Synthesis of Methyl 4-*O*-methyl-β-D-*ribo*-hex-3-ulopyranoside-1-^{13}C and Methyl 4-*O*-methyl-β-D-*ribo*-hex-3-ulopyranoside-3-^{13}C as Fragment Analogues of Oxidized Cellulose Units

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Abstract: Model compounds of oxidized anhydroglucose units in cellulosic materials, carrying ^{13}C isotopic labels at specific positions, have been synthesized starting from commercially available 1-^{13}C-D-glucose (14.7%) and 3-^{13}C-D-glucose (6.3%), respectively, over 10 linear steps. To ensure high yields, the synthetic route was optimized with non-labeled material beforehand. The labeled compounds are used in studies of chromophore formation, yellowing, brightness reversion and aging of cellulosics.

Keywords: Cellulose, aging, yellowing, brightness reversion, isotopic labeling, 3-keto-glucose.

INTRODUCTION

Cellulose is the most abundant, and – with regard to technology and economic impact – also the most important carbohydrate polymer and natural resource. Extraction of celluloses from different sources and refinement of the material towards paper and fiber production requires numerous process steps (cooking and bleaching). Especially bleaching that is based on oxidizing chemicals (O_2, O_3 or H_2O_2 on one hand or ClO_2 on the other hand) might cause oxidation of the cellulose as reflected by introduction of carbonyl and carboxyl groups [1]. Especially the carbonyl groups are known to be the primary cause of brightness reversion effects, i.e. re-yellowing of already bleached materials, and precursor moieties for chromophore formation [2, 3]. This topic is not only scientifically challenging, but also of primary interest and economic importance in the pulp and paper industry. Although such chromophores have been isolated and characterized despite their extremely low content in the ppb range [4,5], the chemical mechanisms of the chromophore formation processes are still completely unclear. To prove the hypotheses that oxidized anhydroglucose units along the cellulose chains are the basic chromophore precursors and that a fragmentation and subsequent re-condensation of these units gives rise to the observed colored, quinoid substances, the ^{13}C-labeled model compound methyl 4-*O*-methyl-β-D-*ribo*-hex-3-ulopyranoside was required that functions as oxidized cellulose fragment analogue [6]. Introduction of the label was especially interesting for the reactive positions 1 and 3. In this study, a high-yield route towards methyl 4-*O*-methyl-β-D-*ribo*-hex-3-ulopyranoside, labeled with >99% ^{13}C at either 1-C or 3-C is presented.

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EXPERIMENTAL

General

All chemicals were available from commercial suppliers and were of the highest purity available and used without further purification. Reagent-grade solvents were used for all extractions and workup procedures. Distilled water was used for all aqueous extractions and for all aqueous solutions. The use of brine refers to saturated aqueous NaCl. All reactions involving non-aqueous conditions were conducted in flame-dried glassware under an argon atmosphere. CH_2Cl_2 was dried by refluxing over CaH, THF by refluxing over Na. Molecular sieves were dried at 300°C. TLC was performed using Merck silica gel 60 F254 pre-coated plates. Flash chromatography was performed using Baker silica gel (40 μm particle size). All given yields refer to isolated, pure products. NMR spectra were generally recorded at 300.13 MHz for ^{1}H and at 75.47 MHz for ^{13}C NMR in $CDCl_3$ as the solvent, if not otherwise stated. The target products were recorded at 400.13 MHz for ^{1}H and at 100 MHz, for ^{13}C NMR. Chemical shifts, relative to TMS as internal standard, are given in δ values, coupling constants in Hz. ^{13}C resonances were assigned by means of COSY, APT, HSQC and HMBC spectra. All syntheses were carried out in parallel with labeled and non-labeled material. In the case of the 3-^{13}C-compound, NMR data were recorded only of the final product, but not of the intermediates.

Synthesis of β-D-glucopyranose pentaacetate (2)

Acetic anhydride (10.58 mmol, 1.0 ml) was placed into a round-bottom flask and cooled to 0°C. A drop of concentrated perchloric acid was added followed by addition of D-glucose (**1**, 0.82 mmol, 150 mg) in small portions.

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During the addition, the reaction temperature was monitored not to exceed 40°C. The reaction mixture was stirred at r.t. for 1 h and was used for the following step without purification. R_f 0.31 (Hex/EtOAc, v/v = 1:1). Analytical data corresponded to the literature [7].

Synthesis of α-bromo-2,3,4,6-tetra-O-acetyl-D-glucose (3)

The reaction mixture containing **2** was cooled to 15°C and phosphorus tribromide (2.13 mmol, 0.20 ml) was added slowly, followed by careful addition of water (5.55 mmol, 0.10 ml). During both steps the temperature of the reaction mixture was monitored to not exceed 25°C. The reaction mixture was stirred at r.t. for 1.5 h, diluted with EtOAc, neutralized with saturated aqueous $NaHCO_3$. The organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to yield the bromide as a white solid. The crude bromide was co-evaporated three times with dry toluene, dried under vacuum and directly used for the following step. R_f 0.50 (Hex/EtOAc, v/v = 1:1). Analytical data corresponded to the literature [7].

Synthesis of methyl 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (4)

Compound **3** was dissolved in dry CH_2Cl_2 (50 mmol, 3.2 ml). Powdered molecular sieves (4Å) and silver carbonate (4.1 mmol, 1.13 g) were added and the suspension was stirred under light protection and under argon at r.t. for 10 min. Dry MeOH (12 mmol, 0.5 ml) was added dropwise by syringe through a septum. The reaction mixture was stirred for 30 min for complete conversion of the starting material. Solids were filtered off and washed with dry CH_2Cl_2, and the combined filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography (CH_2Cl_2 / MeOH, v/v = 20:1, R_f 0.58) providing the methyl β-glucoside peracetate in 86% yield (0.70 mmol, 255 mg).

Synthesis of methyl β-D-glucopyranoside (5)

For deprotection, compound **4** (1.06 mmol, 385 mg) was dissolved in 4 ml of CH_2Cl_2 / MeOH (v/v = 1:4) and cooled to 0°C. After addition of NaOMe (1M in MeOH, 0.42 mmol, 0.42 ml) the mixture was stirred 15 h under argon at r.t., neutralized with Dowex 50W-8X (H^+) resin, filtered and evaporated to dryness, providing 86% (0.91 mmol, 187 mg) of the deprotected glucoside. R_f 0.7 ($MeOH/CHCl_3/H_2O$, v/v/v = 10:10:1). Analytical data of the non-labeled compound (**5**) agreed with those of the commercially available substance. 1-^{13}C-labeled compound (**5a**): ^{1}H NMR (D_2O): δ 3.25-3.34 (m, 1H, H-2), 3.38-3.56 (m, 3H, H-3, H-4, H-5), 3. 61 (d, 3H, O-CH_3, $J_{C\text{-}1,H}$ = 4.4 Hz), 3.76 (m, 1H, H-6a), 3.97 (m, 1H, H-6b), 4.42 (dd, 1H, H-1, $J_{C\text{-}1,H\text{-}1}$ = 160.4 Hz, $J_{H\text{-}1,H\text{-}2}$ = 7.1 Hz). ^{13}C NMR (D_2O): δ103.22 (^{13}C-1).

Synthesis of methyl 4,6-O-benzylidene-β-D-glucopyranoside (6)

Methyl β-D-gluco-pyranoside (**5**) (0.91 mmol, 186 mg) was dissolved in dry DMF (3 ml). Pre-dried *p*-toluenesulfonic acid (0.05 mmol, 8.5 mg) and benzaldehyde dimethylacetal (2.73 mmol, 0.41 ml) were added, and the mixture was heated for 2 h at 50°C and 50 mbar. Solid $NaHCO_3$ was added to neutralize the reaction mixture. Solids (mainly containing excess $NaHCO_3$) were filtered off, and the solution was co-evaporated with dry toluene to afford compound **6** as white solid in quantitative yield, R_f 0.41 (EtOAc). The product was used in the following step without further purification.

Synthesis of methyl 2,3-di-O-benzyl-4,6-O-benzylidene-β-D-glucopyranoside (7)

Benzylidene acetal **6** (0.91 mmol, 256 mg) was dissolved in dry THF (5.5 ml). NaH (4.55 mmol, 182 mg), tetrabutylammonium iodide (10 mg) and benzyl bromide (3.19 mmol, 0.38 ml) were added under cooling with ice water. The reaction mixture was refluxed for 15 h in an argon atmosphere. The reaction mixture was cooled to r.t. and the excess of NaH was quenched with MeOH under cooling with ice water. The mixture was diluted with EtOAc, washed neutral with H_2O, and washed with brine. The organic layer was dried over Na_2SO_4 and the solvents evaporated to dryness. The solid residue was purified by column chromatography (Hex/EtOAc, v/v = 5:1) to afford **7** as a white solid in 73% yield (0.67 mmol, 311 mg). Analytical data of the non-labeled compound agreed with literature data [8]. 1-^{13}C-labeled compound (**7a**): ^{1}H NMR ($CDCl_3$): δ 3.40-3.48 (m, 2H, H-2, H-3), 3.58 (d, CH_3, $J_{C\text{-}1,H}$ = 4.8 Hz), 3.66-3.75 (m, 2H, H-4, H-5), 3.81 (m, 1H, H-6a), 4.37 (m, 1H, H-6b), 4.42 (dd, 1H, H-1, $J_{C\text{-}1,H\text{-}1}$ = 160.9 Hz, $J_{H\text{-}1,H\text{-}2}$ = 7.9 Hz), 4.73-4.95 (m, 4H, 2 x CH_2Ph), 5.55 (s, 1H, C*H*Ph), 7.27-7.91 (m, 15H, 3 x *Ph*). ^{13}C NMR ($CDCl_3$): δ105.23 (C-1).

Synthesis of methyl 2,3,6-tri-O-benzyl-β-D-glucopyranoside (8)

In an argon atmosphere, triethylsilane (4.70 mmol, 0.75 ml) and trifluoracetic acid (4.70 mmol, 0.36 ml) were added to a solution of compound **7** (0.67 mmol, 311 mg) in anhydrous CH_2Cl_2 at –20°C. The reaction was warmed to r.t., stirred for 3 h, diluted with EtOAc, neutralized with saturated aqueous $NaHCO_3$, and washed consecutively with saturated aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$ and brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (toluene/EtOAc, v/v = 9:2, R_f 0.36) to afford the desired product **8** as a white solid in 66% yield (0.44 mmol, 206 mg). Non-labeled compound (**8**): ^{1}H NMR ($CDCl_3$): δ 3.30-3.41 (m, 3H, H-2, H-3, H-4), 3.49 (s, 3H, 1-OCH_3), 3.53 (m, 1H, H-5), 3.63 (m, 1H, H-6a), 3.70 (m, 1H, H-6b), 4.25 (d, H-1, $J_{H\text{-}1,H\text{-}2}$ = 7.5 Hz), 4.38-4.92 (m, 3x O-CH_2Ph), 7.05-7.27 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ57.27 (1-OCH_3), 70.45 (C-6), 71.75 (C-5), 73.84 (O-CH_2-Ph), 74.84 (O-CH_2-Ph), 75.41 (O-CH_2-Ph), 81.81; 81.94; 84.16 (C-2, C-3, C-4), 104. 92 (C-1), 127.28–138.78 (Ph). 1-^{13}C-labeled compound (**8a**): ^{1}H NMR ($CDCl_3$): δ 3.35-3.48 (m, 3H, H-2, H-3, H-4), 3.56 (d, CH_3, $J_{C\text{-}1,H}$ = 4.5 Hz), 3.59-3.63 (m, 1H, H-5), 3.67-3.80 (m, 2H, H-6a, H-6b), 4.32 (dd, 1H, H-1, $J_{C\text{-}1,H\text{-}1}$ = 160.1 Hz, $J_{H\text{-}1,H\text{-}2}$ = 8.0 Hz), 4.59; 4.71; 4.92 (3 x dd, 6H, 3 x CH_2Ph), 7.26-7.38 (m, 15H, 3 x *Ph*). ^{13}C NMR ($CDCl_3$): δ104.60 (C-1).

Synthesis of methyl 2,3,6-tri-O-benzyl-4-O-methyl -β-D-glucopyranoside (9)

Compound **8** (0.44 mmol, 206 mg) was dissolved in anhydrous THF (7.2ml). NaH (1.82 mmol, 73 mg) was added under cooling with ice water and the reaction mixture was stirred in an Ar atmosphere for 30 min at r.t.. Methyl

iodide (1.82 mmol, 0.11 ml) was added to the solution at 0°C, and stirring was continued for 3 h. Excess NaH was quenched with MeOH while cooling with ice water, and the mixture was diluted with EtOAc, neutralized with water and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (first: Hex, then: Hex/EtOAc, v/v = 1:1 to elute the product) to yield compound **9** in 94% yield (0.41 mmol, 198 mg). Non-labeled compound (**9**): ^{1}H NMR ($CDCl_3$): δ3.18–3.23 (m, 3H, H-4, H-5, H-2), 3.38 (s 3H, 1-O*CH*$_3$), 3.43 (d, 1H, H-3), 3.47 (s, 3H, 4-O*CH*$_3$), 3.60 (m, 1H, H-6a), 3.66 (m, 1H, H-6b), 4.12 (d, 1H, H-1, $J_{H\text{-}1,H\text{-}2}$ = 7.1 Hz), 4.46-4.82 (3 x dd, 6H, 3xO-*CH2*-Ph), 7.15-7.27 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ57.07 (4-OCH_3), 60.68 (1-OCH_3), 69.08 (C-6), 73.53 (O-*CH2*-Ph), 74.76 (O-*CH2*-Ph), 74.99 (C-5), 75.59 (O-*CH2*-Ph), 79.83 (C-4), 82.18 (C-2), 84.61 (C-3), 104.71 (C-1), 127.63-138.72 (Ph). 1-^{13}C-labeled compound (**9a**): ^{1}H NMR ($CDCl_3$): δ 3.25-3.41 (m, 3H, H-4, H-5, H-2), 3.48 (s, 3H, OC*H*$_3$), 3.52 (m, 1H, H-3), 3.56 (d, CH_3, $J_{C\text{-}1,H}$ = 4.4 Hz), 3.67-3.78 (m, 2H, H-6a, H-6b), 4.28 (dd, 1H, H-1, $J_{C\text{-}1,H\text{-}1}$ = 159.5 Hz, $J_{H\text{-}1,H\text{-}2}$ = 7.7 Hz), 4.65; 4.73; 4.89 (3 x dd, 6H, 3 x C*H*$_2$Ph), 7.27-7.35 (m, 15H, 3 x *Ph*). ^{13}C NMR ($CDCl_3$): δ104.60 (C-1).

Synthesis of methyl 4-O-methyl-β-D-glucopyranoside (10)

Compound **9** (0.41 mmol, 198 mg) was dissolved in MeOH (20 ml) and 40 mg of Pd/C (10%) were added and stirred under hydrogen (10 bar) overnight at r.t. The catalyst was filtered off and the solution evaporated to dryness to obtain debenzylated compound **10** in quantitative yield (0.41mmol, 86 mg). R_f 0.1 (CH_2Cl_2/MeOH, v/v = 9:1). Non-labeled compound (**10**): ^{1}H NMR (D_2O): δ3.16–3.28 (m, 2H, H-4, H-2), 3.45 (m, 1H, H-5), 3.54 (s, 3H, 1-O*CH*$_3$), 3.55 (s, 3H, 4-O*CH*$_3$), 3.57-3.59 (m, 1H, H-3), 3.73 (dd, 1H, H-6a), 3.91 (dd, 1H, H-6b), 4.33 (d, 1H, H-1). ^{13}C NMR (D_2O): δ57.14 (4-O*CH*$_3$), 59.98 (1-O*CH*$_3$), 60.39 (C-6), 73.05 (C-3), 74.89 (C-2), 75.40 (C-5), 79.28 (C-4), 103.11 (C-1). 1-^{13}C-labeled compound (**10a**): ^{1}H NMR (D_2O): δ 3.15-3.34 (m, 2H, H-4, H-2), 3.41-3.48 (m, 1H, H-5), 3.54 (s, 3H, 4-O*CH*$_3$), 3.56 (d, CH_3, 1-O*CH*$_3$, $J_{C\text{-}1,H}$ = 4.6 Hz), 3.58-3.62 (m, 1H, H-3), 3.73 (dd, 1H, H-6a), 3.91 (dd, 1H, H-6b), 4.33 (dd, 1H, H-1, $J_{C\text{-}1,H\text{-}1}$ = 161.0 Hz, $J_{H\text{-}1,H\text{-}2}$ = 7.8 Hz). ^{13}C NMR (D_2O): δ103.15 (^{13}C-1).

Synthesis of methyl 4-O-methyl-β-D-ribo-hex-3-ulopyranoside (11)

Compound **10** (0.41 mmol, 86 mg) was dissolved in $CHCl_3$ (7 ml) and powdered molecular sieves (3Å) was added followed by tributyltin(IV) oxide (0.82 mmol, 0.42 ml). The suspension was stirred and refluxed for 3 h under argon, cooled to 0°C and bromine (approx. 1 mmol, 55 µl) was added until a faint coloration was observed. The suspension was applied onto a silica gel column and washed with $CHCl_3$ (25 ml). The desired product was then eluted by changing the solvent system to CH_2Cl_2/MeOH, v/v = 9:1. Compound **11** was obtained in 79% yield (0.32 mmol, 67 mg) as a white solid. R_f 0.26 (CH_2Cl_2/MeOH, v/v = 9:1). Non-labeled compound (**11**): ^{1}H NMR ($CDCl_3$): δ3.43–3.47 (m, 1H, H-5), 3.58 (s, 3H, 4-O*CH*$_3$), 3.69 (s, 3H, 1-O*CH*$_3$), 3.86 (dd, 1H, H-6a), 4.01 (dd, 1H, H-6b), 3.99-4.12 (m, 2H, H-2, H-4), 4.26 (d, 1H, H-1, $J_{H\text{-}1,H\text{-}2}$ = 7.9 Hz). ^{13}C NMR ($CDCl_3$): δ57.76 (4-O*CH*$_3$), 59.81 (1-O*CH*$_3$), 61.79 (C-6), 75.35 (C-5), 77.34 (C-2), 80.40 (C-4), 105.75 (C-1), 205.12 (C-3). $C_8H_{14}O_6$ (206.2): C 46.60, H 6.84, found: C 46.85, H 6.96. 1-^{13}C-labeled compound (**11a**): ^{1}H NMR ($CDCl_3$): δ 3.42-3.47 (m, 1H, H-5), 3.58 (s, 3H, 4-O*CH*$_3$), 3.63 (d, 1-O*CH*$_3$, $J_{C\text{-}1,H}$ = 4.9 Hz), 3.86 (dd, 1H, H-6a), 4.01 (dd, 1H, H-6b), 4.04-4.13 (m, 2H, H-2, H-4), 4.26 (dd, 1H, H-1, $J_{C\text{-}1,H\text{-}1}$ = 164.4 Hz, $J_{H\text{-}1,H\text{-}2}$ = 8.0 Hz). ^{13}C NMR ($CDCl_3$) δ 57.77 (4-O*CH*$_3$), 59.81 (C-1-O*CH*$_3$), 61.81 (d, J = 4.6 Hz, C-6), 75.37 (C-5), 77.47 (d, $^1J_{C,C}$ = 21.3 Hz, C-2), 80.43 (C-4), 105.77 (1-^{13}C), 205.13 (C-3). Microanalysis calcd. for $^{13}CC_7H_{14}O_6$ (207.2): C 46.37, H 6.81, found: C 46.32, H 6.89. 3-^{13}C-labeled compound (**11b**): ^{1}H NMR ($CDCl_3$): δ 3.43-3.48 (m, 1H, H-5), 3.59 (s, 3H, 4-O*CH*$_3$), 3.64 (s, 3H, 1-O*CH*$_3$), 3.87 (m, 1H, H-6a), 4.02 (m, 1H, H-6b), 4.07-4.13 (m, 2H, H-2, H-4), 4.27 (d, 1H, H-1, $J_{H\text{-}1,H\text{-}2}$ = 7.1 Hz). ^{13}C

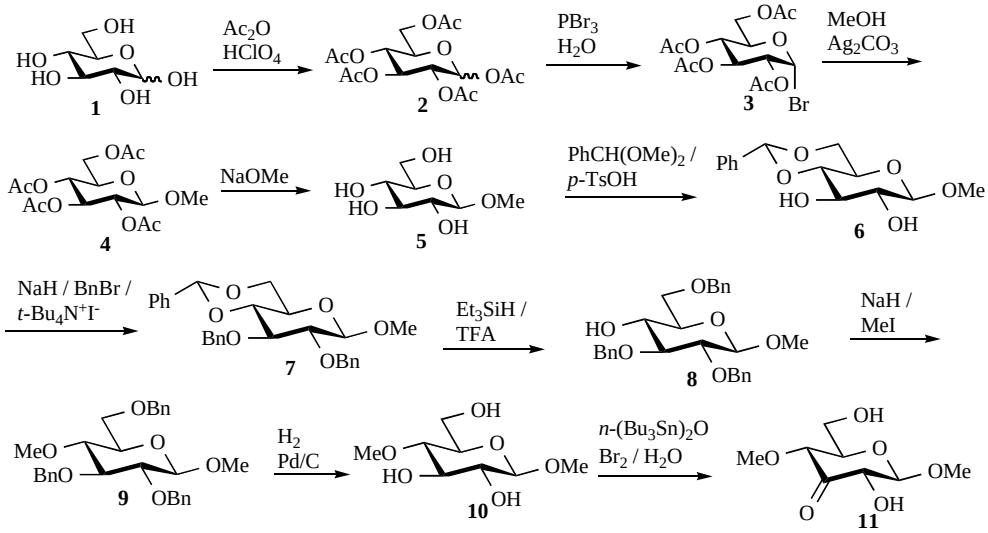

Fig. (1). Synthesis scheme is shown for the non-labeled compound **11**. The paths for the 1-^{13}C compound **11a** and the 3-^{13}C compound **11b** were analogous, starting from correspondingly labeled D-glucose (**1**).

NMR ($CDCl_3$): δ 57.71 (4-O*CH*$_3$), 59.76 (1-O*CH*$_3$), 61.88 (C-6), 75.36 (C-5), 77.52 (C-2, $J_{C-2,C-3}$ = 35.4 Hz), 80.49 (C-4, $J_{C-4,\ C-3}$ = 41.7 Hz), 105.77 (C-1), 205.10 (3-^{13}C). $^{13}CC_7H_{14}O_6$ (207.2): C 46.37, H 6.81, found: C 46.29, H 6.92.

RESULTS AND DISCUSSION

The basic synthetic approaches to build up the desired cellulosic model compounds have been published by our group [6, 8, 9], but had to be extended (Fig. **1**). Careful optimization towards maximum yields was required due to the high costs of the ^{13}C-labeled materials. While work with non-labeled compounds could be based on the use of commercially available methyl β-D-glucopyranoside, the syntheses of the labeled model compounds necessitated the use of labeled D-glucoses as the only commercially available starting materials – which meant four additional synthesis steps including the high-yield glycosidation to form the β-methyl glucoside. The final, optimized reaction sequence implied ten steps (Fig. **1**) and overall yields of 14.7% for the 1-^{13}C-labeled compound **11a** and 6.3% for the 3-^{13}C-labeled compound **11b**. Key steps were the moisture-sensitive glycosylation and the regioselective benzylidene acetal ring opening.

In the initial steps, peracetylated D-glucose (**2**) was converted into its α-bromide according to the Helferich protocol [7] and into the β-methyl glucoside under Koenigs-Knorr conditions [10]. Among commonly used promoters, such as silver triflate, mercuric bromide, mercuric oxide or mercuric cyanide [10-12], 5 equivalents of silver carbonate and the solvent mixture dichloromethane / methanol (v/v = 5:1) worked best. Introduction of the 4,6-*O*-benzylidene group followed by benzylation of the remaining hydroxyl groups resulted in a rather apolar compound that was conveniently purified by column chromatography. Regioselective opening of the benzylidene acetal to obtain **8** bearing a free hydroxyl group at C-4 was achieved by use of

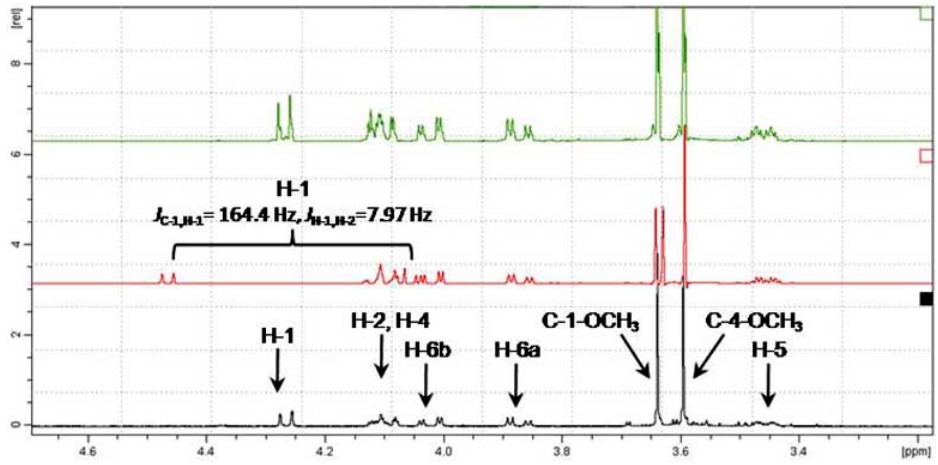

Fig. (2). ^{1}H NMR spectra ($CDCl_3$, 400 MHz) spectra of methyl 4-*O*-methyl-β-D-*ribo*-hex-3-ulopyranoside: non-labeled (**11**, lower spectrum), 1-^{13}C (**11a**, middle spectrum), and 3-^{13}C (**11b**, upper spectrum).

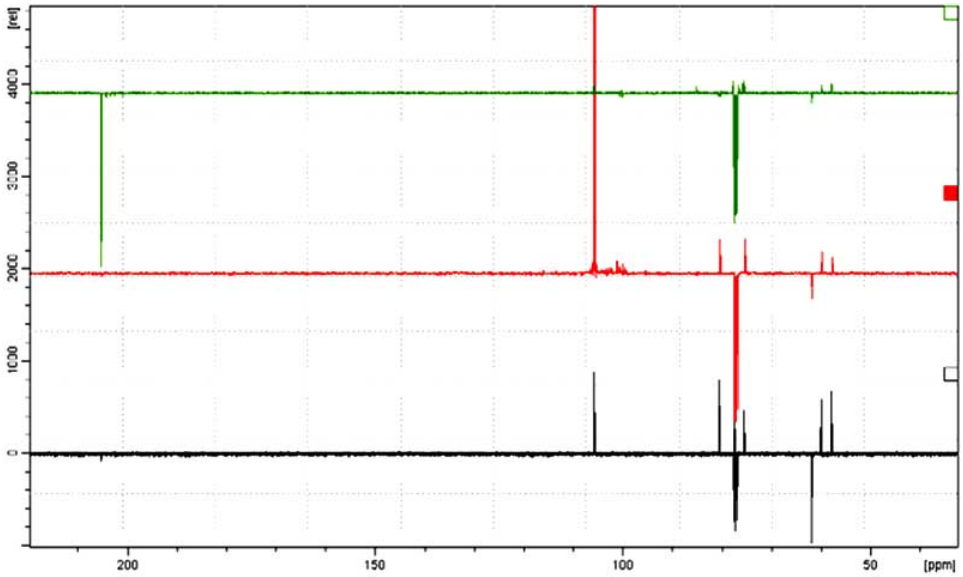

Fig. (3). ^{13}C NMR spectra (APT, $CDCl_3$, 100 MHz) of methyl 4-*O*-methyl-β-D-*ribo*-hex-3-ulopyranoside: non-labeled (**11**, lower spectrum), 1-^{13}C (**11a**, middle spectrum), and 3-^{13}C (**11b**, upper spectrum).

triethylsilane and THF [13]. The alternative ring opening with sodium cyanoborohydride / HCl [14] was tested as well but showed considerably more byproducts. The deprotected 4-OH was methylated with methyl iodide, subsequent debenzylation was performed with Pd/C (10%) and H_2 at 10 bar. Lower hydrogen pressure caused incomplete debenzylation. The final oxidation step, regioselective at position 3, used the bis-tributyltin oxide / bromine protocol [15, 16], whereas Swern oxidation as used in our previous work [6, 8] was much less successful.

NMR analysis of the labeled compounds corresponded to the data achieved with non-labeled material, but the ^{13}C-enriched positions caused additional homo- (C – C) and heteronuclear (C – H) couplings. The ^{1}H and ^{13}C spectra of the non-labeled product **11** in comparison to the 1-^{13}C compound **11a** and the 3-^{13}C substance **11b** are given in Figs. (**2** and **3**), respectively.

CONCLUSIONS

A ten-step synthetic route to ^{13}C-labeled methyl 4-*O*-methyl-β-D-*ribo*-hex-3-ulopyranosides as model compounds for oxidized anhydroglucose units in celluloses was presented. The reaction products, analyzed with modern NMR techniques, will be the basis of further studies into chromophore formation processes in cellulosic materials.

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