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Preparation of cellulose oligomers from cellulose triacetate (standard procedure)

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Abstract

This communication reports the detailed procedure for the cleavage of cellulose triacetate (30 g scale) with pivalic anhydride and boron trifluoride etherate in dichloromethane (*pivaloylysis*). With this mild and efficient method the cellulose oligomers up to the octasaccharide can be obtained in gram scale. Full characteristic data of this compounds are given.

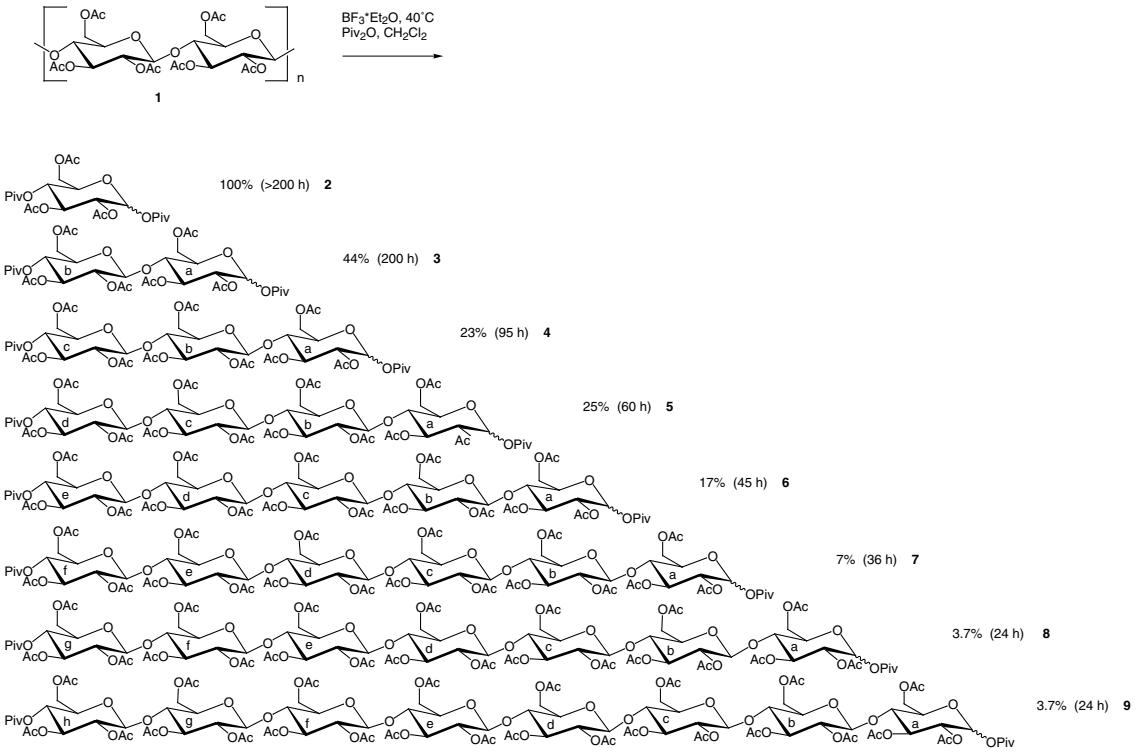
Introduction

As reported before (Redlich et al. 2003) a mild and efficient method for the cleavage of cellulose triacetate has been developed. The most common acylysis methods like using acetic anhydride with additives of solvents and sulphuric acid or *Lewis* acids as catalyst (Franchimont et al. 1879; Wolfrom et al. 1949 and 1952; Lemieux et al. 1955; Lichtenthaler et al. 1971; Dasgupta et al. 1988) are very aggressive and applied on carbohydrates may lead to undesired degradation products. The purification and separation of such reaction mixtures often is troublesome.

Standard procedure for the acylysis (pivaloylysis) of cellulose triacetate

The milder alternative using pivalic anhydride/boron trifluoride etherate in dichloromethane at 40 °C for the acylysis of cellulose triacetate 1 offers an easy access to products up to the hexamer **(2–7)** which can be separated easily by preparative liquid chromatography. Further on the higher oligomers **8–9** are separated by preparative high performance liquid chromatography (HPLC). The procedure described here is very specific for cellulose triacetate. The comparable amylose triacetate with α-linkages is not attached by this system (in a macroscopic view). It has to be pointed out, that all chemical manipulations in the pivaloylysis have to be carried out under strict exclusion of moisture, including the preparation of the cellulose triacetate and the qualities of the reagents and solvent (see experimental part). The pivaloylysis, properly carried out, shows no browning of the reaction mixtures. Depending on the reaction time each cellulose oligomer shows a maximum yield after a specific time (scheme 1).

The experimental details given in the experimental part are elaborated for a medium reaction time of 48 h. Longer reaction times will enhance the amount of short-chain oligomers, shorter reaction times will lead to higher amounts of the longer oligomers. Under the latter conditions we



Scheme 1. Pivaloylysis of cellulose triacetate 1.

could identify and separate by a HPLC intact oligomers up to the tetradecamer.

Experimental

All reactions were monitored by tlc on silica gel (Merck, GF_{254}) using mixtures of ethyl acetate and cyclohexane. All solvents were distilled. Detection was carried out by UV-absorptions, reaction with 0.2% ethanolic naphthoresorcine solution/ $2NH_2SO_4$ (1:1) and heating. Separations were carried out by preparative column chromatography on silica gel 60 (0,063–0,200 mm) at 0.2–0.4 mPa using solvent mixtures mentioned above. Preparative high performance liquid chromatography (HPLC) was carried out with Knauer HPLC equipment (Knauer WellChrom K1000 Maxi-Star or Knauer WellChrom preparative pump K1800, column: Merck LiChrosorb Si-60 (7 μm) 250×25 mm, Merck LiChrospher Si-60 (5 μm) 250×4 mm or Knauer Eurosphere Si-100 (7 μm) 250×40 mm, detection: analytical or preparative differential refractometer, Knauer). Melting points were measured on an electrothermal melting point apparatus and are not corrected. Optical rotations were measured on a Perkin-Elmer polarimeter 241 or 341 using 1 dm cells. Elemental analyses were carried out with a CHN-RAPID of Hereaus. Mass spektra were measured after MALDI-TOF method (Matrix Assisted Laser Desorption Ionisation-Time of Flight; Lazarus II, III or III DE, self-construction: Dr. H. Luftmann, Organisch-Chemisches Institut der Westfälischen Wilhelms-Universität Münster).

*Preparation of 2,3,6-Tri-O-acetyl-cellulose **1** (Tanghe et al. 1964)*

Cellulose acetate (Aldrich, 39.8 wt% acetyl content, average M_n = 30,000 (GPC)) was dried at 110 °C in the oven. Thirty grams of dried cellulose acetate was dissolved in 540 ml acetic acid, 60 ml acetic anhydride and 2.1 ml 72% perchloric acid. The solution was stirred for 2 h and slowly poured

into 2.5 l of water. The fully acetylated cellulose precipitated and was collected by filtration. The raw material was washed several times with sat. sodium hydrogen carbonate solution and water, filtered and washed again until the filtrate was neutral. The polymer was dried at 50 °C under vacuum to yield **1**.

Yield: 31.2 g, colorless solid

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.00 (dd, 1 H, J (3,2) = 8.6, J (3,4) = 9.2, H-3), 4.72 (dd, 1 H, J (2,1) = 8.0, J (2,3) = 8.6, H-2), 4.35 (d, 1 H, J (1,2) = 8.0, H-1), 4.23–4.44 (m, 1 H, H-6), 3.91–4.07 (m, 1 H H-6), 3.64 (dd, 1 H, J (4,3) = 9.2, J (4,5) = 9.2, H-4), 3.41–3.54 (m, 1 H, H-5), 2.05, 1.94, 1.88 (3 × s, 3 × 3H, $OCOCH_3$).

To obtain predominately the cellulose oligomers **3–7** medium reaction time (48 h) was chosen.

*Pivaloylysis of 2,3,6-Tri-O-acetyl-cellulose **1***

Under argon atmosphere 30 g (0.104 M) of carefully dried 2,3,6-tri-*O*-acetyl-cellulose **1** is dissolved in 2.5 l abs. dichloromethane. To the solution 995 ml (4.9 M, 47 eq) pivalic anhydride is dropped over a period of 30 min. Then 200 ml (1.59 mM, 15 eq) boron trifluoride etherate is added and the reaction mixture is warmed to 40 °C. The reaction is controlled by tlc (cyclohexane/ethyl acetate 1/1). After 48 h the reaction is quenched with sat. sodium hydrogen carbonate solution. The aqueous layer is extracted several times with dichloromethane. The combined organic layers are dried with sodium sulphate, filtered and the remaining solvent is reduced in high vacuo. The separation of the different pivaloylysis products 2–6 can be done by preparative liquid chromatography (silica gel 60, 0.063–0.200 mm, 1,5 kg). At the beginning of the separation the column is conditioned with cyclohexane (500 ml). The monosaccharide **2** is eluted with cyclohexane/ethyl acetate 5/1, the disaccharide **3** with cyclohexane/ethyl acetate 3/1, the trisaccharide **4** with cyclohexane/ethyl acetate 2/1 and the tetra-, penta- and hexasaccharide **5–7** (in this order) with cyclohexane/ethyl acetate 1/1. The remaining higher homologues are eluted with ethyl acetate and can be separated by preparative high performance liquid chromatography (HPLC).

Yields: 7.55 g (15.3%) **2**, 7.90 g (19.9%) **3**, 5.3 g (14.5%) **4**, 3.67 g (10.5%) **5**, 3.83 g (11.3%) **6**, 2.4 g (4.3%) **7**

HPLC: 1.15 g (3.5%) **8**, 1.13 g (3.5%) **9**

The data for the different anomers were obtained by analysis of different anomeric mixtures. The assignment for the different ring protons (a–h) was made by ^{1}H–^{1}H-COSY spectra (360 MHz, $CDCl_3$).

*2,3,6-Tri-O-acetyl-1,4-di-O-pivaloyl-α-D-glucopyranose **2**α*

colorless syrup (α:β = 23:1), $[\alpha]_D^{20}$ = + 64.6° (c = 1.0, $CHCl_3$), R_f = 0.59 (cyclohexane/ethyl acetate 1/1)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.35 (d, 1 H, J (1,2) = 3.6, H-1), 5.51 (dd, 1 H, J (3,2) = 9.6, J (3,4) = 10.0, H-3), 5.15 (dd, 1 H, J (4,3) = 10.0, J (4,5) = 10.0, H-4), 5.10 (dd, 1 H, J (2,1) = 3.6, J (2,3) = 9.6, H-2), 4.20 (dd, 1 H, J (6,5) = 4.8, J (6,6′) = 12.4, H-6), 4.04–4.13 (m, 2 H, H-5, H-6′), 2.08, 2.01, 1.99 (3 × s, 3 × 3H, $OCOCH_3$), 1.30, 1.19 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.78, 176.07 ($OCOC(CH_3)_3$), 170.44, 169.70, 169.47 ($OCOCH_3$), 88.96 (C-1), 70.40, 69.76, 69.49, 67.33 (C-5, C-4, C-3, C-2), 61.50 (C-6), 39.23, 38.82 ($OCOC(CH_3)_3$), 26.99, 26.83 ($OCOC(CH_3)_3$), 20.59, 20.59, 20.29 ($OCOCH_3$) ppm.

*2,3,6-Tri-O-acetyl-1,4-di-O-pivaloyl-β-D-glucopyranose **2**β*

colorless crystals (α:β = 1:14), $[\alpha]_D^{20}$ = +9.0 ° (c = 0.1, $CHCl_3$), mp = 127.1 °C, R_f = 0.59 (cyclohexane/ethyl acetate 1/1)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.68 (d, 1 H, J (1,2) = 8.4, H-1), 5.31 (dd, 1 H, J (3,2) = 9.6, J (3,4) = 9.8, H-3), 5.17 (dd, 1 H, J (2,1) = 8.4, J (2,3) = 9.6, H-2), 5.15 (dd, 1 H, J (4,3) = 9.8, J (4,5) = 10.0, H-4), 4.23 (dd, 1 H, J (6,5) = 4.8, J (6,6′) = 12.8, H-6), 4.09 (dd, 1 H, J (6′,5) = 2.0, J (6′,6) = 12.8, H-6′), 3.84 (ddd, 1 H, J (5,4) = 10.0, J (5,6′) = 2.0, J (5,6) = 4.8, H-5), 2.08, 2.00, 1.99 (3 × s, 3 × 3H, $OCOCH_3$), 1.20, 1.16 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.80, 176.44 ($OCOC(CH_3)_3$), 170.55, 169.80, 169.10 ($OCOCH_3$), 91.83 (C-1), 72.99, 70.38, 70.33, 67.53 (C-5, C-4, C-3, C-2), 61.53 (C-6), 38.82, 38.76

($OCOC(CH_3)_3$), 26.90, 26.72 ($OCOC(CH_3)_3$), 20.69, 20.49, 20.44 ($OCOCH_3$) ppm.

$C_{22}H_{34}O_{11}$ (474.21) MS (NH_3-DCI): m/z = 492 ($[M_r + NH_4^+$)

Calcd. C 55.69%, H 7.22%

Found C 55.88%, H 7.22%

4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-α-D-glucopyranose ***3α***

colorless syrup, $[\alpha]_D^{20}$ = + 29.0° (*c* = 0.2, $CHCl_3$), R_f = 0.47 (cyclohexane/ethyl acetate 1/1)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.27 (d, 1 H, *J* (1a,2a) = 3.6, H-1a), 5.41 (dd, 1 H, *J* (3a,2a) = 9.6, *J* (3a,4a) = 9.6, H-3a), 5.20 (dd, 1 H, *J* (3b,2b) = 9.4, *J* (3b,4b) = 9.6, H-3b), 5.10 (dd, 1 H, *J* (4b,3b) = 9.6, *J* (4b,5b) = 9.6, H-4b), 5.02 (dd, 1 H, *J* (2a,1a) = 3.6, *J* (2a,3a) = 9.6, H-2a), 4.93 (dd, 1 H, *J* (2b,1b) = 8.0, *J* (2b,3b) = 9.4, H-2b), 4.55 (d, 1 H, *J* (1b, 2b) = 8.0, H-1b), 4.51 (dd, 1 H, *J* (6a,5a) = 2.0, *J* (6a,6′a) = 12.4, H-6a), 4.31 (dd, 1 H, *J* (6b,5b) = 4.4, *J* (6b,6′b) = 12.4, H-6b), 4.10 (dd, 1 H, *J* (6′a,5a) = 4.4, *J* (6′a,6a) = 12.4, H-6′a), 4.04 (dd, 1 H, *J* (6′b,5b) = 1.6, *J* (6′b,6b) = 12.4, H-6′b), 3.97 (ddd, 1 H, *J* (5a,4a) = 9.6, *J* (5a,6′a) = 4.4, *J* (5a,6a) = 2.0, H-5a), 3.79 (dd, 1 H, *J* (4a,3a) = 9.6, *J* (4a,5a) = 9.6, H-4a), 3.68 (ddd, 1 H, *J* (5b,4b) = 9.6, *J* (5b,6′b) = 1.6, *J* (5b,6b) = 4.4, H-5b), 2.13, 2.09, 2.04, 2.04, 1.98, 1.96 (6 × s, 6 × 3H, $OCOCH_3$), 1.27, 1.14 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (90 MHz, $CDCl_3$): δ = 176.55, 176.14 ($OCOC(CH_3)_3$), 170.26, 170.04, 169.86, 169.58, 169.46, 169.00 ($OCOCH_3$), 100.59 (C-1b), 88.73 (C-1a), 75.90 (C-4a), 72.72, 72.22, 71.88, 70.93, 69.60, 69.37, 67.20 (C-5a/b, C-4a/b, C-3a/b, C-2a/b), 61.51, 61.36 (C-6a/b), 38.70, 38.60 ($OCOC(CH_3)_3$), 26.80, 26.61 ($OCOC(CH_3)_3$), 20.69, 20.64, 20.52, 20.38, 20.34, 20.23 ($OCOCH_3$) ppm.

4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-β-D-glucopyranose ***3β***

colorless crystals (α:β = 1:7), $[\alpha]_D^{20}$ = +2.0 ° (*c* = 0.2, $CHCl_3$), mp = 120.8 °C, R_f = 0.47 (cyclohexane/ethyl acetate 1/1)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.62 (d, 1 H, *J* (1a,2a) = 8.4, H-1a), 5.23 (dd, 1 H, *J* (3a,2a) = 9.6, *J* (3a,4a) = 9.2, H-3a), 5.19 (dd, 1 H, *J* (3b,2b) = 9.6, *J* (3b,4b) = 9.6, H-3b), 5.09 (dd, 1 H, *J* (2a,1a) = 8.4, *J* (2a,3a) = 9.6, H-2a), 5.06 (dd, 1 H, *J* (4b,3b) = 9.6, *J* (4b,5b) = 9.6, H-4b), 4.91 (dd, 1 H, *J* (2b,1b) = 8.0, *J* (2b, 3b) = 9.6, H-2b), 4.53 (d, 1 H, *J* (1b,2b) = 8.0, H-1b), 4.49 (dd, 1 H, *J* (6a,5a) = 2.0, *J* (6a, 6′a) = 12.8, H-6a), 4.27 (dd, 1 H, *J* (6b,5b) = 4.8, *J* (6b,6′b) = 12.8, H-6b), 4.12 (dd, 1 H, *J* (6′a, 5a) = 4.8, *J* (6′a,6a) = 12.8, H-6′a), 4.04 (dd, 1 H, *J* (6′b,5b) = 2.0, *J* (6′b,6b) = 12.8, H-6′b), 3.84 (dd, 1 H, *J* (4a,3a) = 9.2, *J* (4a,5a) = 10.0, H-4a), 3.74 (ddd, 1 H, *J* (5a,4a) = 10.0, *J* (5a,6′a) = 4.8, *J* (5a,6a) = 2.0, H-5a), 3.66 (ddd, 1 H, *J* (5b,4b) = 9.6, *J* (5b,6′b) = 2.0, *J* (5b, 6b) = 4.8, H-5b), 2.14, 2.10, 2.03, 2.02, 2.00, 2.00 (6 × s, 6 × 3H, $OCOCH_3$), 1.18, 1.14 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (90 MHz, $CDCl_3$): δ = 176.55, 176.17 ($OCOC(CH_3)_3$), 170.22, 170.09, 169.62, 169.51, 169.19, 168.90 ($OCOCH_3$), 100.96 (C-1b), 91.57 (C-1a), 76.13 (C-4a), 73.45, 72.56, 72.22, 72.14, 71.75, 70.32, 67.33 (C-5a/b, C-4a/b, C-3a/b, C-2a/b), 61.57, 61.51 (C-6a/b), 38.70, 38.60 ($OCOC(CH_3)_3$), 26.91, 26.77 ($OCOC(CH_3)_3$), 20.52, 20.44, 20.38, 20.38, 20.34, 20.34 ($OCOCH_3$) ppm.

$C_{34}H_{50}O_{19}$ (762.29) MS (NH_3-DCI): m/z = 780 ($[M_r + NH_4^+$)

Calcd. C 53.54%, H 6.61%

Found C 53.66%, H 6.74%

4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-α-D-glucopyranose ***4α***

colorless syrup (α:β = 16:1), $[\alpha]_D^{20}$ = +13.5 ° (*c* = 1.0, $CHCl_3$), R_f = 0.33 (cyclohexane/ethyl acetate 1/1)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.26 (d, 1 H, *J* (1a,2a) = 3.6, H-1a), 5.39 (dd, 1 H, *J* (3a,2a) = 10.2, *J* (3a,4a) = 9.8, H-3a), 5.18 (dd, 1 H, *J* (3c,2c) = 9.6, *J* (3c,4c) = 9.8, H-3c), 5.13 (dd, 1 H, *J* (3b,2b) = 9.6, *J* (3b,4b) = 9.6, H-3b), 5.06 (dd, 1 H, *J* (4c,3c) = 9.8, *J* (4c,5c) = 10.0, H-4c), 5.00 (dd, 1 H, *J* (2a,1a) = 3.6, *J* (2a,3a) = 10.2, H-2a), 4.89 (dd, 1 H, *J* (2c,1c) = 8.0, *J* (2c,3c) = 9.6, H-2c), 4.87 (dd, 1 H, *J* (2b,1b) = 8.0, *J* (2b,3b) = 9.6, H-2b), 4.50 (d, 1 H, *J* (1c,2c) = 8.0, H-1c), 4.50 (d, 1 H, *J* (1b,2b) = 8.0, H-1b), 4.50 (dd, 1 H, *J* (6a,5a) = 2.0, *J* (6a,6′a) = 12.4, H-6a), 4.41

(dd, 1 H, J(6b,5b) = 2.0, J(6b,6′b) = 12.4, H-6b), 4.26 (dd, 1 H, J(6c,5c) = 4.8, J(6c,6′c) = 12.8, H-6c), 4.12 (dd, 1 H, J (6′a,5a) = 4.8, J (6′a,6a) = 12.4, H-6′a), 4.09 (dd, 1 H, J (6′b,5b) = 4.6, J(6′b,6b) = 12.4, H-6′b), 4.03 (dd, 1 H, J(6′c,5c) = 2.0, J(6′c,6c) = 12.8, H-6′c), 3.95 (ddd, 1 H, J (5a,4a) = 10.0, J (5a,6′a) = 4.8, J (5a,6a) = 2.0, H-5a), 3.78 (dd, 1 H, J (4a,3a) = 9.8, J(4a,5a) = 10.0, H-4a), 3.76 (dd, 1 H, J (4b,3b) = 9.6, J (4b,5b) = 9.6, H-4b), 3.64 (ddd, 1 H, J (5c,4c) = 10.0, J (5c,6′c) = 2.0, J (5c,6c) = 4.8, H-5c), 3.60 (ddd, 1 H, J (5b,4b) = 9.6, J (5b,6′b) = 4.6, J (5b,6b) = 2.0, H-5b), 2.14, 2.12, 2.09, 2.03, 2.02, 2.01, 1.99, 1.97, 1.95 (9 × s, 9 × 3H, $OCOCH_3$), 1.26, 1.14 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (90 MHz, $CDCl_3$): δ = 176.68, 176.21 ($OCOC(CH_3)_3$), 170.41, 170.14, 170.14, 169.94, 169.80, 169.67, 169.50, 169.33, 169.10 ($OCOCH_3$), 100.89, 100.82 (C-1b/c), 88.83 (C-1a), 76.29, 76.09 (C-4a/b), 72.89, 72.79, 72.65, 72.35, 71.88, 71.88, 71.00, 69.75, 69.47, 67.26 (C-5a/b/c, C-4c, C-3a/b/c, C-2a/b/c), 62.21, 61.53, 61.36 (C-6a/b/c), 39.22, 38.82 ($OCOC(CH_3)_3$), 27.03, 26.86 ($OCOC(CH_3)_3$), 20.79, 20.79, 20.66, 20.59, 20.59, 20.59, 20.50, 20.46, 20.35 ($OCOCH_3$) ppm.

4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-β-D-glucopyranose ***4****β*

colorless syrup (α:β = 1:7), $[\alpha]_D^{20}$ = − 6.0° (c = 0.1, $CHCl_3$), R_f = 0.33 (cyclohexane/ethyl acetate 1/1)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.61 (d, 1 H, J (1a,2a) = 8.4, H-1a), 5.22 (dd, 1 H, J (3a,2a) = 9.2, J (3a,4a) = 9.3, H-3a), 5.18 (dd, 1 H, J (3c,2c) = 9.6, J (3c,4c) = 9.6, H-3c), 5.12 (dd, 1 H, J (3b,2b) = 9.4, J (3b,4b) = 9.2, H-3b), 5.07 (dd, 1 H, J (2a,1a) = 8.4, J (2a,3a) = 9.2, H-2a), 5.06 (dd, 1 H, J (4c,3c) = 9.6 J (4c,5c) = 9.8, H-4c), 4.89 (dd, 1 H, J (2c,1c) = 8.0, J (2c,3c) = 9.6, H-2c), 4.85 (dd, 1 H, J (2b,1b) = 8.0, J (2b,3b) = 9.4, H-2b), 4.49 (d, 1 H, J (1c,2c) = 8.0, H-1c), 4.49 (d, 1 H, J (1b,2b) = 8.0, H-1b), 4.47 (dd, 1 H, J (6a,5a) = 2.0, J (6a,6′a) = 12.4, H-6a), 4.41 (dd, 1 H, J (6b,5b) = 2.0, J (6b,6′b) = 12.4, H-6b), 4.25 (dd, 1 H, J (6c,5c) = 4.8, J (6c,6′c) = 12.8, H-6c), 4.11 (dd, 1 H, J (6′a,5a) = 4.6, J (6′a,6a) = 12.4, H-6′a), 4.10 (dd, 1 H, J (6′b,5b) = 4.6, J (6′b,6b) = 12.4, H-6′b), 4.03 (dd, 1 H, J (6′c,5c) = 2.0, J (6′c,6c) = 12.8, H-6′c), 3.82 (dd, 1 H, J (4a,3a) = 9.3, J (4a,5a) = 10.0, H-4a), 3.76 (dd, 1 H, J (4b,3b) = 9.2, J (4b,5b) = 9.6, H-4b), 3.73 (ddd, 1 H, J (5a,4a) = 10.0, J (5a,6′a) = 4.6, J (5a,6a) = 2.0, H-5a), 3.63 (ddd, 1 H, J (5c,4c) = 9.8, J (5c,6′c) = 2.0, J (5c,6c) = 4.8, H-5c), 3.59 (ddd, 1 H, J (5b,4b) = 9.6, J (5b,6′b) = 4.6, J (5b,6b) = 2.0, H-5b), 2.15, 2.12, 2.09, 2.03, 2.02, 2.00, 1.99, 1.99, 1.95 (9 × s, 9 × 3H, $OCOCH_3$), 1.17, 1.14 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (90 MHz, $CDCl_3$): δ = 176.65, 176.28 ($OCOC(CH_3)_3$), 170.37, 170.17, 170.17, 169.91, 169.74, 169.53, 169.25, 169.21, 169.07 ($OCOCH_3$), 100.79, 100.40 (C-1b/c), 91.62 (C-1a), 76.21, 76.04 (C-4a/b), 73.54, 72.85, 72.63, 72.63, 72.35, 72.21, 71.85, 71.78, 70.48, 67.28 (C-5a/b/c, C-4c, C-3a/b/c, C-2a/b/c), 62.22, 61.58, 61.52 (C-6a/b/c), 39.20, 38.79 ($OCOC(CH_3)_3$), 26.85, 26.70 ($OCOC(CH_3)_3$), 20.77, 20.73, 20.62, 20.62, 20.50, 20.50, 20.50, 20.42, 20.42 ($OCOCH_3$) ppm.

$C_{46}H_{66}O_{27}$ (1050.38) MS (NH_3-DCI): m/z = 1068 ($[M_r + NH_4^+]$)

Calcd. C 52.57%, H 6.33%

Found C 51.99%, H 6.18%

4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-α-D-glucopyranose ***5****α*

colorless crystals (α:β = 8:1), $[\alpha]_D^{20}$ = + 6.0 ° (c = 1.0, $CHCl_3$), mp = 113.5 °C, R_f = 0.40 (cyclohexane/ethyl acetate 1/2)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.26 (d, 1 H, J (1a,2a) = 3.6, H-1a), 5.41 (dd, 1 H, J (3a,2a) = 10.0, J (3a,4a) = 9.8, H-3a), 5.17 (dd, 1 H, J (3d,2d) = 9.6, J (3d,4d) = 9.8, H-3d), 5.12 (dd, 1 H, J (3b,2b) = 9.4, J (3b,4b) = 9.4, H-3b), 5.10 (dd, 1 H, J (3c,2c) = 9.4, J (3c,4c) = 9.4, H-3c), 5.06 (dd, 1 H, J (4d,3d) = 9.8, J (4d,5d) = 9.8, H-4d), 5.00 (dd, 1 H, J (2a,1a) = 3.6, J (2a,3a) = 10.0, H-2a), 4.89 (dd, 1 H, J (2d,1d) = 8.0, J (2d,3d) = 9.6, H-2d), 4.85 (dd, 1 H, J (2b,1b) = 8.0, J (2b,3b) = 9.4, H-2b), 4.83 (dd, 1 H, J (2c,1c) = 8.0, J (2c,3c) = 9.4, H-2c), 4.50 (d, 1 H, J (1d,2d) = 8.0, H-1d), 4.49 (d, 1 H, J (1b,2b) = 8.0, H-1b), 4.47 (dd, 1 H, J

(6a,5a) = 2.0, *J* (6a,6′a) = 12.8, H-6a), 4.46 (d, 1 H, *J* (1c,2c) = 8.0, H-1c), 4.42 (dd, 1 H, *J* (6c,5c) = 2.0, *J* (6c,6′c) = 12.8, H-6c), 4.39 (dd, 1 H, *J* (6b,5b) = 2.0, *J* (6b,6′b) = 12.4, H-6b), 4.26 (dd, 1 H, *J* (6d,5d) = 4.6, *J* (6d,6′d) = 12.8, H-6d), 4.11 (dd, 1 H, *J* (6′a,5a) = 4.4, *J* (6′a,6a) = 12.8, H-6′a), 4.10 (dd, 1 H, *J* (6′c,5c) = 4.4, *J* (6′c,6c) = 12.8, H-6′c), 4.09 (dd, 1 H, *J* (6′b,5b) = 4.4, *J* (6′b,6b) = 12.4, H-6′b), 4.03 (dd, 1 H, *J* (6′d,5d) = 2.0, *J* (6′d,6d) = 12.8, H-6′d), 3.95 (ddd, 1 H, *J* (5a,4a) = 9.4, *J* (5a,6′a) = 4.4, *J* (5a,6a) = 2.0, H-5a), 3.76 (dd, 1 H, *J* (4a,3a) = 9.8, *J* (4a,5a) = 9.4, H-4a), 3.75 (dd, 1 H, *J* (4c,3c) = 9.4, *J* (4c,5c) = 9.6, H-4c), 3.75 (dd, 1 H, *J* (4b,3b) = 9.4, *J* (4b,5b) = 9.6, H-4b), 3.63 (ddd, 1 H, *J* (5d,4d) = 9.8, *J* (5d,6′d) = 2.0, *J* (5d,6d) = 4.6, H-5d), 3.59 (ddd, 1 H, *J* (5b,4b) = 9.6, *J* (5b,6′b) = 4.4, *J* (5b,6b) = 2.0, H-5b), 3.57 (ddd, 1 H, *J* (5c,4c) = 9.6, *J* (5c,6′c) = 4.4, *J* (5c,6c) = 2.0, H-5c), 2.15, 2.14, 2.11, 2.08, 2.03, 2.02, 2.02, 2.00, 1.99, 1.97, 1.97, 1.95 (12 × s, 12 × 3H, $OCOCH_3$), 1.26, 1.14 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 177.49, 176.68 ($OCOC(CH_3)_3$), 170.41, 170.41, 170.18, 169.94, 169.77, 169.77, 169.69, 169.53, 169.30, 169.30, 169.19 ($OCOCH_3$), 100.86, 100.86, 100.52 (C-1b/c/d), 88.83 (C-1a), 76.29, 76.09, 76.09 (C-4a/b/c), 72.86, 72.86, 72.62, 72.62, 72.62, 72.38, 72.01, 71.84, 71.84, 71.00, 69.76, 69.45, 67.26 (C-5a/b/c/d, C-4d, C-3a/b/c/d, C-2a/b/c/d), 62.21, 62.07, 61.53, 61.40 (C-6a/b/c/d), 39.23, 38.82 ($OCOC(CH_3)_3$), 27.03, 26.86 ($OCOC(CH_3)_3$), 20.79, 20.66, 20.46, 20.35 (12×$OCOCH_3$) ppm.

4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-β-D-glucopyranose ***5****β*

colorless syrup (α:*β* = 1:8), $[\alpha]_D^{20}$ = − 9.0° (*c* = 0.1, $CHCl_3$), R_f = 0.40 (cyclohexane/ethyl acetate 1/2)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.60 (d, 1 H, *J* (1a,2a) = 8.4, H-1a), 5.22 (dd, 1 H, *J* (3a,2a) = 9.2, *J* (3a,4a) = 9.3, H-3a), 5.17 (dd, 1 H, *J* (3d,2d) = 9.6, *J* (3d,4d) = 9.8, H-3d), 5.10 (dd, 1 H, *J* (3b,2b) = 9.4, *J* (3b,4b) = 9.6, H-3b), 5.10 (dd, 1 H, *J* (3c,2c) = 9.4, *J* (3c,4c) = 9.2, H-3c), 5.07 (dd, 1 H, *J* (2a,1a) = 8.4, *J* (2a,3a) = 9.2, H-2a), 5.06 (dd, 1 H, *J* (4d,3d) = 9.8, *J* (4d,5d) = 10.2, H-4d), 4.89 (dd, 1 H, *J* (2d,1d) = 8.0, *J* (2d,3d) = 9.6, H-2d), 4.83 (dd, 1 H, *J* (2b,1b) = 8.0, *J* (2b,3b) = 9.4, H-2b), 4.83 (dd, 1 H, *J* (2c,1c) = 8.0, *J* (2c,3c) = 9.4, H-2c), 4.49 (d, 1 H, *J* (1,2) = 8.0, H-1), 4.48 (d, 1 H, *J* (1,2) = 8.0, H-1), 4.47 (dd, 1 H, *J* (6a,5a) = 4.8, *J* (6a,6′a) = 12.8, H-6a), 4.45 (d, 1 H, *J* (1c,2c) = 8.0, H-1c), 4.41 (dd, 1 H, *J* (6b,5b) = 2.0, *J* (6b,6′b) = 12.8, H-6b), 4.40 (dd, 1 H, *J* (6c,5c) = 2.0, *J* (6c,6′c) = 12.8, H-6c), 4.26 (dd, 1 H, *J* (6d,5d) = 4.6, *J* (6d,6′d) = 12.8, H-6d), 4.11 (dd, 1 H, *J* (6′b,5b) = 5.0, *J* (6′b,6b) = 12.8, H-6′b), 4.11 (dd, 1 H, *J* (6′a,5a) = 2.0, *J* (6′a,6a) = 12.8, H-6′a), 4.07 (dd, 1 H, *J* (6′c,5c) = 4.8, *J* (6′c,6c) = 12.8, H-6′c), 4.03 (dd, 1 H, *J* (6′d,5d) = 2.0, *J* (6′d,6d) = 12.8, H-6′d), 3.81 (dd, 1 H, *J* (4a,3a) = 9.3, *J* (4a,5a) = 9.6, H-4a), 3.75 (dd, 1 H, *J* (4b,3b) = 9.6, *J* (4b,5b) = 10.2, H-4b), 3.74 (dd, 1 H, *J* (4c,3c) = 9.4, *J* (4c,5c) = 9.6, H-4c), 3.63 (ddd, 1 H, *J* (5d,4d) = 10.2, *J* (5d,6′d) = 2.0, *J* (5d,6d) = 4.6, H-5d), 3.58 (ddd, 1 H, *J* (5b,4b) = 10.2, *J* (5b,6′b) = 5.0, *J* (5b,6b) = 2.0, H-5b), 3.56 (ddd, 1 H, *J* (5c,4c) = 9.6, *J* (5c,6′c) = 4.8, *J* (5c,6c) = 2.0, H-5c), 2.15, 2.14, 2.11, 2.08, 2.02, 2.02, 2.01, 2.00, 1.99, 1.99, 1.96, 1.95 (12 × s, 12 × 3H, $OCOCH_3$), 1.17, 1.14 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

$C_{58}H_{82}O_{35}$(1338.46) MS (NH_3-DCI): m/z = 1357.3 ($[M_r + NH_4^+]$)

Calcd. C 52.02%, H 6.17%

Found C 51.68%, H 6.20%

4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-α-D-glucopyranose ***6****α*

colorless syrup (α:*β* = 100:1), $[\alpha]_D^{20}$ = +3.0 ° (*c* = 0.1, $CHCl_3$), R_f = 0.33 (cyclohexane/ethyl acetate 1/2)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.26 (d, 1 H, *J* (1a,2a) = 3.8, H-1a), 5.38 (dd, 1 H, *J* (3a,2a) = 10.2, *J* (3a,4a) = 9.8, H-3a), 5.17 (dd, 1 H, *J* (3e,2e) = 9.4, *J* (3e,4e) = 9.6, H-3e), 5.11 (dd, 1 H, *J* (3b,2b) = 9.2, *J* (3b,4b) = 9.6, H-3b), 5.10 (dd, 1 H, *J* (3d,2d) = 9.2, *J* (3d,4d) = 9.6, H-3d), 5.09 (dd, 1 H, *J* (3c,2c) = 9.4, *J* (3c,4c) = 9.6, H-3c), 5.06 (dd, 1 H, *J*

(4e,3e) = 9.6, *J* (4e,5e) = 9.6, H-4e), 5.00 (dd, 1 H, *J* (2a,1a) = 3.8, *J* (2a,3a) = 10.2, H-2a), 4.88 (dd, 1 H, *J* (2e,1e) = 8.0, *J* (2e,3e) = 9.4, H-2e), 4.85 (dd, 1 H, *J* (2b,1b) = 8.0, *J* (2b,3b) = 9.2, H-2b), 4.82 (dd, 1 H, *J* (2d,1d) = 8.0, *J* (2d,3d) = 9.2, H-2d), 4.80 (dd, 1 H, *J* (2c,1c) = 8.0, *J* (2c,3c) = 9.4, H-2c), 4.49 (d, 1 H, *J* (1e,2e) = 8.0, H-1e), 4.49 (d, 1 H, *J* (1b,2b) = 8.0, H-1b), 4.45 (d, 1 H, *J* (1d,2d) = 8.0, H-1d), 4.45 (d, 1 H, *J* (1c,2c) = 8.0, H-1c), 4.52–4.34 (m, 4 H, 4 × H-6), 4.25 (dd, 1 H, *J* (6e,5e) = 4.8, *J* (6e,6′e) = 12.8, H-6e), 4.16–3.91 (m, 6 H, H-5a, 5 × H-6), 3.76 (dd, 1 H, *J* (4a,3a) = 9.8, *J* (4a,5a) = 9.6, H-4a), 3.75 (dd, 1 H, *J* (4d,3d) = 9.6, *J* (4d,5d) = 10.0, H-4d), 3.75 (dd, 1 H, *J* (4b,3b) = 9.6, *J* (4b,5b) = 10.0, H-4b), 3.73 (dd, 1 H, *J* (4c,3c) = 9.6, *J* (4c,5c) = 9.6, H-4c), 3.67–3.50 (m, 4 H, H-5b, H-5c, H-5d, H-5e), 2.14, 2.14, 2.13, 2.11, 2.08, 2.04, 2.02, 2.02, 2.01, 2.00, 1.98, 1.97, 1.97, 1.96, 1.95 (15 × s, 15 × 3H, $OCOCH_3$), 1.26, 1.14 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.68 ($OCOC(CH_3)_3$), 170.18, 169.78, 169.67, 169.53, 169.23, 169.10 (15 × $OCOCH_3$), 100.82, 100.82, 100.56, 100.45 (C-1b/c/d/e), 88.83 (C-1a), 76.30, 76.22, 76.09, 76.09 (C-4a/b/c/d), 72.86, 72.86, 72.86, 72.62, 72.62, 72.62, 72.62, 72.35, 71.88, 71.88, 71.88, 71.00, 69.78, 69.69, 69.45, 67.26 (C-5a/b/c/d/e, C-4d, C-3a/b/c/d/e, C-2a/b/c/d/e), 62.21, 62.07, 62.07, 61.53, 61.40 (C-6a/b/c/d/e), 39.83, 38.82 ($OCOC(CH_3)_3$), 27.03, 26.89 ($OCOC(CH_3)_3$), 20.79, 20.68, 20.59, 20.51, 20.36 (15 × $OCOCH_3$) ppm.

4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D -glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-β-D-glucopyranose ***6β***

colorless syrup (α:β = 1:50), $[\alpha]_D^{20}$ = − 10.0° (*c* = 0.1, $CHCl_3$), R_f = 0.33 (cyclohexane/ethyl acetate 1/2)

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 5.60 (d, 1 H, *J* (1a,2a) = 8.4, H-1a), 5.21 (dd, 1 H, *J* (3a,2a) = 9.2, *J* (3a,4a) = 9.8, H-3a), 5.17 (dd, 1 H, *J* (3ed,2e) = 9.4, *J* (3e,4e) = 9.6, H-3e), 5.10 (dd, 1 H, *J* (3d,2d) = 9.2, *J* (3d,4d) = 9.2, H-3d), 5.10 (dd, 1 H, *J* (3b,2b) = 9.2, *J* (3b,4b) = 9.2, H-3b), 5.08 (dd, 1 H, *J* (3c,2c) = 9.2, *J* (3c,4c) = 9.2, H-3c), 5.06 (dd, 1 H, *J* (2a,1a) = 8.4, *J* (2a,3a) = 9.2, H-2a), 5.05 (dd, 1 H, *J* (4e,3e) = 9.6, *J* (4e,5e) = 9.6, H-4e), 4.88 (dd, 1 H, *J* (2e,1e) = 8.0, *J* (2e,3e) = 9.4, H-2e), 4.82 (dd, 1 H, *J* (2d,1d) = 8.0, *J* (2d,3d) = 9.2, H-2d), 4.82 (dd, 1 H, *J* (2b,1b) = 8.0, *J* (2b,3b) = 9.2, H-2b), 4.80 (dd, 1 H, *J* (2c,1c) = 8.0, *J* (2c,3c) = 9.2, H-2c), 4.49 (d, 1 H, *J* (1,2) = 8.0, H-1), 4.49 (d, 1 H, *J* (1,2) = 8.0, H-1), 4.44 (d, 1 H, *J* (1d,2d) = 8.0, H-1d), 4.43 (d, 1 H, *J* (1c,2c) = 8.0, H-1c), 4.51–4.35 (m, 4 H, 4 × H-6), 4.25 (dd, 1 H, *J* (6e,5e) = 4.8, *J* (6e,6′e) = 12.8, H-6e), 4.14–3.99 (m, 5 H, 5 × H-6), 3.80 (dd, 1 H, *J* (4a,3a) = 9.3, *J* (4a,5a) = 9.6, H-4a), 3.74 (dd, 1 H, *J* (4d,3d) = 9.2, *J* (4d,5d) = 9.2, H-4d), 3.73 (ddd, 1 H, *J* (5a,4a) = 9.6, *J* (5a,6′a) = 2.0, *J* (5a,6a) = 4.4, H-5a), 3.73 (dd, 1 H, *J* (4c,3c) = 9.2, *J* (4c,5c) = 9.2, H-4c), 3.73 (dd, 1 H, *J* (4b,3b) = 9.2, *J* (4b,5b) = 9.2, H-4b), 3.66–3.51 (m, 4 H, H-5b, H-5c, H-5d, H-5e), 2.14, 2.13, 2.13, 2.11, 2.08, 2.02, 2.02, 2.01, 2.01, 1.99, 1.99, 1.98, 1.96, 1.96, 1.95 (15 × s, 15 × 3H, $OCOCH_3$), 1.17, 1.13 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.68, 173.31 ($OCOC(CH_3)_3$), 170.18, 170.16, 169.74, 169.68, 169.27 (15 × $OCOCH_3$), 100.81, 100.53, 100.46, 100.38 (C-1b/c/d/e), 91.63 (C-1a), 76.24, 76.12, 76.10, 76.06 (C-4a/b/c/d), 73.58, 72.93, 72.88, 72.86, 72.64, 72.64, 72.60, 72.53, 72.38, 72.38, 72.21, 71.95, 71.90, 71.83, 70.47, 67.31 (C-5a/b/c/d/e, C-4e, C-3a/b/c/d/e, C-2a/b/c/d/e), 62.24, 62.07, 62.00, 61.81, 61.54 (C-6a/b/c/d/e), 40.56, 39.75 ($OCOC(CH_3)_3$), 26.88, 26.73 ($OCOC(CH_3)_3$), 20.80, 20.77, 20.65, 20.55, 20.53, 20.48, 20.45 (15 × $OCOCH_3$) ppm.

$C_{70}H_{98}O_{43}$(1626.45) MS (NH_3-DCI): m/z = 1645 ($[M_r + NH_4^+]$)

Calcd. C 51.66%, H 6.07%

Found C 51.72%, H 6.29%

4-O-(4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-α-D-glucopyranose 7α

colorless crystals (α : β = 3.2 : 1), $[\alpha]_D^{20}$ = −12.4 ° (*c* = 1.0, $CHCl_3$), mp 148 °C

^{1}H-NMR (300 MHz, $CDCl_3$): δ = 6.24 (d, 1 H, *J* (1a,2a) = 3.6, H-1a), 5.38 (dd, 1 H, *J* (3a,2a) = 9.5, *J* (3a,4a) = 9.8, H-3a), 5.16 (dd, 1 H, *J* (3,2) = 9.5, *J* (3,4) = 9.5, H-3), 5.16 (dd, 1 H, *J* (3,2) = 9.5, *J* (3,4) = 9.5, H-3), 5.13 (dd, 1 H, *J* (3,2) = 9.7, *J* (3,4) = 9.5, H-3), 5.13–5.04 (m, 4 H, H-3b/c/d/e, H-4f), 4.99 (dd, 1 H, *J* (2a,1a) = 3.8, *J* (2a,3a) = 10.0, H-2a), 4.87 (dd, 1 H, *J* (2,1) = 7.8, *J* (2,3) = 9.1, H-2), 4.84 (dd, 1 H, *J* (2,1) = 7.6, *J* (2,3) = 9.1, H-2), 4.84 (dd, 1 H, *J* (2,1) = 7.2, *J* (2,3) = 9.3, H-2), 4.81 (dd, 1 H, *J* (2,1) = 7.6, *J* (2,3) = 9.1, H-2), 4.79 (dd, 1 H, *J* (2,1) = 7.8, *J* (2,3) = 9.3, H-2), 4.51–4.34 (m, 10 H, H-6a/b/c/d/e, H-1b/c/d/e/f), 4.24 (dd, 1 H, *J* (6f,5f) = 4.8, *J* (6f,6′f) = 12.4, H-6f), 4.14–3.98 (m, 6 H. 6× H-6), 3.94 (ddd, 1 H, *J* (5f,4f) = 9.5, *J* (5f,6′f) = 1.8, *J* (5f,6f) = 4.8, H-5f), 3.80–3.67 (m, 5 H, H-4a/b/c/d/e), 3.66–3.52 (m, 5 H, H-5a/b/c/d/e), 2.14, 2.13, 2.13, 2.12, 2.10, 2.07, 2.01, 2.01, 2.01, 2.01, 2.00, 1.98, 1.98, 1.97, 1.96, 1.95, 1.95, 1.94 (18 × s, 18 × 3H, $OCOCH_3$), 1.25, 1.12 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.66, 176.19 ($OCOC(CH_3)_3$), 170.36, 170.14, 170.14, 170.14, 169.91, 169.75, 169.75, 169.72, 169.67, 169.67, 169.64, 169.64, 169.50, 169.28, 169.28, 169.24, 169.24, 169.06 (18× $OCOCH_3$), 100.84, 100.81, 100.56, 100.44, 100.37 (C-1b/c/d/e/f), 88.82 (C-1a), 77.62, 76.51, 76.30, 76.10, 75.73 (C-4a/b/c/d/e), 72.92, 72.92, 72.89, 72.89, 72.69, 72.64, 72.64, 72.64, 72.59, 72.37, 72.01, 71.96, 71.88, 71.83, 71.00, 69.75, 69.48, 68.76, 67.71 (C-5a/b/c/d/e/f, C-4f, C-3a/b/c/d/e/f, C-2a/b/c/d/e/f), 62.25, 62.12, 61.58, 61.44, 60.33, 60.20 (C-6a/b/c/d/e/f), 39.14, 38.80 ($OCOC(CH_3)_3$), 26.99, 26.85, ($OCOC(CH_3)_3$), 20.72, 20.62, 20.56, 20.52, 20.49, 20.46, 20.42, 20.30 (18 × $OCOCH_3$) ppm.

4-O-(4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-β-D-glucopyranose 7β

^{1} H-NMR (300 MHz, $CDCl_3$): δ = 5.60 (d, 1 H, *J* (1a,2a) = 8.1, H-1a), 5.24–5.04 (m, 7 H, H-3a/b/c/d/e/f, H-4f), 4.91–4.72 (m, 1 H, H-2a), 4.87 (dd, 1 H, *J* (2,1) = 7.8, *J* (2,3) = 9.1, H-2), 4.84 (dd, 1 H, *J* (2,1) = 7.6, *J* (2,3) = 9.1, H-2), 4.87 (dd, 1 H, *J* (2,1) = 7.2, *J* (2,3) = 9.3, H-2), 4.81 (dd, 1 H, *J* (2,1) = 7.6, *J* (2,3) = 9.1, H-2), 4.79 (dd, 1 H, *J* (2,1) = 7.8, *J* (2,3) = 9.3, H-2), 4.51–4.34 (m, 10 H, H-6a/b/c/d/e, H-1b/c/d/e/f), 4.24 (dd, 1 H, *J* (6f,5f) = 4.8, *J* (6f,6′f) = 12.4, H-6f), 4.14–3.98 (m, 6 H, H-4a/b/c/d/e), 3.94 (ddd, 1 H, *J* (5f,4f) = 9.5, *J* (5f,6′f) = 1.8, *J* (5f,6f) = 4.8, H-5f), 3.80–3.67 (m, 5 H, H-5a/b/c/d/e), 2.14, 2.13, 2.13, 2.12, 2.10, 2.07, 2.01, 2.01, 2.01, 2.01, 2.00, 1.98, 1.98, 1.97, 1.96, 1.95, 1.95, 1.94 (18× s, 18× 3H, $OCOCH_3$), 1.25, 1.16 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.66, 176.19 ($OCOC(CH_3)_3$), 170.36, 170.14, 170.14, 170.14, 169.91, 169.75, 169.75, 169.72, 169.67, 169.67, 169.64, 169.64, 169.50, 169.28, 169.28, 169.24, 169.24, 169.06 (18× $OCOCH_3$), 100.84, 100.81, 100.56, 100.44, 100.37 (C-1b/c/d/e/f), 91.55 (C-1a), 77.62, 76.51, 76.30, 76.10, 75.73 (C-4a/b/c/d/e), 72.92, 72.92, 72.89, 72.89, 72.69, 72.64, 72.64, 72.64, 72.59, 72.37, 72.01, 71.96, 71.88, 71.83, 71.00, 69.75, 69.48, 68.76, 67.71 (C-5a/b/c/d/e/f, C-4f, C-3a/b/c/d/e/f, C-2a/b/c/d/e/f), 62.25, 62.12, 61.58, 61.48, 60.33, 60.20 (C-6a/b/c/d/e/f), 39.14, 38.80 ($OCOC(CH_3)_3$), 26.85, 26.71, ($OCOC(CH_3)_3$), 20.72, 20.62, 20.56, 20.52, 20.49, 20.46, 20.42, 20.30 (18× $OCOCH_3$) ppm.

$C_{70}H_{98}O_{43}$(1626.45) MS (MALDI-TOF): m/z = 1938 ($[M_r + Na]^{\oplus}$)

Calcd. C 51.41%, H 6.00%

Found C 51.66%, H 6.14%

*4-O-(4-O-(4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-α-D-glucopyranose **8**α*

colorless crystals (α:*β* = 1.9:1), $[\alpha]_D^{20}$ = −8.6 ° (*c* = 1.0, $CHCl_3$), mp 160 °C

^{1}H-NMR (360 MHz, $CDCl_3$): δ = 6.24 (d, 1 H, *J* (1a,2a) = 3.3, H-1a), 5.38 (dd, 1 H, *J* (3a,2a) = 9.5, *J* (3a,4a) = 9.5, H-3a), 5.24–5.02 (m, 7 H, H-3b/c/d/e/f/g, H-4g), 4.99 (dd, 1 H, *J* (2a,1a) = 3.9, *J* (2a,3a) = 10.5, H-2a), 4.92–4.72 (m, 6 H, H-2b/c/d/e/f/g), 4.52–4.34 (m, 12 H, H-6a/b/c/d/e/f, H-1b/c/d/e/f/g), 4.25 (dd, 1 H, *J* (6g,5g) = 4.8, *J* (6g,6′g) = 12.8, H-6g), 4.16–3.90

(m, 8 H, H-5g, 7× H-6), 3.80–3.67 (m, 6 H, H-4a/b/c/d/e/f), 3.66–3.48 (m, 6 H, H-5a/b/c/d/e/f), 2.14, 2.13, 2.13, 2.11, 2.11, 2.08, 2.08, 2.02, 2.02, 2.02, 2.01, 2.01, 2.01, 1.99, 1.99, 1.98, 1.98, 1.95, 1.94, 1.94, 1.94 (21×s, 21×3H, $OCOCH_3$), 1.25, 1.12 (2×s, 2×9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.66, 176.21 ($OCOC(CH_3)_3$), 170.41, 170.20, 170.20, 170.20, 170.16, 170.16, 170.16, 169.95, 169.78, 169.72, 169.72, 169.69, 169.69, 169.69, 169.54, 169.26, 169.26, 169.26, 169.26, 169.11, 169.11 (21× $OCOCH_3$), 100.85, 100.82, 100.53, 100.47, 100.47, 100.36 (C-1b/c/d/e/f/g), 88.73 (C-1a), 77.15, 77.09, 76.90, 76.26, 75.97, 75.97 (C-4a/b/c/d/e/f), 73.49, 72.80, 72.80, 72.66, 72.57, 72.57, 72.51, 72.51, 72.31, 72.25, 72.25, 71.90, 71.90, 71.82, 71.82, 71.72, 71.55, 71.55, 70.93, 69.68, 67.39, 67.17 (C-5a/b/c/d/e/f/g, C-4g, C-3a/b/c/d/e/f/g, C-2a/b/c/d/e/f/g), 62.14, 62.07, 62.07, 62.07, 62.00, 61.47, 61.31 (C-6a/b/c/d/e/f/g), 39.14, 38.69 ($OCOC(CH_3)_3$), 26.99, 26.83, ($OCOC(CH_3)_3$), 20.77, 20.66, 20.55, 20.49, 20.44, 20.34 (21 × $OCOCH_3$) ppm.

4-O-(4-O-(4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl-β-d-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D- glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-β-D-glucopyranose ***8β***

^{1}H-NMR (360 MHz, $CDCl_3$): δ = 5.60 (d, 1 H, *J* (1a,2a) = 8.3, H-1a), 5.24–5.02 (m, 8 H, H-3a/b/c/d/e/f/g, H4-g), 4.92–4.72 (m, 7 H, H-2a/b/c/d/e/f/g), 4.52–4.34 (m, 12 H, H-6a/b/c/d/e/f, H-1b/c/d/e/f/g), 4.25 (dd, 1 H, *J* (6g,5g) = 4.8, *J* (6g,6′g) = 12.8, H-6g), 4.16–3.90 (m, 8 H, H-5g, 7× H-6), 3.80–3.67 (m, 6 H, H-4a/b/c/d/e/f), 3.66–3.48 (m, 6 H, H-5a/b/c/d/e/f), 2.14, 2.13, 2.13, 2.11, 2.11, 2.08, 2.08, 2.02, 2.02, 2.02, 2.01, 2.01, 2.01, 1.99, 1.99, 1.98, 1.98, 1.95, 1.94, 1.94, 1.94 (21 × s, 21 × 3H, $OCOCH_3$), 1.22, 1.16 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.66, 176.21 ($OCOC(CH_3)_3$), 170.41, 170.20, 170.20, 170.20, 170.16, 170.16, 170.16, 169.95, 169.78, 169.72, 169.72, 169.69, 169.69, 169.69, 169.54, 169.26, 169.26, 169.26, 169.26, 169.11, 169.11 (21× $OCOCH_3$), 100.85, 100.82, 100.53, 100.47, 100.47, 100.36 (C-1b/c/d/e/f/g), 91.55 (C-1a), 77.15, 77.09, 76.90, 76.26, 75.97, 75.97 (C-4a/b/c/d/e/f), 73.49, 72.80, 72.80, 72.66, 72.57, 72.57, 72.51, 72.51, 72.31, 72.25, 72.25, 71.90, 71.90, 71.82, 71.82, 71.72, 71.55, 71.55, 70.93, 69.68, 67.39, 67.17 (C-5a/b/c/d/e/f/g, C-4g, C-3a/b/c/d/e/f/g, C-2a/b/c/d/e/f/g), 62.14, 62.07, 62.07, 62.07, 62.00, 61.47, 61.31 (C-6a/b/c/d/e/f/g), 39.14, 38.69 ($OCOC(CH_3)_3$), 27.58, 26.68, ($OCOC(CH_3)_3$), 20.77, 20.66, 20.55, 20.49, 20.44, 20.34 (21× $OCOCH_3$) ppm.

$C_{94}H_{130}O_{59}$ (2204.0) MS (MALDI-TOF): m/z = 2224 ($[M_r + Na]^{\oplus}$)

Calcd. C 51.23%, H 5.94%

Found C 51.02%, H 6.00%

4-O(4-O-(4-O-(4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl- β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-αD-glucopyranose ***9α***

colorless crystals (α:β = 1.5:1), $[\alpha]_D^{20}$ = −6.9 ° (*c* = 1.0, $CHCl_3$), mp 163 °C

^{1}H-NMR (360 MHz, $CDCl_3$): δ = 6.24 (d, 1 H, *J* (1a,2a) = 3.3, H-1a), 5.38 (dd, 1 H, *J* (3a,2a) = 9.5, *J* (3a,4a) = 9.5, H-3a), 5.24–5.02 (m, 8 H, H-3b/c/d/e/f/g/h, H-4h), 4.99 (dd, 1 H, *J* (2a,1a) = 3.9, *J* (2a,3a) = 10.5, H-2a), 4.92–4.72 (m, 7 H, H-2b/c/d/e/f/g/h), 4.52–4.34 (m, 14 H, H-6a/b/c/d/e/f/g, H-1b/c/d/e/f/g/h), 4.25 (dd, 1 H, *J* (6h,5h) = 4.8, *J* (6h,6′h) = 12.8, H-6h), 4.16–3.90 (m, 9 H, H-5h, 8× H-6), 3.80–3.67 (m, 7 H, H-4a/b/c/d/e/f/g), 3.66–3.48 (m, 7 H, H-5a/b/c/d/e/f/g), 2.14, 2.13, 2.13, 2.12, 2.11, 2.11, 2.08, 2.08, 2.02, 2.02, 2.02, 2.01, 2.01, 2.01, 2.00, 1.99, 1.99, 1.98, 1.98, 1.96, 1.95, 1.94, 1.94, 1.94 (24 × s, 24 × 3H, $OCOCH_3$), 1.25, 1.12 (2 ×,s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.66, 176.21 ($OCOC(CH_3)_3$), 170.41, 170.20, 170.20, 170.20, 170.16, 170.16, 170.16, 170.16, 169.95, 169.78, 169.72, 169.72, 169.69, 169.69, 169.69, 169.69, 169.54, 169.26, 169.26, 169.26, 169.26, 169.26, 169.11, 169.11 (24× $OCOCH_3$), 100.85, 100.82, 100.61, 100.53, 100.47, 100.47, 100.36 (C-1b/c/d/e/f/g), 88.73 (C-1a), 77.15, 77.09, 76.90,

76.68, 76.26, 75.97, 75.97 (C-4a/b/c/d/e/f/g), 73.49, 72.80, 72.80, 72.66, 72.57, 72.57, 72.51, 72.51, 72.31, 72.31, 72.25, 72.25, 71.90, 71.90, 71.82, 71.82, 71.72, 71.64, 71.55, 71.55, 70.93, 69.84, 69.68, 67.39, 67.17 (C-5a/b/c/d/e/f/g/h, C-4h, C-3a/b/c/d/e/f/g/h, C-2a/b/c/d/e/f/g/h), 62.14, 62.07, 62.07, 62.07, 62.00, 62.00, 61.47, 61.31 (C-6a/b/c/d/e/f/g/h), 39.14, 38.69 ($OCOC(CH_3)_3$), 26.99, 26.83, ($OCOC(CH_3)_3$), 20.77, 20.66, 20.55, 20.49, 20.44, 20.34 (21× $OCOCH_3$) ppm.

4-O(4-O-(4-O-(4-O-(4-O-(4-O-(4-O-(2,3,6-Tri-O-acetyl-4-O-pivaloyl- β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-β-D-glucopyranosyl)-2,3,6-tri-O-acetyl-1-O-pivaloyl-β-D-glucopyranose ***9β***

^{1}H-NMR (360 MHz, $CDCl_3$): δ = 5.60 (d, 1 H, J (1a,2a) = 8.3, H-1a), 5.24–5.02 (m, 9 H, H-3a/b/c/d/e/f/g/h, H4-h), 4.92–4.72 (m, 8 H, H-2a/b/c/d/e/f/g/h), 4.52–4.34 (m, 14 H, H-6a/b/c/d/e/f/g, H-1b/c/d/e/f/g/h), 4.25 (dd, 1 H, J (6h,5h) = 4.8, J (6h,6′h) = 12.8, H-6h), 4.16–3.90 (m, 9 H, H-5h, 8× H-6), 3.80–3.67 (m, 7 H, H-4a/b/c/d/e/f/g), 3.66–3.48 (m, 7 H, H-5a/b/c/d/e/f/g), 2.14, 2.13, 2.13, 2.12, 2.11, 2.11, 2.08, 2.08, 2.02, 2.02, 2.02, 2.01, 2.01, 2.01, 2.00, 1.99, 1.99, 1.98, 1.98, 1.95, 1.95, 1.94, 1.94, 1.94 (24 × s, 24 × 3H, $OCOCH_3$), 1.22, 1.16 (2 × s, 2 × 9H, $OCOC(CH_3)_3$) ppm.

^{13}C-NMR (75 MHz, $CDCl_3$): δ = 176.66, 176.21 ($OCOC(CH_3)_3$), 170.41, 170.20, 170.20, 170.20, 170.16, 170.16, 170.16, 170.16, 169.95, 169.78, 169.72, 169.72, 169.69, 169.69, 169.69, 169.69, 169.54, 169.26, 169.26, 169.26, 169.26, 169.11, 169.11 (24× $OCOCH_3$), 100.85, 100.82, 100.61, 100.53, 100.47, 100.47, 100.36 (C-1b/c/d/e/f/g), 91.75 (C-1a), 77.15, 77.09, 76.90, 76.68, 76.26, 75.97, 75.97 (C-4a/b/c/d/e/f/g), 73.49, 72.80, 72.80, 72.66, 72.57, 72.57, 72.51, 72.51, 72.31, 72.31, 72.25, 72.25, 71.90, 71.90, 71.82, 71.82, 71.72, 71.64, 71.55, 71.55, 70.93, 69.84, 69.68, 67.39, 67.17 (C-5a/b/c/d/e/f/g/h, C-4h, C-3a/b/c/d/e/f/g/h, C-2a/b/c/d/e/f/g/h), 62.14, 62.07, 62.07, 62.07, 62.00, 62.00, 61.47, 61.31 (C-6a/b/c/d/e/f/g/h), 39.14, 38.69 ($OCOC(CH_3)_3$), 27.58, 26.68, ($OCOC(CH_3)_3$), 20.77, 20.66, 20.55, 20.49, 20.44, 20.34 (21 × $OCOCH_3$) ppm.

$C_{106}H_{146}O_{67}$ (2492.3) MS (MALDI-TOF): m/z = 2516 ($[M_r + Na]^{\oplus}$)

Calcd. C 51.08%, H 5.90%

Found C 51.10%, H 5.84%

Acknowledgements

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