C-1′β), 95.6 (C-1β), 92.7 (C-1α), 77.3 (C-4β), 74.9 (C-4α), 73.2 (C-3β), 71.9 (C-3α), 70.5 (C-2α), 70.4 (C-2β), 66.9 (C-5β), 64.6 (C-5α), 34.4, 35.5 (C-2′α, C-2′β), 32.5 (C-9′), 29.4, 29.5, 29.6, 29.7, 29.8, 29.9, 30.0, 30.1, 30.2, 30.3 (C-4′, C-5′, C-6′, C-7′, C-8′), 25.3, 25.4 (C-3′α, C-3′β), 23.2 (C-10′), 14.3 (C-11′); HRMS: calcd for $[M+Na]^+$ 341.1940, found 341.1953.

Acknowledgements

This work was supported by the 'Contrat d'objectifs' in 'Europol'Agro' framework (Glycoval program). We are grateful to the public authorities of Champagne-Ardenne for a fellowship to C.D. and material funds.

References

1. (a) Muzart, J.; Hénin, F.; Estrine, B.; Bouquillon, S. French Patent CNRS No. 0116363, PCT WO 03053987, 2001; (b) Estrine, B.; Bouquillon, S.; Hénin, F.; Muzart, J. *Eur. J. Org. Chem.* **2004**, 2914–2922; (c) Estrine, B.; Bouquillon, S.; Hénin, F.; Muzart, J. *Green Chem.* **2005**, *7*, 219–223; (d) Bessmertnykh, A.; Hénin, F.; Muzart, J. *J. Mol. Catal. A: Chem.* **2005**, *238*, 199–206; (e) Damez, C.; Estrine, B.; Bessmertnykh, A.; Bouquillon, S.; Hénin, F.; Muzart, J. *J. Mol. Catal. A: Chem.* **2006**, *244*, 93–98.
2. Satgé, C.; Le Bras, J.; Hénin, F.; Muzart, J. *Tetrahedron* **2005**, *61*, 8405–8409.
3. (a) Konstantinovic, S.; Predojevic, J.; Gojkovic, S.; Ratkovic, Z.; Dimitrijevic, B.; Mojsilovic, B. *Ind. J. Chem., Sect. B.* **2001**, *40B*, 802–805; (b) Konstantinovic, S.; Predojevic, J.; Gojkovic, S.; Pavlovic, V. *Ind. J. Chem., Sect. B.* **2003**, *42B*, 666–669; (c) Roy, R.; Dominique, R.; Das, S. K. *J. Org. Chem.* **1999**, *64*, 5408–5412; (d) Behler, A.; Schmid, K. H.; Koester, R. Eur. Pat. Appl. EP 1205536 A2 20020515 2002; *Chem. Abstr.* **2002**, 136, 371507; (e) de Smet, L. C. P. M.; Pukin, A. V.; Stork, G. A.; de Vos, C. H. R.; Visser, G. M.; Zuilhof, H.; Sudhoelter, E. J. R. *Carbohydr. Res.* **2004**, *339*, 2599–2605.
4. Baker, I. J. A.; Matthews, B.; Suares, H.; Krodkiewska, I.; Furlong, D. N.; Grieser, F.; Drummond, C. J. *J. Surf. Deterg.* **2000**, *3*, 1–11.
5. McGeary, R. P.; Amini, S. R.; Tang, V. W. S.; Toth, I. *J. Org. Chem.* **2004**, *69*, 2727–2730.
6. (a) Nevin, C. S.; Short, R. G. (Staley, A. E. Manufg. Co.), US Patent 3375243 19680326, Appl. US 67-622476 19670313, 1967; *Chem. Abstr.* **1968**, *68*, 106243; (b) Davis, J. E.; Letton, J. C., (Procter and Gamble Co. USA), Eur. Pat. Appl., Appl. EP 84-303874 19840608, Prior. US 83-504647 19830615, 1984; *Chem. Abstr.* **1985**, *102*, 149713; (c) Song, X.; Cui, Y.; Guo, J. *Xandai Huagong* **1999**, *19*, 30–31; *Chem. Abstr.* **1999**, *132*, 310016.
7. (a) Ballou, C. E.; Roseman, S.; Link, K. P. *J. Am. Chem. Soc.* **1951**, *73*, 1140–1144; (b) Helm, R. F.; Ralph, J. *J. Org. Chem.* **1991**, *56*, 7015–7021.
8. Schmid, K.; Tesmann, H. *Surfact. Sci. Ser.* **2001**, *98*, 1–69.
9. Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212–235.
10. Bock, K.; Pedersen, C. *Adv. Carbohydr. Chem. Biochem.* **1984**, *41*, 27–66.
11. (a) Utille, J. P.; Vottero, P. J. A. *Carbohydr. Res.* **1980**, *85*, 289–297; (b) Utille, J. P.; Gagnaire, D. *Carbohydr. Res.* **1982**, *106*, 43–57.
12. Decoster, E.; Lacombe, J. M.; Strebler, J. L.; Ferrari, B.; Pavia, A. *J. Carbohydr. Chem.* **1983**, *2*, 329–341.
13. (a) Lubineau, A.; Queneau, Y. *Tetrahedron Lett.* **1985**, *26*, 2653–2654; (b) Bliard, C.; Massiot, G.; Nazabadiokon, S. *Tetrahedron Lett.* **1994**, *35*, 6107–6108.
14. Matsumura, S.; Imai, K.; Yoshikawa, S.; Kawada, K.; Uchibori, T. *J. Am. Oil Chem. Soc.* **1990**, *67*, 996–1001.
15. Garofalakis, G.; Murray, B. S.; Sarney, D. B. *J. Colloid Interface Sci.* **2000**, *9*, 391–398.
16. Ross, J.; Miles, G. D. Am. Soc. For Testing Materials, Method D1173-53, Philadelphia, PA, 1953.
17. Rosen, M. J.; Solash, J. *J. Am. Oil Chem. Soc.* **1969**, *46*, 399.
18. Legrand, F.; Millequant, J. M. Fr. Demande 2003; *Chem. Abstr.* **2004**, *138*, 373805.