Stereoselective 1,4-Addition of Thiols to (2*E*)-4,6-Di-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose

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A thermodynamically controlled Michael-type 1,4-addition of 2-methyl-2-propanethiol and ethanethiol to (2*E*)-4,6-di-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**1**) in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) gives 3-alkylthio-2,3-dideoxy-*arabino*-hexopyranose (**4**) after deprotection with sodium methoxide.

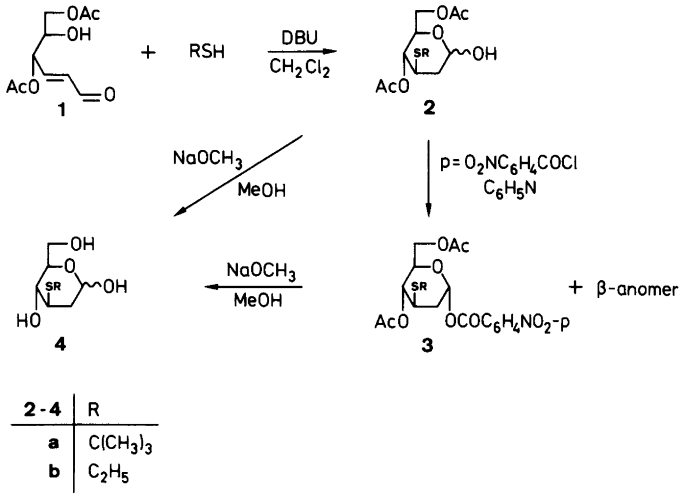
There has been considerable interest in 2,3-dideoxy-3-substituted carbohydrates. In particular, 3-amino sugars,[1] a component of several antibiotics, has been an attractive synthetic target, but other substituents at C-3 of 2,3-dideoxy pyranoses have been introduced as well. Thus, carbon-branched carbohydrates with different alkyl groups,[2] cyanomethyl,[3] aminomethyl,[4] nitromethyl[5] and hydroxymethyl[6] as well as formyl[7] and cyano[8] groups have been of interest.

Previously, we have reported the preparation of various 3-substituted-2,3-dideoxy pyranoses and furanoses by Michael-type addition of different nitrogen nucleophiles to α,β-unsaturated aldehydes. The addition of nitrogen nucleophiles was carried out either in a matrix of phosphorus pentaoxide, tributylamine and water in chloroform together with 2-deoxyribose creating an α,β-unsaturated aldehyde *in situ*[9] or, more recently, by using α,β-unsaturated carbohydrate aldehydes as the substrates.[10] In some instances the resulting products proved to be interesting new precursors for the synthesis of various 3′-amino-2′,3′-dideoxy nucleosides with potential antiviral activity.[10] For this reason and the fact that the application of α,β-unsaturated carbohydrates in this type of reaction has received very little attention, we decided to gain a better insight into this area by using other nucleophiles.

In this investigation we report the stereoselective 1,4-addition of thiols to the α,β-unsaturated carbohydrate aldehyde (2*E*)-4,6-di-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose[10a,11] (**1**) to produce 2,3-dideoxy-3-alkylthio-D-*arabino*-hexopyranoses (**4**) after deprotection of the hydroxy groups.

Results and discussion

Dropwise addition of a solution of α,β-unsaturated aldehyde **1** in dichloromethane at 0 °C to a solution of 2-



2-4	R
a	$C(CH_3)_3$
b	C_2H_5

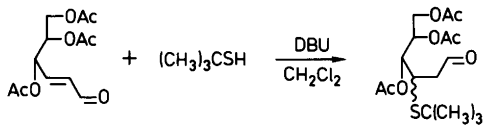
Scheme 1.

methyl-2-propanethiol and DBU in dichloromethane resulted in 1,4-addition of the thiol to produce the *arabino* isomer **2a** in 94 % crude yield; a 65 % yield of an analytically pure product was obtained after recrystallization from ethanol/water (2:1).

When the less bulky ethanethiol was used as the nucleophile, **2b** was obtained in 82 % purified yield after flash chromatography. The NMR spectrum of the crude 1,4-adduct showed the *arabino*/*ribo* ratio to be 10:1 for **2a** and 15:1 for **2b**. In a similar reaction with phthalimide together with one equivalent of DBU, and acetyl migration from 4-*O* to 5-*O* during the reaction resulted in ring closure to give the furanose forms.[10a] Different ratios of alkanethiol and DBU were tried in order to investigate the possibility of an acetyl migration, but no appreciable migration was ever observed.

In order to confirm the *arabino* configuration of the products, compounds **2** were *p*-nitrobenzoylated at the anomeric center to give **3** which for **3b** could be isolated as pure α-anomer with a simplified ^{1}H NMR spectrum. The unprotected 2,3-dideoxy-3-alkylthio-D-*arabino*-hexopyranoses **4** were either obtained by deprotection with sodium methoxide in methanol of compounds **3** or directly from the hemiacetals **2**.

The coupling pattern of the proton NMR spectrum clearly showed all structures possessing $^4C_1$-conformation with all substituents except the anomeric orientated equatorially. For instance, the ^{1}H NMR spectrum of **3b** showed a triplet (*J* 10.6 Hz) at 5.05 ppm from 4-H and a triplet of doublets (*J* 10.6, 4.2 Hz) at 3.19 ppm from 3-H in accordance with an *arabino* configuration with $^4C_1$ conformation. In order to verify whether the stereoselective formation of **2** was of thermodynamic origin we performed the 1,4-addition of 2-methyl-2-propanethiol to the tri-*O*-acetyl α,β-unsaturated aldehyde **5**[12] obtained by acetylation of **1**. In this case the 1,4-adduct of **5** could not undergo ring closure and a nearly 1:1 mixture of the *ribo* and *arabino* isomers of **6** was isolated. Thus, the highly stereoselective formation of **2** must be reversible and thermodynamically controlled.



5 **6**

Scheme 2.

Experimental

NMR spectra were recorded on a Bruker AC 250 FT NMR spectrometer at 250 MHz for ^{1}H NMR and 62.5 MHz for ^{13}C NMR spectroscopy. Microanalyses were carried out at NOVO Microanalytical Laboratory A/S, Novo Allé, DK-2880 Bagsværd. EI mass spectra were recorded on a Varian MAT 311 A spectrometer.

4,6-Di-O-*acetyl-3*-tert-*butylthio-2,3-dideoxy*-D-arabino-*hexopyranose* (**2a**). 2-Methyl-2-propanethiol (2.30 g, 26.0 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.00 g, 13.1 mmol) were dissolved in dichloromethane (60 ml) and cooled to 0 °C. (2*E*)-4,6-di-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose (**1**)[10a,11] (3.00 g, 13.00 mmol) dissolved in dichloromethane (30 ml) was added dropwise over 1 h at 0 °C. After 4 h at 0 °C and 1 h at room temperature the reaction mixture was washed with ice-cold 1 M sulfuric acid (3×25 ml), a saturated solution of sodium hydrogen carbonate (25 ml) and water (25 ml). After drying of the organic phase over magnesium sulfate the solvent was removed at reduced pressure to give crude **2a** as a white solid. Yield 3.90 g (94 %). Recrystallization from 96 % ethanol/water (v/v = 2:1) gave an analytically pure compound, α:β ratio = 4:1 in $CDCl_3$. Yield 2.70 g (65 %), m.p. 138–140 °C. ^{1}H NMR ($CDCl_3$): δ 5.30 (br s, 1α-H), 4.84 (td, 1β-H), 4.75 (t, *J* 11.0 Hz, 4α-H), 4.71 (t, *J* 11.0 Hz, 4β-H), 4.23–4.02 (m, 6α-H, 6β-H, 5α-H), 3.70–3.61 (m, 5β-H), 3.15 (ddd, *J* 13.0, 11.0, 4.5 Hz, 3α-H), 2.75 (ddd, *J* 12.9, 11.0, 4.5 Hz, 3β-H), 2.32 (ddd, 2β-H^a), 2.23 (dd, *J* 13.0, 4.5 Hz, 2α-H^e), 1.93 (dt, *J* 13.0, 2.7 Hz, 2α-H^a), 1.78 (dd, 2β-H^e). ^{13}C NMR ($CDCl_3$): α-anomer, δ 170.91 (C=O), 169.71 (C=O), 91.06 (C-1), 69.50 (C-4), 69.28 (C-5), 63.17 (C-6), 43.62 [*C*(CH_3)$_3$], 40.43 (C-3), 38.28 (C-2), 31.16 (CH_3), 20.83 (CH_3), 20.83 (CH_3), 20.69 (CH_3). β-anomer, δ 170.62 (C=O), 169.66 (C=O), 94.88 (C-1), 74.94 (C-4), 68.77 (C-5), 63.06 (C-6), 43.62 [*C*(CH_3)$_3$], 42.84 (C-3), 41.58 (C-2), 31.07 (CH_3), 20.83 (CH_3), 20.69 (CH_3). MS [*m*/*z* (% rel. int.)]: 320 (M^+, 5.7 %), 200 (45), 187 (23), 185 (24), 171 (18), 144 (100), 131 (59), 111 (23), 103 (22). Anal. ($C_{14}H_{24}O_6S$): C, H.

4,6-Di-O-*acetyl-2,3-dideoxy-3-ethylthio*-D-arabino-*hexopyranose* (**2b**). Ethanethiol (1.50 g, 24.1 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (0.40 g, 2.6 mmol) were dissolved in dichloromethane (150 ml) and cooled to −5 °C. (2*E*)-4,6-*O*-acetyl-2,3-dideoxy-*aldehydo*-D-*erythro*-hex-2-enose **1**[10a,11] (3.00 g, 13.0 mmol) dissolved in dichloromethane (100 ml) was added dropwise over 30 min at −5 °C. After 1 h at −5 °C and 2 h at room temperature the reaction mixture was washed with ice-cold 1 M sulfuric acid (3.50 ml), a saturated solution of sodium hydrogen carbonate (50 ml) and water (50 ml). After being dried over anhydrous magnesium sulfate, the organic phase was concentrated to a yellow oil (3.9 g) under reduced pressure. The crude oil was purified by flash chromatography (Merck silica 230–400 mesh, 3.5×45 cm, dichloromethane/methanol (v/v = 95:5)) to give **2b** as an oil. Yield 3.1 g (82 %). α:β ratio = 3:1 in $CDCl_3$. ^{1}H NMR ($CDCl_3$): δ 5.32–5.35 (m, 1α-H, 1β-H), 4.86 (t, *J* 10.6 Hz, 4α-H), 4.83 (t, *J* 10.6 Hz, 4β-H), 4.28–4.03 (m, 5α-H, 6α-H, 6β-H), 3.65 (ddd, *J* 10.6, 5.6, 2.6 Hz, 5β-H), 3.18 (ddd, *J* 13.5, 10.6, 4.3 Hz, 3α-H), 2.80 (ddd, *J* = 13.3, 10.6, 4.3 Hz, 3β-H), 2.57 (q, *J*

7.5 Hz, CH_2), 2.37–2.30 (m, 2β-H), 2.22 (dd, *J* 13.5, 4.3 Hz, 2α-H^e), 2.11 (s, CH_3), 2.09 (s, CH_3), 1.91 (td, *J* 13.5, 3.4 Hz, 2α-H^a), 1.83–1.71 (m, 2β-H), 1.22 (t, *J* 7.5 Hz, CH_3). ^{13}C NMR ($CDCl_3$): α-anomer, δ 170.89 (C=O), 169.80 (C=O), 90.86 (C-1), 69.73 (C-4), 68.94 (C-5), 62.98 (C-6), 40.58 (C-3), 37.11 (C-2), 23.89 (CH_2), 20.87 (CH_3), 20.59 (CH_3), 14.59 (CH_3). β-anomer, δ 170.83 (C=O), 169.76 (C=O), 95.02 (C-1), 74.48 (C-4), 68.94 (C-5), 62.90 (C-6), 43.80 (C-3), 39.20 (C-2), 23.51 (CH_2), 30.87 (CH_3), 20.59 (CH_3), 14.45 (CH_3). MS [*m/z* (% rel. int.)] 292 (M^+, 1), 172 (100), 159 (99), 143 (38), 103 (23). Anal. ($C_{12}H_{20}O_6S$): C, H.

*4,6-Di-*O*-acetyl-3-*tert*-butylthio-2,3-dideoxy-1-*O*-p-nitrobenzoyl-*D*-arabino-hexopyranose* (**3a**). **2a** (1.05 g, 3.28 mmol) was dissolved in dry pyridine (30 ml) and cooled to 0 °C. *p*-Nitrobenzoyl chloride (0.61 g, 3.29 mmol) was added and the reaction mixture was stirred for 4 h during which time, the temperature was gradually increased to 20 °C. The reaction mixture was diluted with dichloromethane (100 ml) and washed with ice-cold 1 M sulfuric acid (3×50 ml) and then with a saturated solution of sodium hydrogencarbonate (50 ml) and finally with water (50 ml). The organic phase was dried over anhydrous magnesium sulfate and then concentrated under reduced pressure. Yield 1.40 g (91 %). Flash chromatographic purification [Merck silica 230–400 mesh, 3.5×40 cm, dichloromethane/methanol (v/v = 95:5)] gave **3a** as a white hygroscopic foam. Yield 0.85 g (55 %). α:β ratio = 8:3. ^{1}H NMR ($CDCl_3$): δ 8.22 (m, arom.), 6.42 (d, *J* 2.1 Hz, 1α-H), 6.02 (dd, *J* 9.0, 2.0 Hz, 1β-H), 4.92 (t, *J* 10.5 Hz, 4α-H), 4.84 (t, *J* 10.0 Hz, 4β-H), 4.29 (dd, *J* 11.9, 4.3 Hz, 6β-H), 4.27 (dd, *J* 11.9, 4.3 Hz, 6α-H), 4.15–4.04 (m, 5α-H, 6α-H, 6β-H), 3.88–3.83 (m, 5β-H), 3.14 (ddd, *J* 14.5, 10.5, 4.5 Hz, 3α-H), 2.88 (ddd, *J* 14.5, 10.0, 4.5 Hz, 3β-H), 2.44 (dd, *J* 14.5, 4.5 Hz, 2α-H^e), 2.22 (td, *J* 14.5, 2.1 Hz, 2α-H^a). 2β-H protons are hidden behind 2α-H protons. ^{13}C NMR ($CDCl_3$): α-anomer, δ 170.58 (C=O), 169.31 (C=O), 162.61 (C=O), 150.74 (arom.), 134.88 (arom.), 130.62 (arom.), 123.70 (arom.), 92.60 (C-1), 72.41 (C-4), 68.23 (C-5), 62.41 (C-6), 43.68 [*C*(CH_3)$_3$], 39.03 (C-3), 38.70 (C-2), 31.17 (CH_3), 20.74 (CH_3), 20.60 (CH_3). β-anomer 170.58 (C=O), 169.44 (C=O), 162.61 (C=O), 150.74 (arom.), 134.43 (arom.), 131.00 (arom.), 123.46 (arom.), 93.23 (C-1), 75.84 (C-4), 68.23 (C-5), 62.53 (C-6), 43.87 [*C*(CH_3)$_3$], 41.05 (C-3), 39.55 (C-2), 31.17 (CH_3), 20.74 (CH_3), 20.63 (CH_3). MS [*m/z* (% rel. int.)] 469 (M^+, 1), 349 (13), 187 (10), 185 (20), 150 (38), 127 (10), 126 (34), 113 (11), 57 (100), 43 (56). Peak matching on M^+. Calc. for $C_{19}H_{23}NO_9S$: 469.1404. Found: 469.1406.

*4,6-Di-*O*-acetyl-2,3-dideoxy-3-ethylthio-1-*O*-p-nitrobenzoyl-*D*-arabino-hexopyranose* (**3b**). **2b** (4.20 g, 14.4 mmol) was dissolved in dry pyridine (25 ml) and cooled to 0 °C. *p*-Nitrobenzoyl chloride (2.70 g, 15.0 mmol) was added and the reaction mixture was stirred for 3.5 h at 25 °C. The reaction mixture was diluted with dichloromethane (150 ml), washed with ice-cold 1 M sulfuric acid (3×50 ml) and then with a saturated solution of sodium hydrogencarbonate (50 ml) and finally with water (50 ml). After being dried over anhydrous magnesium sulfate, the organic phase was concentrated to a yellow oil which crystallized as a mixture of α- and β-anomers of **3b** on addition of dry diethyl ether. Yield 5.3 g (83 %). Recrystallization from 96 % ethanol gave the analytically pure α-isomer, m.p. 125–127 °C. ^{1}H NMR ($CDCl_3$): δ 8.35 (d, *J* 8.7 Hz, arom), 8.24 (d, *J* 8.7 Hz, arom.), 6.48 (br s, 1-H), 5.05 (t, *J* 10.6 Hz, 4-H), 4.30 (dd, *J* 12.3, 4.3 Hz, 6-H), 4.12–4.04 (m, 5-H, 6-H), 3.19 (ddd, *J* 14.3, 10.6, 4.0 Hz, 3-H), 2.57–2.65 (m, CH_2), 2.43 (dd, *J* 14.3, 4.0 Hz, 2-H^e), 2.22 (td, *J* 14.3, 2.8 Hz, 2-H^a), 2.14 (s, CH_3), 2.01 (s, CH_3), 1.25 (t, 7.4 Hz, CH_3). ^{13}C NMR ($CDCl_3$): δ 170.35 (C=O), 169.46 (C=O), 162.51 (C=O), 150.60 (arom.), 134.70 (arom.), 130.63 (arom.), 123.48 (arom.), 93.32 (C-1), 71.81 (C-4), 68.52 (C-5), 62.19 (C-6), 40.87 (C-3), 35.58 (C-2), 23.52 (CH_2), 20.46 (2×CH_3), 14.36 (CH_3). MS-FAB [*m/z*, sulf. H_2O, NaCl] 464 (M + Na^+, 2 %). Anal. ($C_{19}H_{23}NO_9S$): C, H, N.

*3-*tert*-Butylthio-2,3-dideoxy-*D*-arabino-hexopyranose* (**4a**). *From* **3a**. Freshly cut sodium (10 mg) was treated with anhydrous methanol (10 ml) whereupon **3a** (0.40 g, 0.85 mmol) was added. After 2 h at room temperature analytical TLC showed all compounds to be totally deprotected. The reaction mixture was treated with carbon dioxide and the solvent removed under reduced pressure. The crude product was then purified by flash chromatography [Merck silica 230–400 mesh, 2×40 cm, dichloromethane/methanol (v/v = 95:5)] to give **4a** as a white solid. Yield 0.20 g (99 %), m.p. 153–154 °C. α:β ratio = 1:6 in $(CD_3)_2SO$.

From **2a**. **2a** (1.0 g, 3.12 mmol) was deprotected using the procedure described for the deprotection of **3a**. Yield 0.61 g (83 %). ^{1}H NMR [$(CD_3)_2SO$]: β-anomer, δ 6.49 (d, *J* 5.4 Hz, 1-H), 4.80 (4-OH), 4.67 (1-OH), 4.46 (6-OH), 3.65 (dd, *J* 11.3, 5.1 Hz, 6-H), 3.46 (td, *J* 11.3, 5.7 Hz, 6-H), 3.19 (dd, *J* 5.7, 5.1 Hz, 5-H), 2.86 (td, *J* 12.0, 5.7 Hz, 4-H), 2.65 (td, *J* 12.0, 3.9 Hz, 3-H), 2.04 (dd, *J* 13.0, 3.9 Hz, 2-H^e), 1.43 (dd, *J* 13.0, 12.0 Hz, 2-H^a), 1.29 (s, CH_3). ^{13}C NMR [$(CD_3)_2SO$]: β-anomer, δ 93.93 (C-1), 79.31 (C-4), 68.57 (C-5), 61.59 (C-6), 43.56 (C-2), 42.99 [*C*(CH_3)$_3$], 31.40 (3×CH_3). α-anomer, δ 89.51 (C-1), 73.67 (C-4), 68.88 (C-5), 61.59 (C-6), 42.87 [*C*(CH_3)$_3$], 41.57 (C-3), 41.40 (C-2), 31.40 (3×CH_3). MS [*m/z*, % rel. int.] 236 (M^+, 82), 163 (18), 162 (56), 146 (35), 131 (24), 129 (100), 119 (47), 101 (47). Peak matching on M^+. Calc. for $C_{10}H_{20}O_4S$: 236.1082. Found: 236.1075.

*2,3-Dideoxy-3-ethylthio-*D*-arabino-hexopyranose* (**4b**). *From* **3b**. Freshly cut sodium (30 mg) was treated with absolute methanol (30 ml) whereupon **3b** (1.00 g, 2.27 mmol) was added. After 3.5 h at room temperature analytical TLC showed all compounds to be totally deprotected. The reaction mixture was treated with carbon dioxide and the solvent removed at reduced pressure. Flash chroma-

tographic purification [Merck silica 230–400 mesh, 2×40 cm, dichloromethane/methanol (v/v = 80:20)] gave **4b** as a white solid. Yield 0.45 g (95 %), m.p. 102–103 °C. α:β ratio = 3:5 in $(CD_3)_2SO$.

From **2b**. 1.00 g (3.42 mmol) was deprotected using the procedure described for the deprotection of **3b**. Yield 0.74 g (81 %). ^{1}H NMR [$(CD_3)_2SO$]: δ 6.55 (d, *J* 6.5 Hz, 1β-H), 6.21 (d, *J* 3.6 Hz, 1α-H), 5.08 (d, OH), 4.96 (d, *J* 6.0 Hz, OH), 4.95 (d, *J* 6.7 Hz, OH), 4.49 (t, *J* 6.0 Hz, OH), 4.37 (t, *J* 5.6 Hz, OH), 3.75–3.40 (m, 5α-H, 6α-H, 6β-H), 3.20–2.90 (m, 3α-H, 4α-H, 4β-H, 5β-H), 2.75–2.50 (m, CH_2, 3β-H), 2.00 (ddd, *J* 12.6, 2.5, 1.0 Hz, 2β-H^e), 1.90 (dd, *J* 12.6, 4.2 Hz, 2α-H^e), 1.53 (td, *J* 12.6, 3.0 Hz, 2α-H^a), 1.38 (td, *J* 12.6, 9.4 Hz, 2β-H^a), 1.16 (t, *J* 7.4 Hz, CH_3). ^{13}C NMR [$(CD_3)_2SO$]: α-anomer, δ 94.19 (C-1), 79.26 (C-4), 70.28 (C-5), 61.35 (C-6), 45.91 (C-3), 39.87 (C-2), 23.97 (CH_2), 14.97 (CH_3). β-anomer, δ 99.49 (C-1), 73.49 (C-4), 70.80 (C-5), 61.35 (C-6), 42.69 (C-3), 37.89 (C-3), 23.97 (CH_2), 14.97 (CH_3). MS [*m/z* rel. int.] 208 (M^+, 100), 159 (31), 147 (78), 146 (35), 129 (63), 118 (88), 117 (27), 104 (57). Peak matching on M^+. Calc. for $C_8H_{16}O_4S$: 208.0769. Found: 208.0762. Anal. ($C_8H_{16}O_4S$): C, H.

*4,5,6-Tri-*O*-acetyl-3-*tert*-butylthio-2,3-dideoxy*-aldehydo-D-*hexose* (**6**). **5**[12] (3.0 g, 13.0 mmol) was dissolved in dichloromethane (30 ml) and dropwise added over 1 h to a solution of 2-methyl-2-propanethiol (2.30 g, 26.0 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.00 g, 13.1 mmol) in dichloromethane (60 ml) cooled to 0 °C. After 3 h at 0 °C and 1 h at room temperature, the reaction mixture was washed with ice-cold 1 M sulfuric acid (3×25 ml), saturated sodium hydrogencarbonate (25 ml) and water (25 ml). After drying of the organic phase over magnesium sulfate, the solvent was removed under reduced pressure. Flash chromatographic purification [Merck silica 230–400 mesh, 3×40 cm, diethyl ether/hexane (v/v = 1:1)] gave a nearly 1:1 mixture of the *arabino* and *ribo* isomers of **6** as an oil. Yield 1.9 g (40 %). ^{13}C NMR ($CDCl_3$) 199.37, 199.10 (C-1), 170.42, 170.28, 169.76, 169.71, 169.52, 169.38 (OAc), 73.77, 72.33 (C-4), 70.43, 70.10 (C-5), 62.00, 61.57 (C-6), 48.66, 45.43 (C-3), 44.22, 43.69 [$C(CH_3)_3$], 36.74, 36.20 (C-2), 30.98, 30.68 [$C(CH_3)_3$], 20.91, 20.52 (OAc). Anal. ($C_{16}H_{26}O_7S$): C, H.

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