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Note

Tin-mediated regioselective etherification and esterification of unprotected xylitol

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Abstract

Regioselective alkylation and acylation of xylitol stannylene acetal derivatives with alkyl and acyl halides is reported. The coupling reaction was promoted when necessary by cesium fluoride under mild conditions, affording mono- and di-ethers of xylitol at the primary hydroxyl groups in good overall yields (50–60%). The additional salt was not required in acylation reactions which afforded diesters of xylitol in excellent yields (~96%). © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Xylitol; Alditols; Regioselective; Etherification; Esterification; Stannylene acetal

1. Introduction

Regioselective etherification and esterification are among widely used reactions in carbohydrate chemistry. They provide protected hydroxyl groups in multistep processes [1] and various non ionic amphiphilic sugars with long hydrocarbon chains [2]. Furthermore, several examples have shown the interest of esterified alditols as biologically active compounds [3].

Recently, we have described the efficient two-steps synthesis of α,ω-dithioalkylalditols from the corresponding peracetylated α,ω-dibromoalditol derivatives and alkane thiolate [4]. When attempting to obtain the α,ω-di-*O*-alkylalditol analogues, the same indirect strategy met with serious limitations including alcoholate deacetylation and subsequent heterocyclisation reaction.

The other alternative which could be explored is the regioselective *O*-alkyl etherification of unprotected alditols with alkyl halides. The result of this method depends on the nucleophilic enhancement mode of the hydroxyl groups. In this way, with sodium hydride and an alkyl halide in *N,N*-dimethylformamide, each hydroxyl group was indiscriminately affected and no regioselective etherification at primary hydroxyl dominated, in agreement with other reported results [5].

In the present work, results concerning both etherification and esterification of unprotected xylitol are reported. The nucleophilic enhancement of hydroxyl groups was carried out by means of oxygen–tin coordination involving the dibutyltin oxide reagent (Bu_2SnO) [6]. This type of reaction has been extensively studied since the first report by Valade [7]. However, to our knowledge, apart

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from glycerol [8], no example with other unprotected symetrical alditols has been reported since then.

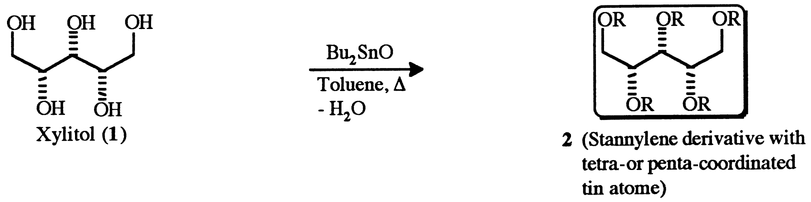
The dibutylstannylene acetal intermediate could be prepared from diol and dibutyltin oxide either in methanol or in toluene as solvent. With the latter, the azeotropic removal of water was carried out. Although the reaction in methanol was faster, it resulted in lower yields [9]. Consequently, preparation in toluene was preferred (Scheme 1).

The solid dibutylstannylene acetal of xylitol **2**, prepared from xylitol (1.3 mmol) and dibutyltin oxide (2.5 equiv) was allowed to react first with an excess of benzylbromide (4 equiv) in toluene as the solvent (Scheme 2) (Table 1, entry 1). After 65 h at 65 °C, no reaction had occurred and the substrate was recovered. In contrast, under the same conditions and using chloroform as the solvent, benzylation occurred with high regioselectivity at primary hydroxyl groups (entry 2) with complete disappearance of the starting material. After acetylation of the crude product, 2,3,4-tri-*O*-acetyl-1,5-di-*O*-benzylxylitol (**3**) and 2,3,4,5-tetra-*O*-acetyl-1-*O*-benzyl-DL-xylitol (**4**) were obtained in 52 and 28% yields respectively. Unsymmetrical 3,4-di-*O*-acetyl-1,2,5-tri-*O*-benzyl-DL-xylitol (**5**) was also isolated, but in lower yield (17%).

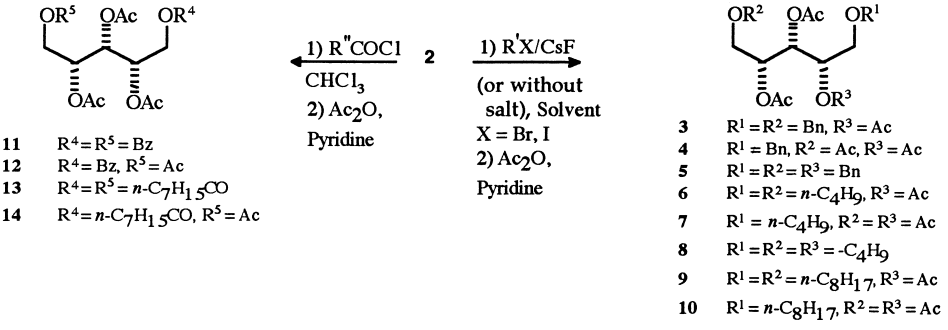
Though the use of only 2 equiv of Bu_2SnO minimized the benzylation at secondary hydroxyl groups, the targeted 1,5-di-*O*-benzyl derivative **3** was not favored (entry 3). However, a decrease in the proportion of both reagents (2 equiv of Bu_2SnO, and 2.5 equiv of BnBr) regioselectively favored one primary position, and the monobenzylated xylitol derivative **4** was isolated in reasonable yield (57%, entry 4). Under the same conditions, but in the presence of added cesium fluoride (2 equiv, entry 8), the benzylation occurred much faster (5 h instead of 65 h for complete reaction), without heating, and approximately with the same regiochemistry. This salt effect has already been reported by Naguashima et al. [8b].

In both dimethylformamide and 1,4-dioxane (entries 5 and 6, respectively), a dramatic decrease in the reaction rate was observed. Use of acetonitrile as the solvent increased the reaction rate, leading to a significant amount of tri-*O*-benzyl derivative **5** (42% yield, entry 7). This is probably due to the coordination ability of CH_3CN towards tin in the stannylene intermediate, leading to further nucleophilic enhancement at oxygen. Based on this result, acetonitrile seems to have the same effect on reaction rate as the fluoride ion catalyst but without the same regioselectivity.

Alkylation with long alkyl chain was also investigated. The *n*-butyl etherification occurred with moderate yield, even when using a large excess of *n*-butyl iodide and cesium fluoride with heating. Thus, the 1-*O*-*n*-butyl-DL-xylitol derivative **7** was



Scheme 1.



11 $R^4 = R^5 = Bz$
12 $R^4 = Bz, R^5 = Ac$
13 $R^4 = R^5 = n\text{-}C_7H_{15}CO$
14 $R^4 = n\text{-}C_7H_{15}CO, R^5 = Ac$

3 $R^1 = R^2 = Bn, R^3 = Ac$
4 $R^1 = Bn, R^2 = Ac, R^3 = Ac$
5 $R^1 = R^2 = R^3 = Bn$
6 $R^1 = R^2 = n\text{-}C_4H_9, R^3 = Ac$
7 $R^1 = n\text{-}C_4H_9, R^2 = R^3 = Ac$
8 $R^1 = R^2 = R^3 = \text{-}C_4H_9$
9 $R^1 = R^2 = n\text{-}C_8H_{17}, R^3 = Ac$
10 $R^1 = n\text{-}C_8H_{17}, R^2 = R^3 = Ac$

Scheme 2.

Table 1
Etherification and esterification of xylitol under various conditions; isolated yields (%) in mono-, di- and tri-akylether and ester after acetylation with Ac_2O in pyridine

Conditions								Isolated yields (%)						
Entry	Bu_2SnO (equiv)	R′X or (equiv)	R′COCl	Salt (equiv)	Solvent	t (h)	T (°C)	di-(%)		mono-(%)		tri-(%)		Xyl (%)
1	2.5	BnBr	(4)	no salt	Toulene	65	65	**3**	(o)	**4**	(o)	**5**	(0)	(100)
2	2.5	BnBr	(4)	no salt	$HCCl_3$	65	reflux	**3**	(52)	**4**	(28)	**5**	(17)	(0)
3	2	BnBr	(4)	no salt	$HCCl_3$	65	reflux	**3**	(41)	**4**	(38)	**5**	(4)	(13)
4	2	BnBr	(2.5)	no salt	$HCCl_3$	65	reflux	**3**	(17)	**4**	(57)	**5**	(3)	(21)
5	2.5	BnBr	(4)	no salt	1,4-dioxane	65	70	**3**	(13)	**4**	(21)	**5**	(4)	(58)
6	2.5	BnBr	(4)	no salt	DMF	65	100	**3**	(18)	**4**	(15)	**5**	(4)	(56)
7	2.5	BnBr	(4)	no salt	CH_3CN	22	reflux	**3**	(32)	**4**	(17)	**5**	(42)	(0)
8	2	BnBr	(2.5)	CsF(2)	$HCCl_3$	5	R.T.	**3**	(25)	**4**	(51)	**5**	(8)	(9)
9	2.5	*n*-BuI	(8)	CsF(3.5)	$HCCl_3$	20	R.T.	**6**	(0)	**7**	(0)	**8**	(0)	(100)
10	2.5	*n*-BuI	(8)	CsF(3.5)	$HCCl_3$	20	50	**6**	(0)	**7**	(35)	**8**	(0)	(61)
11	2.5	*n*-BuI	(4)	CsF(3.5)	DMF	20	R.T.	**6**	(40)	**7**	(42)	**8**	(6)	(6)
12	2.5	*n*-BuI	(4)	CsF(4)	DMF	20	R.T.	**6**	(60)	**7**	(27)	**8**	(6)	—
13	2.5	*n*-BuI	(4)	*n*-Bu_4I(4)	DMF	20	R.T.	**6**	(0)	**7**	(5)	**8**	(0)	(90)
14	2.5	*n*-$C_8H_{17}I$	(4)	CsF(4)	DMF	20	R.T.	**9**	(58)	**10**	(29)	—	—	
15	2.5	BzCI	(2)	no salt	$HCCI_3$	0.25	−15 to R.T.	**11**	(96)	**12**	(0)	—	—	
16	2.5	BzCl	(1)	no salt	$HCCl_3$	0.25	−15 to R.T.	**11**	(24)	**12**	(65)	—	(10)	
17	2.5	$C_7H_{15}COCl$	(2)	no salt	$HCCl_3$	0.25	−15 to R.T.	**13**	(95)	**14**	(—)		—	—
18	2.5	$C_7H_{15}COCl$	(1)	no salt	$HHCl_3$	0.25	0 to R.T.	**13**	(20)	**14**	(60)		—	(15)

isolated as sole product in 35% yield (entry 10). When the reaction was performed in DMF with 4 equiv of *n*-BuI and 3.5 equiv of CsF, acylated 1,5-di-*O*-*n*-butylxylitol (**6**) and 1-*O*-*n*-butyl-DL-xylitol (**7**) derivatives were isolated after acetylation in equal amounts with good yields (40 and 42%, respectively, entry 11). It is important to emphasize that a small increase of CsF amount seems to be crucial since 4 equiv (instead of 3.5) led to the dialkylated derivative **3** as a major product in good yield (60%, entry 12). A similar result was obtained with *n*-octyl iodide as alkylating reagent (entry 14).

In contrast to *O*-alkylation, *O*-acylation was carried out under very mild conditions in chloroform. Thus, a mixture of benzoyl chloride or octanoyl chloride (2 equiv) and the stannylene derivative (prepared from 2.5 equiv of Bu_2SnO and xylitol) in chloroform led to the 1,5-diacylated derivatives **11** and **13** in excellent yields (~ 96%) and a short time (15 mn, entries 15 and 17). When only 1 equiv of acylating reagent was used, the acylation was carried out mainly at one of the primary hydroxyl groups and the monoacylated derivatives **12** and **14** were obtained in good yields (65 and 60%, respectively).

In conclusion, we have described an efficient direct *O*-alkylation and *O*-acylation of xylitol, via their stannylene derivative. Both mono- and di-*O*-alkyl xylitolether derivatives (and mono- and di-*O*-acylester derivatives) were obtained in good to excellent yields.

2. Experimental

General methods.—Melting points were determined with a Büchi 535 digital melting point apparatus and are uncorrected. Optical rotations were measured with a DIP-370 digital polarimeter. ^1H and ^{13}C NMR spectra were recorded on a Bruker 300 WB spectrometer; chemical shifts are reported in δ (ppm) relative to Me_4Si. All ^{13}C NMR signals were assigned through C,H-correlated spectra. TLC was performed on Silica Gel 60 F_{254} 230 mesh (E. Merck) with hexane–EtOAc as eluent, and zones were detected by the vanillin-H_2SO_4 reagent. The silica gel used in column chromatography was 35–70 μ (Amicon).

General procedure for acylation and alkylation.—A mixture of xylitol (0.2 g, 1.3 mmol) and dibutyltin oxide in toluene was refluxed for 16 h with azeotropic removal of water. The white powder, obtained after removal of the solvent, was dried under vacuum and treated with alkylating or acylating reagent (with or without added CsF) under the conditions reported in Table 1. The crude product obtained was subsequentely acetylated (with Ac_2O in pyridine overnight at room temperature).

Evaporation to dryness gave a residue which was processed by column chromatography on silica gel using a mixture of hexane–EtOAc as eluant. The resulting products were isolated with yields as reported in the table.

*2,3,4-Tri-*O*-acetyl-1,5-di-*O*-benzylxylitol* (**3**). Syrup, R_f 0.49 in 5–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 68.1 (C-1), 70.5 (C-2), 69.8 (C-3), 73.2 (CH_2Ph), 128.3, 127.7 (Ph), 137.5 (C-ipso), 170.1, 169.4 (carbonyl×3), 20.8, 20.5 (CH_3); ^{1}H: δ 3.55 (dd, 2 H, $J_{1a,1b}$ 10.6, $J_{1a,2}$ 5.2 Hz, H-1a,5a), 3.5 (dd, 2 H, $J_{1b,2}$ 4.6 Hz, H-1b,5b), 5.2 (m, 2 H, $J_{2,3}$ 5.4 Hz, H-2,4), 5.6 (t, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 4.4 (d , 2 H, CH_2Ph), 7.3 (m, 5 H, Ph), 2, 2.1 (2 s, 6H, CH3). Anal. Calcd for $C_{25}H_{30}O_8$: C, 65.55; H, 6.55; O, 27.95. Found: C, 65.67; H, 6.51.

*2,3,4,5-Tetra-*O*-acetyl-1-*O*-benzyl-*DL*-xylitol* (**4**). Syrup, R_f 0.37 in 5–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 67.72 (C-1), 69.27 (C-2 = C-4), 70.31 (C-3), 61.83 (C-5), 73.2 (C_H2Ph), 128.3, 127.7 (Ph), 137.4 (C-ipso), 169.83, 169.95, 169.6, 170.21 (carbonyl × 4), 20.7, 20.6, 20.45 (CH_3); ^{1}H: δ 2.4 (dd, 1 H, $J_{1a,1b}$ 10.7, $J_{1a,2}$ 4.8 Hz, H-1a), 2.4 (dd, 1 H, $J_{1b,2}$ 4.7 Hz, H-1b), 5.1 (m, 1 H, $J_{2,3}$ 5.4 Hz, H-2), 5.4 (t, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 5.2 (m, 1 H, $J_{4,5a}$ 4.6, $J_{4,5b}$ 6.2 Hz, H-4), 4.2 (dd, $J_{5a,5b}$ 11.9 Hz, H-5a), 4.4 (s, 2 H, CH_2Ph), 7.2 (m, 5 H, Ph), 2, 1.98, 1.93 (3s, 12 H, CH_3). Anal. Calcd for $C_{20}H_{26}O_9$: C, 58.54; H, 6.34; O, 35.12. Found: C, 58.35; H, 6.21.

*2,3-Di-*O*-acetyl-1,2,5-tri-*O*-benzylylitol* (*5*). Syrup, R_f 0.65 in 5–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 69.70 (C-1), 76.22 (C-2), 71.20 (C-3), 71.06 (C-4), 68.17 (C-5), 73.49, 73.08, 72.51 (CH_2Ph), 128.34, 127.91, 127.7 (Ph), 137.92, 137.68 (C-ipso), 170.06 (carbonyl × 2), 20.94, 20.77 (CH_3); ^{1}H: δ 3.61 (d, 2 H, $J_{1a,2} = J_{1b,2}$ 5 Hz, H-1a = H-1b), 3.8 (m, 1 H, $J_{2,3}$ 6.2 Hz, H-2), 5.5 (dd, 1 H, $J_{3,4}$ 4.4 Hz, H-3), 5.3 (m, 1 H, $J_{4,5a}$ 4, $J_{4,5b}$ 5.2 Hz, H-4), 3.5 (dd, 1 H, H-5a), 3.4 (dd, 1 H, H-5b), 4.3–4.7 (m, 2 H, CH_2Ph), 7.3 (m, 5 H, Ph), 2.1 (s, 6 H, CH_3). Anal. Calcd for $C_{30}H_{34}O_7$: C, 71.15; H, 6.72; O, 22.13. Found: C, 71.02; H, 6.68.

*2,3,4-Tri-*O*-acetyl-1,5-di-*O*-n-butylxylitol* (**6**). Syrup, R_f 0.5 in 5–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 71.14 (C-1,5), 70.54 (C-2,4), 69.89 (C-3), 68.78 (OCH_2, *n*-butyl), 31.41 (OCH_2CH_2, *n*-butyl) 19.03 (CH_2-CH_3, *n*-butyl), 13.68 (CH_3, *n*-butyl), 170.03, 169.58 (carbonyl × 3), 20.75, 20.45 (CH_3, Ac); ^{1}H: 3.3 (m, 4 H, H-1a, H-5a, H-1b, H-5b), 5.1 (m, 2 H, $J_{2,3}$ 5.4 Hz, H-2,4), 5.4 (t, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 3.3 (m, 4 H, OCH_2, *n*-butyl), 1.4 (m, 4 H, OCH_2CH_2, *n*-butyl) 1.2 (m, 4 H, CH_2-CH_3, *n*-butyl), 0.8 (t, 6 H, CH_3, *n*-butyl), 2 (CH_3, Ac). Anal. Calcd for $C_{19}H_{34}O_8$: C, 58.46; H, 8.72; O, 32.82. Found: C, 58.24; H, 8.70.

*2,3,4,5-Tetra-*O*-acetyl-1-*O*-n-butyl-*DL*-xylitol* (**7**). Syrup, R_f 0.33 in 5–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 71.32 (C-1), 70.46 (C-2), 69.41 (C-3), 69.3 (C-4), 61.8 (C-5), 68.52 (OCH_2, *n*-butyl), 31.36 (OCH_2CH_2, *n*-butyl) 19.05 (CH_2-CH_3, *n*-butyl), 13.71 (CH_3, *n*-butyl), 170.24, 169.89, 169.62 (carbonyl × 4), 20.65, 20.48 (CH_3, Ac); ^{1}H: 3.3 (m, 2 H, H-1a, H-1b), 5.1 (m, 1 H, $J_{2,3}$ 4.98 Hz, H-2), 5.4 (t, 1 H, $J_{3,4}$ 5.7 Hz, H-3), 5.2 (m, 1 H, $J_{4,5a}$ 6.2, $J_{4,5b}$ 4.6 Hz, H-4), 3.9 (dd, 1 H, $J_{5a,5b}$ 11.8 Hz, H-5a), 4.3 (dd, 1 H, H-5b), 3.3 (m, 2 H, OCH_2, *n*-butyl), 1.4 (m, 2 H, OCH_2CH_2, *n*-butyl), 1.3 (m, 2 H, CH_2-CH_3, *n*-butyl), 0.8 (t, 3 H, CH_3, *n*-butyl), 2.03 (s), 1.98 (s) (12 H, CH_3, Ac). Anal. Calcd for $C_{17}H_{28}O_9$: C, 54.26; H, 7.45; O, 38.30. Found: C, 53.99; H, 7.39.

*2,3,4-Tri-*O*-acetyl-1,5-di-*O*-n-octylxylitol* (**9**). Syrup, R_f 0.58 in 7–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 71.55 (C-1,5), 70.58 (C-2,4), 69.97 (C-3), 68.85 (OCH_2, *n*-octyl), 29.36, 29.29, 29.15, 25.80, 22.54 (6 × CH_2, *n*-octyl), 13.96 (CH_3, *n*-octyl), 170.11, 169.66 (carbonyl × 3), 20.82, 20.51 (CH_3, Ac); ^{1}H: 3.4 (m, 4 H, H-1a, H-5a, H-1b, H-5b), 5.2 (m, 2 H, $J_{2,3}$ 5.4 Hz, H-2,4), 5.4 (t, 1 H, $J_{3,4}$ 5.4 Hz, H-3), 3.4 (4 H, OCH_2, *n*-octyl), 1.5 (4 H, OCH_2CH_2), 1.2 (20 H, 5 × CH_2, *n*-octyl), 0.8 (6 H, CH_3, *n*-octyl), 2.1 (9 H, CH_3, Ac). Anal. Calcd for $C_{27}H_{50}O_8$: C, 64.54; H, 9.96; O, 25.50. Found: C, 64.22; H, 9.90.

*2,3,4,5-Tetra-*O*-acetyl-1-*O*-n-octyl-*DL*-xylitol* (**10**). Syrup, R_f 0.32 in 7–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 71.63 (C-1), 70.45 (C-2), 69.43 (C-3), 69.29 (C-4), 61.81 (C-5), 68.53 (OCH_2, *n*-octyl), 31.67, 29.24, 29.09, 25.84, 22.50 (6 × CH_2, *n*-octyl), 13.94 (CH_3, *n*-octyl), 170.23, 170, 169.87, 169,61 (carbonyl × 4), 20.72, 20.62, 20.43 (CH_3, Ac); ^{1}H: 3.3 (m, 2 H, H-1a, H-1b), 5.1 (m, 1 H, $J_{2,3}$ 4.8 Hz, H-2), 5 (t, 1 H, $J_{3,4}$ 5.7, H-3), 5.22 (m, 1 H, $J_{4,5a}$ 6.2, $J_{4,5b}$ 4.6 Hz, H-4), 3.9 (dd, 1 H, $J_{5a,5b}$ 11.9 Hz, H-5a), 4.2 (dd, 1 H, H-5b), 3.2 (2 H, OH_2, *n*-octyl), 1.4 (m, 2 H, OCH_2CH_2), 1.2 (m, 10 H, 5 × CH_2), 0.8 (t, 3 H, CH_3, *n*-octyl), 2.1 (9 H, CH_3, Ac). Anal. Calcd for $C_{21}H_{36}O_9$: C, 58.33; H, 8.33; O, 33.33. Found: C, 58.28; H, 8.29.

*2,3,4-Tri-*O*-acetyl-1,5-di-*O*-benzoylxylitol* (**11**). Mp 112–113°C (from MeOH); R_f 0.53 in 5–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 62.19 (C-1,5), 69.14 (C-2,4), 68.88 (C-3), 128.43, 129.63, 133.24 (Ph), 165.8 (carbonyl × 2, Bz), 169.58, 169,89

(3 × carbonyl, Ac), 20.50, 20.73 (3 × CH_3, Ac); ^{1}H: δ 4.3 (dd, 2 H, $J_{1a,1b}$ 12, $J_{1a,2}$ 5.9 Hz, H-1a,5a), 4.5 (dd, 2 H, $J_{1b,2}$ 4.2 Hz, H-1b,5b), 5.4 (m, 2 H, $J_{2,3}$ 5.3 Hz, H-2,4), 5.6 (t, 1 H, $J_{3,4}$ 5.3 Hz, H-3), 7.3 (t, 4 H), 7.5 (t, 2 H), 7.9 (dd, 4 H, Ph), 2.1, 2 (9 H, CH_3, Ac). Anal. Calcd for $C_{25}H_{26}O_{10}$: C, 61.73; H, 5.35; O, 32.92. Found: C, 61.63; H, 5.25.

2,3,4,5-Tetra-O-*acetyl-1*-O-*benzoyl*-DL-*xylitol* (**12**). Mp 78–79 °C (from MeOH), R_f 0.42 in 5–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 62.36 (C-1), 69.04 (C-2,3,4), 61.68 (C-5), 128.42, 129.61, 133.27 (Ph),165.78 (carbonyl, Bz), 169.63, 169.87, 170.26 (4 × carbonyl, Ac), 20.50, 20.67 (CH_3, Ac); ^{1}H: δ 4.3 (dd, 1 H, $J_{1a,1b}$ 12, $J_{1a,2}$ 6.2 Hz, H-1a), 4.5 (dd, 1 H, $J_{1b,2}$ 4.1 Hz, H-1b), 5.4 (m, 1 H, $J_{2,3}$ 5.3 Hz, H-2), 5.5 (t, 1 H, $J_{3,4}$ 5.3, H-3), 5.3 (m, 1 H, $J_{4,5a}$ 5.9, $J_{4,5b}$ 4.4 Hz, H-4), 3.9 (dd, 1 H, $J_{5a,5b}$ 12.1 Hz, H-5a), 4.3 (dd, 1 H, H-5b), 7,4 (t, 2 H), 7.5 (t, 1 H), 7.9 (d, 2 H), 2-2.1 (12 H, CH_3, Ac). Anal. Calcd for $C_{20}H_{24}O_{10}$: C, 56.60; H, 5.66; O, 37.74. Found: C, 55.75; H, 5.83.

2,3,4-Tri-O-*acetyl-1,5-di*-O-n-*octanoylxylitol* (**13**). Syrup, R_f 0.58 in 7–2 hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 61.45 (C-1,5), 69.11 (C-2,4), 68.89 (C-3), 33.85 ($OCOCH_2$, *n*-octanoyl), 31.54 ($OCOH_2\underline{C}H_2$), 28.93, 28.9, 24.6, 22.5 (4×CH_2), 13.96 (CH_3, *n*-octanoyl), 173.05 (carbonyl×2, *n*-octanoyl), 169.81, 169.54 (3 × carbonyl, Ac), 20.65, 20.42 (3×CH_3, Ac); ^{1}H: δ 3.93 (dd, 2 H, $J_{1a,1b}$ 12, $J_{1a,2}$ 6 Hz, H-1a,5a), 4.3 (dd, 2 H, $J_{1b,2}$ 4.3 Hz, H-1b,5b), 5.2 (dd, 2 H, $J_{2,3}$ 5.3 Hz, H-2,4), 5.3 (t, 1 H, $J_{3,4}$ 5.3 Hz, H-3), 2.2 (t, 4 H, $OCOCH_2$, *n*-octanoyl), 1.5 (m, 4 H, $OCOH_2\underline{C}H_2$), 1.2 (m, 16 H, 4×CH_2), 0.8 (t, 6 H, CH_3, *n*-octanoyl), 2 (s, 3 H), 2.1 (s, 6 H) (CH_3, Ac). Anal. Calcd for $C_{27}H_{46}O_{10}$: C, 61.13; H, 8.67; O, 30.19. Found: C, 61.42; H, 8.71.

2,3,4,5-Tetra-O-*acetyl-1*-O-n-*octanoyl*-DL-*xylitol* (**14**). Syrup, R_f 0.32 in hexane–EtOAc; ^{13}C NMR ($CDCl_3$): δ 61.47 (C-1), 69.04 (C-2,3,4), 61.7 (C-5), 33.63 ($OCOCH_2$, *n*-octanoyl), 31.51, 28.78, 24.61, 22.46 (5 × CH_2), 13.93 (CH_3, *n*-octanoyl), 173.1 (2 × carbonyl, *n*-octanoyl), 170.3, 169.87, 169.63 (3 × carbonyl, Ac), 20.61 (CH_3, Ac); ^{1}H: δ 3.9 (dd, 1 H, $J_{1a,1b}$ 12, $J_{1a,2}$ 6.1 Hz, H-1a), 4.3 (dd, 1 H, $J_{1b,2}$ 4.3 Hz, H-1b), 5.2 (m, 2 H, $J_{2,3}$ 5.4 Hz, H-2,4), 5.3 (t, 1 H, $J_{3,4}$ 5.4, H-3), 3.9 (dd, 1 H, $J_{5a,5b}$ 12 Hz, H-5a), 4.3 (dd, 1 H, H-5b), 2.2 (t, 2 H, $OCOCH_2$), 1.52 (m, $OCOCH_2C\underline{H}_2$), 1.2 (m, 8 H, 4×CH_2), 0.8 (t, 3 H, CH_3, *n*-octanoyl), 2–2.1 (4×s, 12 H, CH_3, Ac). Anal. Calcd for $C_{21}H_{34}O_{10}$: C, 56.50; H, 7.62; O,35.87. Found: C, 56.18; H, 7.53.

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