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DMF promoted xylosylation of terpenols

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Abstract—The glycosidation of 2,3,4-triacetyl-1-bromo-α-D-xylopyranose with various terpenols occurs at 50 °C in DMF without the requirement of any additive. The decisive role of DMF as solvent on the coupling efficiency is highlighted.

1. Introduction

The progressive changeover of the chemical industry to renewable instead of fossil feedstocks is ineluctable. In this context, the use of cheap and abundant carbohydrates is of great interest,[1] their transformation into biodegradable surfactants being one possibility for their valorisation.[2] As the lipophilic moiety of the surfactants, it would be of interest to use renewable materials such as terpenols. Over the last past years, we have been involved in the valorization of pentoses, which are easily extracted from wheat straw and bran.[3] Consequently, we envisaged to carry out the glycosydation of a D-xylose derivative with terpenols by variations of the Koenigs–Knorr methodology.[4] To the best of our knowledge, such couplings have never been reported using pentose derivatives, while modifications of the Koenigs–Knorr procedure have been used for the coupling of tetra-*O*-protected-glucosyl bromides with terpenols.[5]

2. Results and discussion

The Koenigs–Knorr method was attempted with tri-*O*-acetylxylosyl bromide **1**. This substrate was obtained in two steps via the acetylation of D-xylose and the reaction of the corresponding peracetylated compound with a solution of HBr in acetic acid in 70–75% overall yield.[6–10]

This compound has already been documented in various papers[6–15] but without specification of the configuration of the C-1 center,[6] or with either a rather arbitrarily α-[9–11] or β-[7,8] stereochemistry of the bromine atom, and also with various melting points[10,13,15] and optical rotations.[10,13,15] In fact, we observed that our compound is rapidly decomposed on the bench and should be stored at low temperature, and that best yields were obtained with new solutions of HBr. It has been reported that the α-bromide is more stable than the β-bromide,[13] and, for our compound, we assumed the α-stereochemistry on the basis of the value of $J_{1,2}=4.0$ Hz of the doublet at $\delta=6.58$ ppm, this coupling constant corresponding to an equatorial/axial arrangement of the two vicinal hydrogens.

The reaction of **1** with (±)-citronellol in the presence of $AgBF_4$ and collidine in anhydrous CH_2Cl_2 at 0 °C[16] led to the expected β-D-xyloside **2** in only 14% yield (Table 1, entry 1). Variations of the experimental conditions were then attempted in order to improve the efficiency of the process. In DMF at 50 °C with Ag_2CO_3 as both base and

Table 1. Reaction of **1** with (±)-citronellol[a]

Entry	Additive (equiv)	Solvent	**2**, Yield %[b]	α/β[c]
1[d]	$AgBF_4$ (1.1)+collidine (1.1)	CH_2Cl_2	14	0:100
2	Ag_2CO_3 (0.5)	DMF	21	17:83
3	K_2CO_3 (0.5)	DMF	22	38:62
4	$AgBF_4$ (1)	DMF	19	30:70
5	NaBr (1)	DMF	46	45:55
6	NaI (2)	DMF	42	45:55
7		DMF	53	41:59
8		CH_2Cl_2	Traces	
9		THF	<5	40:60
10		Pyridine	Traces	

[a] Conditions: **1** (0.6 mmol), citronellol (1.5 mmol), additive (as indicated), solvent (1.0 mL), 50 °C, 16 h.
[b] Isolated yield.
[c] Ratio determined by ^{1}H NMR.
[d] Reaction at 0 °C for 18 h.

Keywords: Glycosylation; Xylosylation; Terpenols; Acid sensitive compounds.
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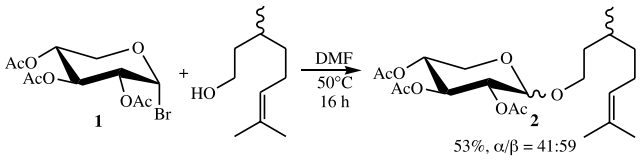
metal halophile, a 17/83 mixture of α- and β- anomers was obtained in 21% yield (entry 2). The use of K_2CO_3 or $AgBF_4$ instead of Ag_2CO_3 afforded similar yields (entries 3 and 4). The glycosydation in DMF was improved to 42–46% yield in the presence of NaBr or NaI (entries 5 and 6) but, surprisingly, the best yield was reached over 16 h[17] in the absence of any additive (entry 7, Eq. 1). The very low amounts of **2** obtained in CH_2Cl_2, THF and pyridine under similar conditions (entries 8–10) highlighted the decisive role of DMF on the efficiency of the coupling. Experiment carried out with (−)-citronellol under conditions of entry 7 led to a mixture of the two corresponding diastereoisomers.



(1)

Recently, ^{1}H NMR studies by Nishida et al. have allowed to demonstrate the formation of a kind of Vilsmeier–Haack intermediate between glycosyl bromides and DMF.[18] An ^{1}H NMR spectra of **1** in DMF-d_7 showed a doublet at 6.86 ppm (J=3.8 Hz), which disappeared with time. According to Nishida et al., this signal would be due to the formation of sensitive *O*-[tri-*O*-acetylxylosyl]-methylene-*N*,*N*-dimethylammonium bromide. We suggest that the glycosylation occurs, at least in part, via the reaction of this adduct with the alcohol and that HBr is neutralized by DMF.

The above results led us to use the conditions of Table 1, entry 7, for the glycosidation of **1** with other terpenols (Table 2). Similar yields have been obtained with (+)-menthol and (−)-borneol (entries 1 and 2), while primary and secondary allylic alcohols afforded lower yields (entries 3–5). No glycosidation of **1** was observed with a tertiary allylic alcohol such as linalol.

3. Conclusion

DMF can have a key role in the glycosidation of 2,3,4-triacetyl-1-bromo-α-D-xylopyranose with primary and secondary alcohols; modest yields, even from sensitive alcohols, can be obtained in this solvent in the absence of any additive.

Table 2. Xylosylation of terpenols[a]

Entry	Terpenol	Products	Yield %[b]	α/β[c]
1	(+)-Menthol	**3**	45	44:56
2	(−)-Borneol	**4**	42	34:66
3	Nerol	**5**	34	42:58
4	Geraniol	**6**	36	40:60
5	(−)-Carveol	**7**	16	43:57

[a] Conditions: **1** (0.6 mmol), terpenol (1.5 mmol), DMF (1.0 mL), 50 °C, 16 h.
[b] Isolated yield.
[c] Ratio determined by ^{1}H NMR.

4. Experimental

4.1. General methods

All reagents used were commercially available and with high purity grade. (−)-Carveol was a mixture of epimers at C(1). TLC were achieved with Silica Gel $60F_{254}$ (E. Merck). Column chromatographies were conducted over silica gel 63–200 μm (SDS). Melting points were measured on a Büchi Schmelzpunktbestimmungsapparat. NMR spectroscopies were performed with a Bruker Avance DRX 500 apparatus. FT-IR spectra were recorded on Avatar 320 FT-IR as KBr pellets or films. $[\alpha]_D^{20}$ were measured with a Perkin Elmer 241 Polarimeter. Mass spectra using electrospray ionization were performed with a Q-TOF micro from micromass.

4.1.1. 1,2,3,4-Tetraacetyl-D-xylopyranose. Acetyl chloride (3.0 mL, 42 mmol) was added dropwise to a solution at 0 °C of xylose (1.0 g, 6.7 mmol) in dichloromethane (25 mL) and pyridine (2.6 mL, 32 mmol). The mixture was allowed to stir overnight, and then quenched with water (50 mL). The organic layer was washed with 2 M HCl (2×50 mL), saturated $NaHCO_3$ (50 mL), water (50 mL), and dried over $MgSO_4$. The removing of the solvent under reduced pressure afforded a yellow paste (2.1 g, 97%, α/β=88/12). R_f 0.61 (1:1 petroleum ether/EtOAc). IR (KBr): ν 2961, 1756. ^{1}H NMR ($CDCl_3$): δ 6.26 (d, 0.88H, $J_{1,2}$=3.6 Hz, H-1α), 5.72 (d, 0.12H, $J_{1,2}$=6.9 Hz, H-1β), 5.47 (t, 0.88H, $J_{2,3,4}$=9.8 Hz, H-3α), 5.21 (t, 0.12H, $J_{2,3,4}$=8.2 Hz, H-3β), 5.03 (m, 2H, H-2α, H-4α, H-2β, H-4β), 4.16 (dd, 0.12H, $J_{4,5a}$=5.0 Hz, $J_{5a,5b}$=12.2 Hz, H-5aβ), 3.94 (dd, 0.88H, $J_{4,5a}$=5.9 Hz, $J_{5a,5b}$=11.2 Hz, H-5aα), 3.72 (t, 0.88H, $J_{4,5b,5a}$=10.9 Hz, H-5bα), 3.53 (dd, 0.12H, $J_{4,5b}$=8.5 Hz, $J_{5a,5b}$=12.0 Hz, H-5bβ), 2.10 (m, 12H, acetyls). ^{13}C NMR: δ 170.1, 169.7 (2), 169.0 (carbonyls), 91.9 (C-1β), 89.1 (C-1α), 70.9 (C-3β), 69.4 (C-2β), 69.2 (2) (C-3α, C-2α), 68.6 (C-4α), 68.2 (C-4β), 62.7 (C-5β), 60.6 (C-5α), 21.0, 20.8, 20.7, 20.6, 20.5, 20.4 (acetyls). ESHRMS: calcd for $C_{13}H_{18}O_9Na^+$: 341.0849; found: 341.0820.

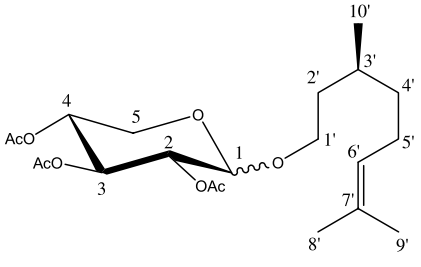
4.1.2. 2,3,4-Triacetyl-1-bromo-α-D-xylopyranose (1).[6–10] 1,2,3,4-Tetraacetyl-D-xylopyranose (4.1 g, 12.8 mmol) was dissolved in dichloromethane (40 mL) and HBr (33% w/v in AcOH) was added dropwise at 0 °C. After 1 h, the reaction was allowed to stir overnight at room temperature. Dichloromethane (60 mL) was added and the reaction was quenched with ice water (100 mL). The organic layer was washed twice with saturated aq. $NaHCO_3$ (100 mL), saturated aq. NaCl (100 mL) and dried over $MgSO_4$. After removing dichloromethane under reduced pressure, the crude product was dissolved in hot diethyl ether (minimum) and crystallized with petroleum ether (150 mL). The product was obtained as light brown crystals (3.3 g, 75%). Mp 75–82 °C (decomposition); lit. 83–85 °C[9]; 97–98 °C[10]; 96–97 °C[13]; 101–102 °C[15]. $[\alpha]_D^{20}$ +192 (*c* 0.87, $CHCl_3$); lit. +215 ($CHCl_3$)[9]; lit. +183 (*c* 2.5 $CHCl_3$)[10]; +206 (*c* 2.3 $CHCl_3$)[13]; +211.9 ($CHCl_3$)[15]. R_f 0.70 (4:1 petroleum ether/EtOAc). IR (KBr): ν 1754. ^{1}H NMR ($CDCl_3$): δ 6.58 (d, 1H, $J_{1,2}$=4.0 Hz, H-1), 5.56 (t, 1H, $J_{2,3,4}$=10.0 Hz, H-3), 5.04 (ddd, 1H, $J_{4,5a}$=5.5 Hz, $J_{3,4}$=9.5 Hz, $J_{4,5b}$=10.5 Hz, H-4), 4.77 (dd, 1H, $J_{1,2}$=4.3 Hz, $J_{2,3}$=10.0 Hz, H-2), 4.06 (dd, 1H, $J_{4,5a}$=6.0 Hz, $J_{5a,5b}$=11.2 Hz, H-5a), 3.88 (t, 1H, $J_{4,5b,5a}$=

10.7 Hz, H-5b), 2.08 (m, 9H, acetyls). ^{13}C NMR: δ 170.0, 169.9 (carbonyls), 87.7 (C-1), 71.0 (C-2), 69.7 (C-3), 68.2 (C-4), 62.7 (C-5), 20.9, 20.8 (2) (acetyls). ESHRMS: calcd for $C_{11}H_{15}O_7BrNa^+$: 360.9899; found: 360.9897. Due to the instability of the product, it should be noted that this signal was not always observed.

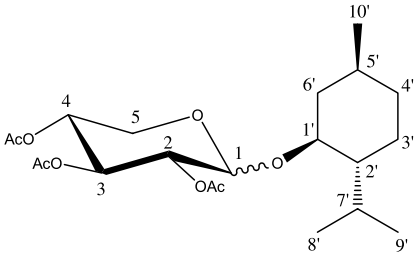
4.2. General method for xylosylation

2,3,4-Triacetyl-1-bromo-α-D-xylopyranose (0.6 mmol) and alcohol (1.5 mmol) were dissolved in anhydrous DMF (1.0 mL) and kept under Ar at 50 °C for 16 h. EtOAc (20 mL) was added and the organic layer was washed with saturated $NaHCO_3$ (20 mL) and water (20 mL), then dried over $MgSO_4$. The mixture was filtered, CH_2Cl_2 (5 mL) and pyridine (2.2 mmol, 0.18 mL) were added. $ClCOCH_3$ (1.8 mmol, 0.13 mL) was added dropwise at 0 °C and the mixture was stirred for 1 h. CH_2Cl_2 (5 mL) was added, the mixture was successively washed with water (10 mL), HCl 2 M (2×10 mL), saturated aq. $NaHCO_3$ (10 mL) and water (10 mL). The organic phase was dried over $MgSO_4$, filtered, then purified by silica gel column chromatography (9:1 then 4:1 petroleum ether/EtOAc). The products were obtained as a mixture of two anomers.

4.2.1. (3′*S*)-3′,7′-Dimethyloct-6′-enyl 2,3,4-triacetyl-D-xylopyranoside (2). Colourless oil. Yield=53%; α/β=41/59. $R_f\alpha$ 0.45; $R_f\beta$ 0.34 (4:1 petroleum ether/EtOAc). IR (KBr): ν 2927, 1755. ^{1}H NMR ($CDCl_3$): δ 5.48 (t, 0.41H, $J_{2,3,4}$=9.7 Hz, H-3α), 5.16 (t, 0.59H, $J_{2,3,4}$=8.5 Hz, H-3β), 5.09 (m, 1H, H-6′), 4.99 (m, 0.41H, H-1α), 4.94 (m, 1.59H, H-4α, H-2β, H-4β), 4.79 (dd, 0.41H, $J_{2,1}$=3.4 Hz, $J_{2,3}$=9.9 Hz, H-2α), 4.47 (d, 0.59H, $J_{1,2}$=6.9 Hz, H-1β), 4.12 (dd, 0.59H, $J_{4,5a}$=5.1 Hz, $J_{5a,5b}$=11.8 Hz, H-5aβ), 3.87 (m, 0.59H, H-1′aβ), 3.77 (m, 0.41H, H-5aα), 3.73 (m, 0.82H, H-1′aα, H-5bα), 3.49 (m, 0.59H, H-1′bβ), 3.44 (m, 0.41H, H-1′bα), 3.37 (m, 0.59H, H-5bβ), 2.05 (m, 9H, acetyls), 2.04 (m, 1H, H-5′a), 1.68 (s, 3H, H-8′), 1.66 (m, 1H, H-2a′), 1.60 (m, 3H, H-9′), 1.55 (m, 1H, H-3′), 1.41 (m, 1H, H-2′b), 1.34 (m, 1H, H-4′a), 1.21 (m, 1H, H-5′b), 1.16 (m, 1H, H-4′b), 0.88 (m, 3H, H-10′). ^{13}C NMR: δ 170.4, 170.3, 170.2, 170.1, 170.0, 169.5 (carbonyls), 131.4, 131.3 (C-7′), 124.8, 124.7 (C-6′), 100.9 (C-1β), 95.7 (C-1α), 71.7 (C-3β), 71.3 (C-2α), 71.0 (C-2β), 69.9 (C-3α), 69.6 (C-4α), 69.1 (C-4β), 68.1 (C-1′β), 66.9 (C-1′α), 62.1 (C-5β), 58.4 (C-5α), 37.2 (2) (C-4′), 36.5, 36.3 (C-2′), 29.7, 29.4 (C-3′), 25.8 (C-8′), 25.6, 25.5 (C-5′), 20.7 (4), 20.6 (2) (acetyls), 19.6, 19.4 (C-10′), 17.7 (C-9′). ESHRMS: calcd for $C_{21}H_{34}O_8Na^+$: 437.2151; found: 437.2159.

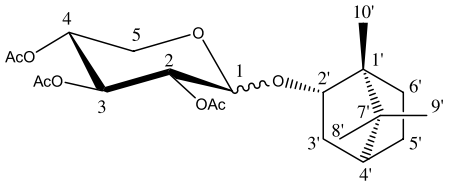


4.2.2. (1′*S*,2′*R*,5′*S*)-2′-(Prop-2-yl)-5′-methylcyclohexyl 2,3,4-triacetyl-D-xylopyranoside (3). White paste. Yield=45%; α/β=44/56. $R_f\alpha$ 0.49; $R_f\beta$ 0.39 (4:1 petroleum ether/EtOAc). IR (KBr): ν 2956, 1747. ^{1}H NMR ($CDCl_3$): δ 5.45 (t, 0.44H, $J_{2,3,4}$=9.8 Hz, H-3α), 5.17 (m, 0.56H, H-1α, H-3β), 4.96 (m, 1.56H, H-4α, H-2β, H-4β), 4.77 (dd, 0.44H, $J_{1,2}$=3.9 Hz, $J_{2,3}$=10.3 Hz, H-2α), 4.52 (d, 0.56H, $J_{1,2}$=7.4 Hz, H-1β), 4.14 (dd, 0.56H, $J_{5a,4}$=5.5 Hz, $J_{5a,5b}$=11.8 Hz, H-5aβ), 3.75 (m, 0.88H, H-5α), 3.38 (dt, 0.44H, $J_{1',6'}$=4.0 Hz, $J_{6',1',2'}$=10.6 Hz, H-1′α), 3.33 (m, 0.56H, H-5bβ), 3.30 (m, 0.56H, H-1′β), 2.24 (m, 0.44H, H-7′α), 2.15 (m, 0.56H, H-6′aβ), 2.08 (m, 0.56H, H-7′β), 2.05 (m, 19.8H, acetyls), 1.84 (m, 0.44H, H-6′aα), 1.65 (m, 0.88H, H-4′aα, H-3′aα), 1.63 (m, 0.56H, H-4′aβ), 1.61 (m, 0.56H, H-3′aβ), 1.37 (m, 0.56H, H-5′β), 1.35 (m, 0.44H, H-2′α), 1.30 (m, 0.44H, H-5′α), 1.22 (m, 0.56H, H-2′β), 1.06 (m, 0.56H, H-6′bβ), 0.95 (d, 1.32H, $J_{7',8'}$=7.0 Hz, H-8′α), 0.94 (m, 1H, H-3′b), 0.89 (m, 3H, H-10′), 0.88 (m, 1.68H, H-8′β), 0.83 (m, 0.44H, H-4′bα), 0.80 (m, 1H, H-6′bα, H-4′bβ), 0.77 (d, 1.32H, $J_{7,9}$=7.0 Hz, H-9′α), 0.75 (d, 1.68H, $J_{7',9'}$=7.1 Hz, H-9′β). ^{13}C NMR: δ 170.3 (2), 170.0 (2), 169.8, 169.3 (carbonyls), 102.3 (C-1β), 92.6 (C-1α), 82.3 (C-1′β), 77.3 (C-1′α), 72.1 (C-3β), 71.5 (C-2β), 71.1 (C-2α), 69.5 (2) (C-3α, C-4α), 69.0 (C-4β), 62.2 (C-5β), 58.6 (C-5α), 48.2 (C-2′β), 47.4 (C-2′α), 43.0 (C-6′β), 40.0 (C-6′α), 34.2 (C-4′α), 34.1 (C-4′β), 31.6 (C-5′β), 31.2 (C-5′α), 25.3 (C-7′α), 24.9 (C-7′β), 22.7 (C-3′β), 22.5 (C-3′α), 22.2 (C-10′β), 22.1 (C-10′α), 21.1 (C-8′α), 21.0 (C-8′β), 20.8 (3), 20.7 (2), 20.5 (acetyls), 15.8 (C-9′β), 14.9 (C-9′α). ESHRMS: calcd for $C_{21}H_{34}O_8Na^+$: 437.2151; found: 437.2148.

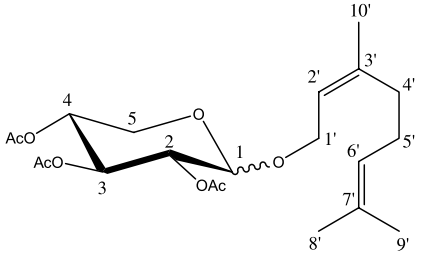


4.2.3. (1′*S*,2′*S*,4′*S*)-1′,7′,7′-Trimethylbicyclo[2.2.1]hept-2′-yl 2,3,4-triacetyl-D-xylopyranoside (4). White paste. Yield=42%; α/β=34/66. $R_f\alpha$ 0.42; $R_f\beta$ 0.32 (4:1 petroleum ether/EtOAc). IR (KBr): ν 2953, 1751. ^{1}H NMR ($CDCl_3$): δ 5.50 (t, 0.34H, $J_{2,3,4}$=9.8 Hz, H-3α), 5.16 (t, 0.66H, $J_{2,3,4}$=8.5 Hz, H-3β), 5.04 (d, 0.34H, $J_{1,2}$=3.7 Hz, H-1α), 4.94 (m, 1.66H, H-4α, H-2β, H-4β), 4.76 (dd, 0.34H, $J_{1,2}$=3.7 Hz, $J_{2,3}$=10.1 Hz, H-2α), 4.47 (d, 0.66H, $J_{1,2}$=6.7 Hz, H-1β), 4.12 (dd, 0.66H, $J_{4,5a}$=4.9 Hz, $J_{5a,5b}$=11.7 Hz, H-5aβ), 3.99 (d, 0.66H, $J_{2',3'}$=8.8 Hz, H-2′β), 3.76 (dd, 0.34H, $J_{4,5a}$=6.1 Hz, $J_{5a,5b}$=10.6 Hz, H-5aα), 3.76 (m, 0.34H, H-2′α), 3.69 (t, 0.34H, $J_{4,5b,5a}$=10.8 Hz, H-5bα), 3.34 (dd, 0.66H, $J_{4,5b}$=8.9 Hz, $J_{5a,5b}$=11.8 Hz, H-5bβ), 2.18 (m, 0.34H, H-3′aα), 2.13 (m, 0.66H, H-3′aβ), 2.10 (m, 0.34H, H-6′aα), 2.08 (m, 9H, acetyls), 1.90 (m, 0.34H, H-6′bα), 1.72 (m, 2H, H-5′), 1.66 (m, 1H, H-4′), 1.20 (m, 1.32H, H-6′β), 1.11 (m, 0.34H, H-3′bα), 0.91 (m, 0.66H, H-3′bβ), 0.86 (s, 1.98H, H-10′β), 0.85 (s, 1.98H, H-8′β), 0.84 (2s, 3H, H-8′α H-9′β), 0.83 (s, 1.02H, H-9′α), 0.80 (s, 1.02H, H-10′α). ^{13}C NMR: δ 170.5, 170.3 (2), 170.2, 170.0, 169.4 (carbonyls), 99.1 (C-1β), 97.2 (C-1α), 85.5 (C-2′α), 82.7 (C-2′β), 71.5 (C-2α), 71.4 (C-3β), 70.9 (C-2β), 69.9 (C-3α), 69.8 (C-4α), 69.0 (C-4β), 62.0 (C-5β), 58.6 (C-5α), 49.7 (C-7′α), 49.1 (C-7′β), 48.0 (C-1′β), 47.8 (C-1′α), 45.1

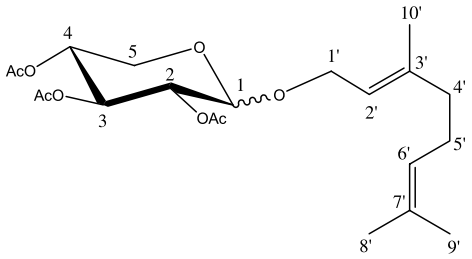
(C-4′α), 45.0 (C-4′β), 37.0 (C-3′α), 35.9 (C-3′β), 28.5 (C-5′β), 28.4 (C-5′α), 26.6 (C-6′α), 26.5 (C-6′β), 21.0, 20.9 (3), 20.8 (2) (acetyls), 19.8 (C-8′), 19.0 (C-9′β), 18.9 (C-9′α), 13.8 (C-10′α), 13.5 (C-10′β). ESHRMS: calcd for $C_{21}H_{32}O_8Na^+$: 435.1995; found: 435.2012.



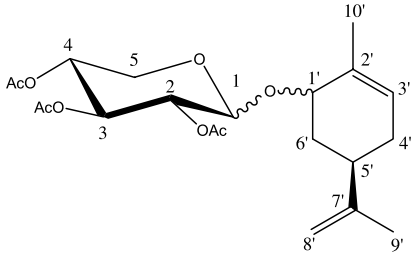
4.2.4. (2′*Z*)-3′,7′-Dimethyloct-2′,6′-dienyl 2,3,4-triacetyl-D-xylopyranoside (5). Colourless oil. Yield=34%; α/β=42/58. $R_f\alpha$ 0.39; $R_f\beta$ 0.31 (4:1 petroleum ether/EtOAc). IR (KBr): ν 2933, 1754. ^{1}H NMR ($CDCl_3$): δ 5.49 (t, 0.42H, $J_{2,3,4}$=9.8 Hz, H-3α), 5.28 (m, 1H, H-2′), 5.16 (t, 0.58H, $J_{2,3,4}$=8.7 Hz, H-3β), 5.07 (m, 1H, H-6′), 5.01 (d, 0.42H, $J_{1,2}$=3.6 Hz, H-1α), 4.94 (m, 1H, H-4α, H-4β), 4.91 (dd, 0.58H, $J_{1,2}$=6.9 Hz, $J_{2,3}$=8.6 Hz, H-2β), 4.81 (dd, 0.42H, $J_{1,2}$=3.6 Hz, $J_{2,3}$=10.2 Hz, H-2α), 4.51 (d, 0.58H, $J_{1,2}$=6.9 Hz, H-1β), 4.22 (dd, 0.58H, $J_{1'a,2'}$=5.6 Hz, $J_{1'a,1'b}$=12.0 Hz, H-1′aβ), 4.13 (m, 1.58H, H-1′aα, H-1′bβ, H-5aβ), 4.01 (dd, 0.42H, $J_{1'a,1'b}$=11.8 Hz, $J_{1'b,2'}$=7.6 Hz, H-1′bα), 3.78 (dd, 0.42H, $J_{4,5a}$=6.0 Hz, $J_{5a,5b}$=10.8 Hz, H-5aα), 3.65 (t, 0.42H, $J_{4,5b,5a}$=10.8 Hz, H-5bα), 3.34 (dd, 0.58H, $J_{4,5b}$=8.9 Hz, $J_{5a,5b}$=11.7 Hz, H-5bβ), 2.07 (m, 4H, H-4′, H-5′), 2.05 (m, 9H, acetyls), 1.76 (s, 3H, H-10′), 1.68 (s, 3H, H-8′), 1.60 (s, 3H, H-9′). ^{13}C NMR: δ 170.4 (2), 170.3, 170.2, 170.0, 169.6 (carbonyls), 142.0 (C-3′β), 141.8 (C-3′α), 132.3 (C-7′), 123.7 (C-6′), 120.5 (C-2′β), 120.4 (C-2′α), 99.2 (C-1β), 94.5 (C-1α), 71.7 (C-3β), 71.1 (C-2α), 71.0 (C-2β), 69.8 (C-3α), 69.7 (C-4α), 69.1 (C-4β), 65.1 (C-1′β), 64.0 (C-1′α), 62.1 (C-5β), 58.4 (C-5α), 32.3 (C-4′), 26.8 (C-5′β), 26.7 (C-5′α), 25.8 (C-8′), 23.7 (C-10′β), 23.6 (C-10′α), 20.9 (6) (acetyls), 17.8 (C-9′). ESHRMS: calcd for $C_{21}H_{32}O_8Na^+$: 435.1995; found: 435.1994.



4.2.5. (2′*E*)-3′,7′-Dimethyloct-2′,6′-dienyl 2,3,4-triacetyl-D-xylopyranoside (6). Colourless oil. Yield=36%; α/β=40/60. $R_f\alpha$ 0.38; $R_f\beta$ 0.28 (4:1 petroleum ether/EtOAc). IR (KBr): ν 2930, 1754. ^{1}H NMR ($CDCl_3$): δ 5.52 (t, 0.4H, $J_{2,3,4}$=9.9 Hz, H-3α), 5.30 (m, 1H, H-2′), 5.19 (t, 0.6H, $J_{2,3,4}$=8.6 Hz, H-3β), 5.11 (m, 1H, H-6′), 5.04 (d, 0.40H, $J_{1,2}$=3.6 Hz, H-1α), 4.97 (m, 1.6H, H-4α, H-2β, H-4β), 4.84 (dd, 0.4H, $J_{1,2}$=3.6 Hz, $J_{2,3}$=10.2 Hz, H-2α), 4.53 (d, 0.6H, $J_{1,2}$=6.9 Hz, H-1β), 4.27 (dd, 0.6H, $J_{1'a,2'}$=6.2 Hz, $J_{1'a,1'b}$=12.0, Hz, H-1′aβ), 4.17 (m, 1.6H, H-1′aα, H-1′bβ, H-5aβ), 4.07 (dd, 0.4H, $J_{1'b,2'}$=7.5 Hz, $J_{1'a,1'b}$=12.0 Hz, H-1′bα), 3.80 (dd, 0.4H, $J_{4,5a}$=5.9 Hz, $J_{5a,5b}$=10.8 Hz, H-5aα), 3.68 (t, 0.4H, $J_{4,5b,5a}$=10.8 Hz, H-5bα), 3.36 (dd, 0.6H, $J_{4,5b}$=8.9 Hz, $J_{5a,5b}$=11.8 Hz, H-5bβ), 2.09 (m, 4H, H-4′, H-5′), 2.07 (m, 9H, acetyls), 1.71 (s, 3H, H-8′), 1.68 (s, 3H, H-10′), 1.63 (s, 3H, H-9′). ^{13}C NMR: δ 170.4, 170.3, 170.2 (2), 170.0, 169.6 (carbonyls), 142.0 (C-3′β), 141.8 (C-3′α), 131.9 (C-7′), 123.9 (C-6′), 119.5 (C-2′), 99.1 (C-1β), 94.5 (C-1α), 71.7 (C-3β), 71.2 (C-2α), 71.0 (C-2β), 69.8 (C-3α), 69.6 (C-4α), 69.1 (C-4β), 65.2 (C-1′β), 64.3 (C-1′α), 62.2 (C-5β), 58.4 (C-5α), 39.7 (C-4′), 26.4 (C-5′), 25.8 (C-8′), 17.8 (C-9′), 17.8 (6) (acetyls), 16.6 (C-10′α), 16.5 (C-10′β). ESHRMS: calcd for $C_{21}H_{32}O_8Na^+$: 435.1995; found: 435.1985.



4.2.6. (1′*RS*,5′*R*)-2′-Methyl-5′-(prop-1-en-2-yl)cyclohex-2′-enyl 2,3,4-triacetyl-D-xylopyranoside (7). The product was obtained as a mixture of two (1′)-epimers. Colourless oil. Yield=16%; α/β=43/57. $R_f\alpha$ 0.41; $R_f\beta$ 0.32 (4:1 petroleum ether/EtOAc). IR (KBr): ν 2922 (alkyl), 1754 (ester). ^{1}H NMR ($CDCl_3$): δ 5.60 (m, 1H, H-3′), 5.50 (m, 0.43H, H-3α), 5.16 (m, 1H, H-1α, H-3β), 4.94 (m, 1.57H, H-4α, H-2β, H-4β), 4.80 (m, 0.43H, $J_{1,2}$=3.7 Hz, $J_{2,3}$=10.4 Hz, H-2α), 4.71 (m, 2H, H-8′), 4.64 (m, 0.57H, H-1β), 4.13 (m, 0.57H, H-5aβ), 3.94 (m, 1H, H-1′), 3.80 (m, 0.86H, H-5α), 3.37 (m, 0.57H, H-5bβ), 2.17 (m, 3H, H-5′ and H-4′ or H-6′), 2.06 (m, 9H, acetyls), 1.90 (m, 6H, H-9′, H-10′), 1.50 (m, 2H, H-4′ or H-6′). ^{13}C NMR: δ 170.5, 170.4, 170.2, 170.0, 169.5 (carbonyls), 149.4, 149.3, 148.8, 148.7 (C-2′), 134.6, 134.4, 131.9 (C-7′), 127.4, 126.8, 125.2, 125.0 (C-3′), 109.4, 109.3, 109.2, 108.8 (C-8′), 102.6, 98.2 (C-1β), 98.0, 93.8 (C-1α), 79.4, 76.9 (C-1′β), 80.9, 74.6 (C-1′α), 72.0, 71.6 (C-3β), 71.5, 71.3 (C-2α), 71.2, 70.9 (C-2β), 69.8, 69.6 (C-3α, C-4β), 69.1, 68.9 (C-4α), 62.2, 61.8 (C-5β), 58.8, 57.8 (C-5α), 40.8, 40.5, 35.2, 34.9 (C-5′), 36.4, 35.0, 33.9, 32.1, 30.7 (C-4′, C-6′), 21.6, 21.1, 20.5 (C-9′, C-10′), 21.0, 20.9, 20.8, 20.7 (acetyls). ESHRMS: calcd for $C_{21}H_{30}O_8Na^+$: 433.1838; found: 433.1841.



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