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Novel Cellulose Ethers: Synthesis and Structure Characterization of 3-Mono-*O*-(3′-hydroxypropyl) Cellulose

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Summary: The synthesis of 3-mono-*O*-(3′-hydroxypropyl) cellulose via 3-mono-*O*-allyl-2,6-di-*O*-thexyldimethylsilyl cellulose was studied. Conversion of the double bond with 9-borabicyclo[3.3.1]nonane and subsequent alkaline oxidation lead to the 3′-hydroxypropyl group. Finally, the treatment with tetrabutylammonium fluoride trihydrate yields the complete cleavage of the protecting groups. The structure of the polymer was confirmed by one- and two dimensional NMR spectroscopic techniques. 3-mono-*O*-(3′-hydroxypropyl) cellulose is soluble in water and aprotic-dipolar organic media.

Keywords: cellulose; etherification; hydroboration; NMR; protecting group

Introduction

Hydroxypropyl cellulose (HPC) and methylhydroxypropyl cellulose (MHPC) are important commercially produced cellulose ethers that find widespread application in various fields, e.g., as stabilizer of whipped cream and in cosmetic emulsions[1], hydrogels as drug delivery devices, materials for chromatography and superabsorbency capabilities[2], fibres for wound dressing, as catalysts, or membranes.[3] Commercial HPC is manufactured under pressure from alkali cellulose in a slurry process using propylene oxide as etherifying agent. Thus, the ether moieties introduced, which are randomly distributed both in the anhydroglucose unit (AGU) and along the polymer chain, possess secondary hydroxyl groups. These newly formed hydroxyl groups may be even more reactive than the hydroxyl group of the AGU. As a consequence, during the etherification reaction the formation of side chains (oxyalkylene chains) may occur. One to three propylene oxide molecules are involved in the side chain formation.[4] In addition, in case of the preparation of mixed ethers like MHPC, the methylation does not only occur on the OH groups of the AGU but also on the hydroxyl groups of the hydroxypropyl moieties. As a result of the various possible reactions, cellulose ethers like HPC and MHPC show a very complex structure that is hard to analyze in detail. Therefore, it is difficult to get comprehensive information about structure property relationships.

Applying the protecting group technique, it is possible to control the distribution of substituents within the AGU.[5,6] Recently, various cellulose ethers functionalized selectively at position 3 were synthesized via 2,6-di-*O*-thexyldimethylsilyl cellulose and characterized in detail by two-dimensional NMR spectroscopy.[7–9] Thus, it is possible to introduce allyl ether functions at position 3 by reaction with allyl chloride as well. It is well-known in organic chemistry that double bonds undergo hydroboration yielding hydroxyl groups after oxidation under alkaline conditions.[10] Applying 9-borabicyclo[3.3.1]-nonane[11] a regioselective hydroboration is

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possible that finally may lead to the primary alcohol moiety. In the present paper, the synthesis and detailed structure characterisation of 3-mono-*O*-(3′-hydroxypropyl) cellulose via 3-mono-*O*-allyl-2,6-di-*O*-thexyldimethylsilyl cellulose is discussed.

Experimental Part

Materials

Cellulose **1** (Avicel®, degree of polymerization 222) was dried in vacuum over KOH at 100 °C and LiCl was dried in vacuum over KOH at 100 °C prior to use. *N,N*–Dimethylacetamide (DMA, Fluka), tetrahydrofuran (THF, Aldrich) and pyridine (Fluka) were stored over molecular sieves. Sodium hydride (Fluka, suspension in mineral oil) was washed with *n*-hexane and was dried in vacuum at room temperature. Thexyldimethylchlorosilane (TDMS-Cl, ABCR), 9-borabicyclo[3.3.1]nonane (9-BBN, Aldrich) and all other chemicals were used as received. 1 L phosphate buffer solution consists of 3.54 g KH_2PO_4 and 11.65 g $K_2HPO_4 \cdot 3H_2O$ in deionised water.

2,6-Di-*O*-thexyldimethylsilyl Cellulose 2

Cellulose **1** (10.0 g, 0.0617 mol) was slurried in 300 mL DMA and stirred for 2 h at 120 °C under exclusion of moisture. After cooling to 80 °C and addition of 18 g LiCl, stirring was continued over night at room temperature. To the solution formed, 20.10 g (0.295 mol) imidazole and 49.0 mL (0.249 mol) TDMS-Cl were added. The temperature was increased to 100 °C and stirring was continued for 24 h. After cooling to room temperature, the polymer was precipitated with 2 L phosphate buffer solution, filtered off, washed with water and ethanol. The product was dried in vacuum at 40 °C.

Yield: 26.1 g (95%)

Degree of substitution: 1.89 (based on the silicon content of 26.32%)

The product is soluble in toluene, THF, chloroform and *n*-hexane.

SEC (THF): $M_w = 2.55 \cdot 10^5$ g/mol, $M_n = 7.02\ 10^5$ g/mol

FT-IR (KBr, cm^{-1}): 3512 ν(O–H); 2960, 2872 ν(C–H); 1468, 1375 $\delta(CH_3)$; 1255 δ(Si–C); 1121, 1078 ν(C–O–C); 777 ν(Si–C).

^{1}H-NMR ($CDCl_3$, ppm): $\delta = 0.04$–0.19, Si–C$\underline{H_3}$; 0.85, Si–C(C$\underline{H_3}$)$_2$CH(C$\underline{H_3}$)$_2$; 1.62, Si–C(CH$_3$)$_2$C$\underline{H}$(CH$_3$)$_2$; 3.00–5.55, H-1-H-6.

^{13}C-NMR ($CDCl_3$, ppm): $\delta = -3.5$, -2.6, -1.6, -0.5, Si–(C$\underline{H_3}$)$_2$; 18.6, 18.7, 18.8, Si–C(C$\underline{H_3}$)$_2$(CH(CH$_3$)$_2$; 20.3, 20.4, 20.6, Si–C(CH$_3$)$_2$(CH(C$\underline{H_3}$)$_2$; 25.1, Si–C$\underline{(CH_3)_2}$-CH(CH$_3$)$_2$; 34.2, Si–C(CH$_3$)$_2$C$\underline{H}$(CH$_3$)$_2$; 60.3–61.8, C-4, C-6; 71.9–82.0, C-2, C-3, C-5; 101.9, C-1.

3-Mono-*O*-allyl-2,6-di-*O*-thexyldimethylsilyl Cellulose 3

To a solution of 10.0 g (0.0224 mol) **2** in 100 mL THF, 5.37 g (0.224 mol) sodium hydride were added under vigorous stirring followed by the dropwise addition of 18.3 mL (0.224 mol) allyl chloride. The slurry was stirred for 23 h at room temperature and 3 d at 50 °C. After cooling to room temperature, about 20 mL isopropanol and subsequently 20 mL H_2O were carefully added in order to destroy excess of NaH. The mixture was poured into phosphate buffer solution and neutralized with acetic acid. The product was filtered off, washed with water and ethanol, and dried in vacuum at 40 °C.

Yield: 8.33 g (76%)

The product is soluble in toluene, THF, chloroform.

SEC (THF): $M_w = 2.92 \cdot 10^4$ g/mol, $M_n = 9.11\ 10^3$ g/mol

FT-IR (KBr, cm^{-1}): 3079 ν(C–H); 2959, 2872 ν(C–H); 1466, 1378 $\delta(CH_3)$; 1252 δ(Si–C); 1123, 1086 ν(C–O–C); 777 ν(Si–C).

^{1}H-NMR ($CDCl_3$, ppm): $\delta = 0.13$, Si–C$\underline{H_3}$; 0.87, Si–C(C$\underline{H_3}$)$_2$CH(C$\underline{H_3}$)$_2$; 1.63–1.68, Si–C(CH$_3$)$_2$C$\underline{H}$(CH$_3$)$_2$; 3.15–5.15, H-1-H-6, OC$\underline{H_2}$CHC$\underline{H_2}$; 6.00, OCH$_2$-C$\underline{H}$C$\underline{H_2}$.

^{13}C-NMR ($CDCl_3$, ppm): $\delta = -3.6$, -3.1, -2.1, -1.4, Si–(C$\underline{H_3}$)$_2$; 18.5, 18.8, Si–C(C$\underline{H_3}$)$_2$-CH(CH$_3$)$_2$; 20.3, 20.6, Si–C(C$\underline{H_3}$)$_2$CH(CH$_3$)$_2$; 24.8, 25.4, Si–C$\underline{(CH_3)_2}$CH(CH$_3$)$_2$; 33.8, 34.0, Si–C(CH$_3$)$_2$C$\underline{H}$(CH$_3$)$_2$; 61.4, C-6;

73.6–75.0, C-2, C-4, C-5, $O\underline{C}H_2CHCH_2$; 82.5, C-3; 101.3, C-1; 115.8, $OCH_2CH\underline{C}H_2$; 137.2, $OCH_2\underline{C}HCH_2$.

3-Mono-*O*-(3′-hydroxypropyl)-2,6-di-*O*-thexyldimethylsilyl Cellulose 4

To a solution of 3.0 g (0.00616 mol) **3** in 15 mL THF, 130.5 mL (0.0645 mol) of a 0.5 M 9-BBN in THF were added dropwise under argon at 0 °C. After stirring at room temperature for 24 h, the reaction mixture was cooled to 0 °C and 15.5 mL (0.116 mol, 30%) aqueous NaOH and 134 mL (1.30 mol, 33%) H_2O_2 were added dropwise. After stirring for 1 h at room temperature, about 50 mL THF were removed by distillation. The mixture was stirred for 48 h at 60 °C. After cooling to room temperature, the two phases formed were separated. The upper organic phase was poured into 1 L methanol/water 1:1 (v/v) and the polymer was filtered off, washed with methanol/water 1:1 (v/v) and dried under vacuum at 40 °C.

Yield: 2.24 g (72%)

The product is soluble in toluene, THF, chloroform, DMA, 1-methyl-2-pyrrolidinone (NMP).

SEC (THF): $M_w = 7.07 \cdot 10^5$ g/mol, $M_n = 4.86\ 10^4$ g/mol

FT-IR (KBr, cm^{-1}): 3455 ν(O–H); 2958, 2873 ν(C–H); 1427, 1379 $\delta(CH_3)$; 1253 δ(Si–C); 1117, 1084 ν(C–O–C); 777 ν(Si–C).

^{1}H-NMR ($CDCl_3$, ppm): $\delta = 0.13$, Si–$C\underline{H}_3$; 0.87, Si–$C(C\underline{H}_3)_2CH(C\underline{H}_3)_2$; 1.64–1.80, Si–$C(CH_3)_2C\underline{H}(CH_3)_2$, $OCH_2C\underline{H}_2CH_2O\underline{H}$; 2.88–4.63, H-1-H-6, $OC\underline{H}_2CH_2C\underline{H}_2OH$.

^{13}C-NMR ($CDCl_3$, ppm): $\delta = -3.3$, -3.1, -2.4, -1.2, Si–$\underline{C}H_3$; 18.6, Si–$C(\underline{C}H_3)_2$-$CH(CH_3)_2$; 20.4, Si–$C(CH_3)_2CH(\underline{C}H_3)_2$; 24.8, 25.4, Si–$\underline{C}(CH_3)_2CH(CH_3)_2$; 32.8, $OCH_2\underline{C}H_2CH_2OH$; 33.7, 33.9, Si–$C(CH_3)_2$-$\underline{C}H(CH_3)_2$; 59.6, $OCH_2CH_2\underline{C}H_2OH$; 61.7, $O\underline{C}H_2CH_2CH_2OH$; 70.4–74.9, C-2-C-6; 101.7, C-1.

3-Mono-*O*-(3′-hydroxypropyl) Cellulose 5

To a solution of 2.0 g ($3.96 \cdot 10^{-3}$ mol) **4** in 36 mL THF, 5.0 g (0.0158 mol) tetrabutylammonium fluoride trihydrate ($TBAF \cdot 3H_2O$) were added and the mixture was stirred for 24 h at 50 °C. After cooling to room temperature, the polymer was precipitated with diethyl ether/isopropanol 3:1 (v/v) and filtered off. The polymer was dissolved in 30 mL DMSO containing 3.27 g (0.0103 mol) $TBAF \cdot 3H_2O$ and stirred for 24 h at 50 °C with. The product was precipitated with diethyl ether/isopropanol 2:1 (v/v), filtrated off, washed with diethyl ether/isopropanol 2:1 (v/v), and dried in vacuum at 40 °C.

Yield: 0.76 g (87%)

The product is soluble in dimethyl sulfoxide (DMSO), DMA, *N,N*-dimethyl formamide and water.

SEC (DMSO): $M_w = 3.74 \cdot 10^4$ g/mol, $M_n = 1.84\ 10^4$ g/mol

FT-IR (KBr, cm^{-1}): 3415 ν(O–H); 2932, 2884 ν(C–H); 1417, 1369 $\delta(CH_3)$; 1110, 1064 ν(C–O–C).

^{1}H-NMR (DMSO, ppm): $\delta = 1.64$, $OCH_2C\underline{H}_2CH_2OH$; 2.74–5.82, H-1-H-6, $OC\underline{H}_2CH_2C\underline{H}_2OH$.

^{13}C-NMR (DMSO, ppm): $\delta = 33.5$, $OCH_2\underline{C}H_2CH_2OH$; 58.8, $OCH_2CH_2\underline{C}H_2OH$; 60.6, $O\underline{C}H_2CH_2CH_2OH$; 69.7, C-6; 74.1, C-2; 75.2, C-5; 76.0, C-4; 84.0, C-3; 103.1, C-1.

2,6-Di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) Cellulose 6

A mixture of 0.15 g (0.000681 mol) **5**, 5 mL pyridine, 5 mL acetic anhydride, and 0.01 g 4–*N,N*–dimethylaminopyridine was stirred for 24 h at 80 °C. After cooling to room temperature, the product was precipitated with methanol, filtered off, washed with methanol, and dried in vacuum at 40 °C.

Yield: 0.13 g (55%)

The product is soluble in chloroform, DMSO, NMP.

SEC (THF): $M_w = 4.84 \cdot 10^4$ g/mol, $M_n = 2.60\ 10^4$ g/mol

FT-IR (KBr, cm^{-1}): 2965, 2895 ν(C–H); 1741 ν(C=O); 1433, 1372 $\delta(CH_3)$; 1047 ν(C–O–C).

^{1}H-NMR ($CDCl_3$, ppm): $\delta = 1.73$, $OCH_2C\underline{H}_2CH_2OC(O)CH_3$; 2.01, 2.07, $OCH_2CH_2CH_2OC(O)C\underline{H}_3$, $OC(O)C\underline{H}_3$; 2.96, H-2″; 3.10, H-2′; 3.19, H-3″; 3.31, H-

3; 3.39, H-5; 3.47, H-6; 3.63, H-4, H-4′, H-4″; 3.81, H-6; 4.00, $OCH_2CH_2C\underline{H}_2OC(O)CH_3$; 4.07, $OC\underline{H}_2CH_2C\underline{H}_2OC(O)CH_3$; 4.33, H-1, H-1′, H-1″, $OC\underline{H}_2CH_2CH_2OC(O)CH_3$; 4.77, H-2; 5.02, H-3′.

^{13}C-NMR ($CDCl_3$, ppm): $\delta = 20.7$, 20.9, $OCH_2CH_2CH_2OC(O)\underline{C}H_3$, $OC(O)\underline{C}H_3$; 29.2, $OCH_2\underline{C}H_2CH_2OC(O)CH_3$; 61.5, $OCH_2CH_2\underline{C}H_2OC(O)CH_3$; 62.2, $O\underline{C}H_2CH_2CH_2OC(O)CH_3$; 69.2, C-6; 73.1, C-2; 73.5, C-5; 76.4–77.7, C-4; 80.7, C-3; 100.6, C-1; 169.2, $C^2O\underline{C}(O)CH_3$; 170.3, $OCH_2CH_2CH_2O\underline{C}(O)CH_3$; 170.9, $C^6O\underline{C}(O)CH_3$.

Measurements

FTIR spectra were acquired with a NICOLET AVATAR 370 DTGS spectrometer using the KBr technique. NMR spectra were obtained with Bruker Avance 250 (250 MHz) or Avance 400 (400 MHz) in $CDCl_3$ or DMSO-d_6 (sample concentration 5–10%) at 25 °C or 50 °C using standard pulse sequences for ^{1}H-, ^{13}C-, TOCSY, selective TOCSY, and two-dimensional (COSY, TOCSY, HSQC-DEPT, HMBC) NMR spectra.

A JASCO SEC system was applied consisting of a degasser DG 980-50, pump PU 980, UV detector 975 ($\lambda = 354$ nm), refractive index detector 930, column oven and guard column.

SEC in THF: A flow rate of 1 mL/min at 30 °C was chosen. Three SDV-Gel columns (10^6, 10^4, and 10^3 Å, Polymer Standards Service, Mainz, Germany) were used.

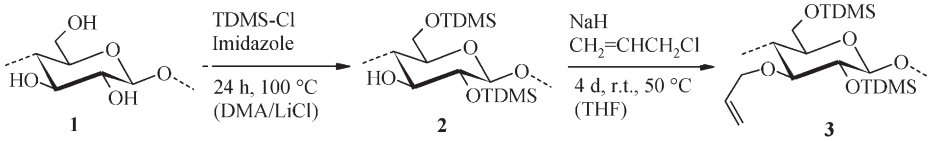
SEC in DMSO: A flow rate of 0.5 mL/min at 70 °C was chosen. The columns used were Novema-Gel columns (3 10^3 and 0.3 10^3 Å, Polymer Standards Service, Mainz, Germany).

Results and Discussion

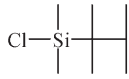
It is known that the silylation of cellulose **1** dissolved in *N,N*-dimethyl acetamide (DMA)/LiCl with thexyldimethylchlorosilane (TDMS-Cl) in the presence of imidazole yields 2,6-di-*O*-TDMS cellulose **2**. Subsequent allylation of **2** yielding 3-mono-*O*-allyl-2,6-di-*O*-TDMS cellulose **3** was carried out with allyl chloride in the presence of NaH based on a procedure published in ref.[9] (Scheme 1).

Preparation and Structural Characterization of 3-Mono-*O*-(3′-hydroxypropyl) Cellulose

Hydroboration of 3-mono-*O*-allyl-2,6-di-*O*-TDMS cellulose **3** was carried out with an excess of 9-borabicyclo[3.3.1]nonane in tetrahydrofuran (THF) at 0 °C and subsequently at room temperature. The intermediate formed was treated with aqueous NaOH solution (30%) and hydrogen peroxide (33%) at room temperature. The temperature was increased carefully (gas formation) and THF was partly removed by distillation. Subsequently, the solution was stirred for 48 h at 60 °C, forming two phases. The upper organic phase was isolated by



r. t.: room temperature
DMA: *N,N*-Dimethylacetamide
THF: Tetrahydrofuran
TDMS-Cl: Thexyldimethylchlorosilane



Scheme 1.
Reaction scheme for the preparation of 3-*O*-allyl-2,6-di-*O*-TDMS cellulose **3**.

precipitation with methanol/water 1:1, filtered off, washed with methanol/water 1:1 (v/v) and dried in vacuum at 40 °C Scheme 2.

The product 3-mono-*O*-(3′-hydroxypropyl)-2,6-di-*O*-thexyldimethylsilyl cellulose **4** is soluble in organic solvents like toluene, chloroform, THF, DMA, 1-methyl-2-pyrrolidinone. In the FTIR spectrum the typical absorption bands of the modified repeating unit appear at: 3455 ν(O–H); 2958, 2873 ν(C–H); 1427, 1379 $\delta(CH_3)$; 1253 δ(Si–C); 1117, 1084 ν(C–O–C) and at 777 ν(Si–C) cm^{-1}. For desilylation, the polymer **4** was treated with tetrabutylammonium fluoride trihydrate (TBAF · $3H_2O$) in THF and subsequently in dimethyl sulfoxide. ^{1}H- and ^{13}C NMR spectra of the cellulose derivative obtained do not show signals of silicon containing moieties, but signals of TBAF · $3H_2O$. Thus, the sample was additionally purified by dialysis. After freeze drying a pure product, i. e. free of silicon and TBAF, was obtained. Structure characterization of 3-mono-*O*-(3′-hydroxypropyl) cellulose **5** was carried out by means of NMR spectroscopy.

In the ^{13}C NMR spectrum (Figure 1), the expected signals of the modified anhydroglucose unit (AGU) appear; C-1 occurred at 103.1 ppm indicting the absence of substituents at position 2. The peak for C-3 bearing the 3′-hydroxypropyl ether is shifted downfield to 84.0 ppm. Further peaks of the modified AGU appear at 76.0 (C-4), 75.2 (C-5), 74.1 (C-2), and 69.7 ppm (C-6). In addition, the signals at 60.6 (C-9), 58.8 (C-11) and 33.5 ppm (C-10) can be assigned to the carbon atoms of the functional group $CH_2CH_2CH_2OH$.

The structure was confirmed by means of two-dimensional NMR measurements. For this purpose, **5** was converted to 2,6-di-*O*-

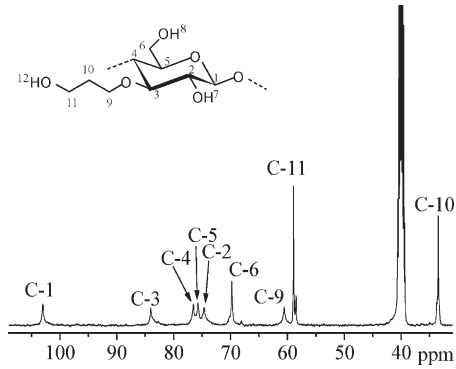
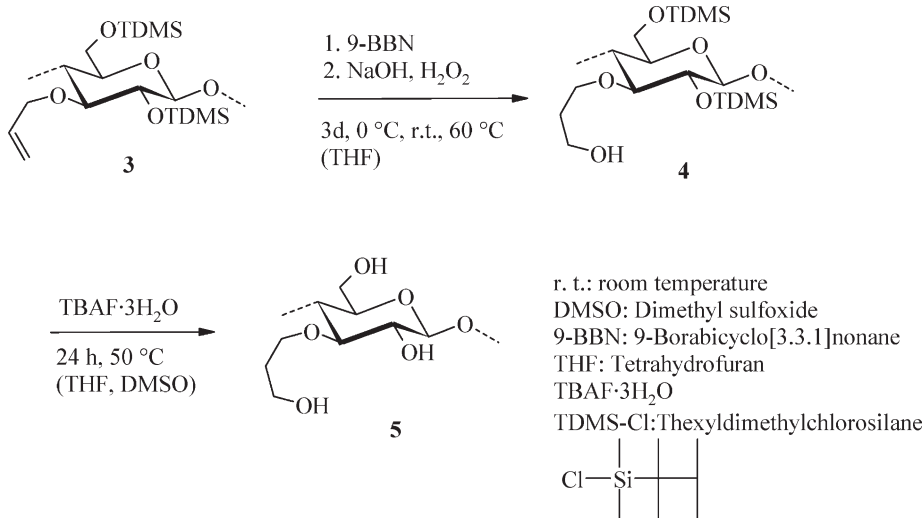
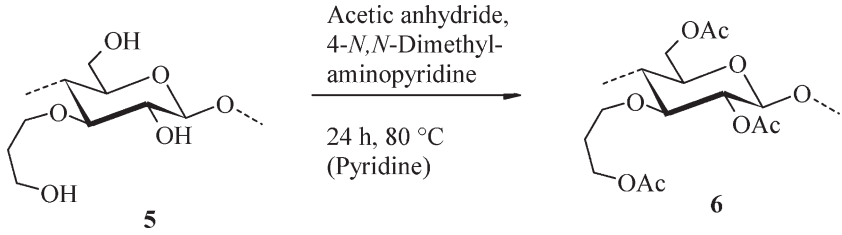


Figure 1.
^{1}H NMR spectrum of 3-mono-*O*-(3′-hydroxypropyl) cellulose **5** (recorded in dimethylsulfoxide-d_6) after desilylation and dialysis.



Scheme 2.
Reaction scheme for the preparation of 3-mono-*O*-(3′-hydroxypropyl) cellulose **5**.



Scheme 3.
Preparation of 2,6-di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose **6**.

acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose **6**, see Scheme 3. Thus, the spectral resolution is increased due to decrease of intermolecular interactions of the dissolved polymer that is well soluble in $CDCl_3$. In case of partly functionalized cellulose products and cellulose derivatives bearing hydroxyl groups in the substituent, hydrogen bonds may cause intensive interactions that may be a reason for badly resolved NMR spectra. Sample **6** was subjected to NMR analysis in $CDCl_3$ solution.

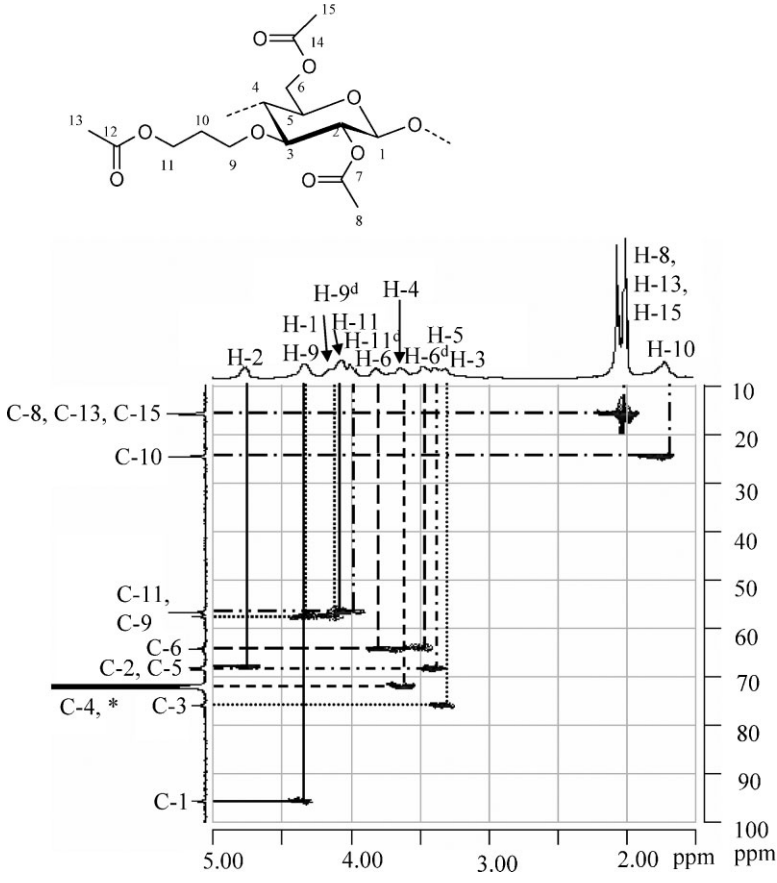


Figure 2.
$^1H/^{13}C$ HSQC DEPT NMR spectrum of 2,6-di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose **6** ($CDCl_3$), ^{d} = diastereotop protons.

The $^{1}H/^{13}C$ HSQC DEPT NMR spectrum of 2,6-di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose (**6**, Figure 2) proves that the signal of C-6 appears at 69.2 ppm, because two signals are observed for H-6 at 3.47 and 3.81 ppm due to the neighbouring chiral carbon atom at position 5. The carbon atom of C-6 is shifted downfield compared to other 3-*O*-ethers of cellulose like 3-mono-*O*-methyl cellulose.[9] Further signals of the modified AGU appear at 4.77 (H-2), 4.33 (H-1), 3.63 (H-4), 3.39 (H-5) and 3.31 ppm (H-3) and at 100.6 (C-1), 80.7 (C-3), 76.4–77.7 (C-4), 73.5 (C-5) and 73.1 (C-2). In addition, two signals are found for the CH_2 groups of the propyl-3′-acetyl moiety adjacent to oxygen atom at 4.33 and 4.07 (H-9) as well as 4.00 and 4.07 ppm (H-11). The corresponding signals for carbon atoms are observed at 61.5 (C-11) and 62.2 ppm (C-9). A peak at 1.73 (H-10)/29.2 ppm (C-10) is clearly assigned to the CH_2-group (10) of the 3′-hydroxypropyl. The signals of the methyl protons (H-8, H-13, H-15) are found in the range from 1.06 ppm to 2.14 ppm and interact with C-8, C-13, and C-15 that appear as a peak group at about 20.8 ppm as well. One peak for each carbon atom at 170.9 (C-14), 170.3 (C-12), 169.2 (C-7) ppm (not shown) appears in the carbonyl region of the ^{13}C NMR spectrum.

In further investigations, the novel 3-mono-*O*-(3′-hydroxypropyl) cellulose was analyzed by means of COSY-, TOCSY- and HMBC NMR spectroscopy (Figures 3–5). In addition to the relevant signals that proof the structure of the 3-mono-*O*-(3′-hydroxypropyl) cellulose, some small signals appear indicating a slight deviation from the ideal molecular structure. It must be pointed out that the 2,6-di-*O*-protected cellulose derivatives are not completely uniform. That means there are some non-protected hydroxyl groups at position 2 that are allylated and oxidized subsequently. As a consequence a side structure occurred

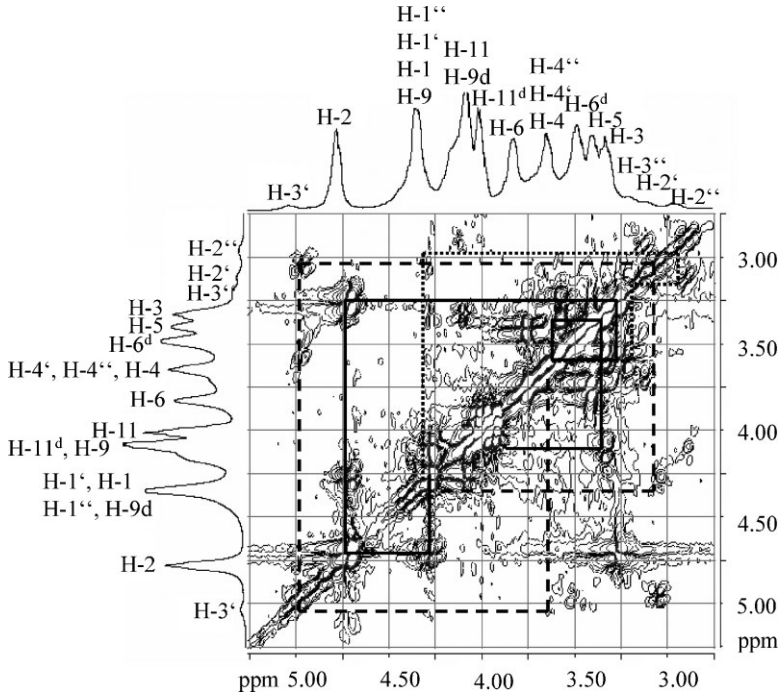


Figure 3.
$^{1}H/^{1}H$ COSY NMR spectrum of 2,6-di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose **6** ($CDCl_3$). Signals < 2.75 are not shown. – = 2,6-di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose, --- = 3,6-di-*O*-acetyl-2-mono-*O*-(propyl-3′-acetyl) cellulose, ··· = 6-mono-*O*-acetyl-2,3-di-*O*-(propyl-3′-acetyl) cellulose, ^{d} = diastereotop protons.

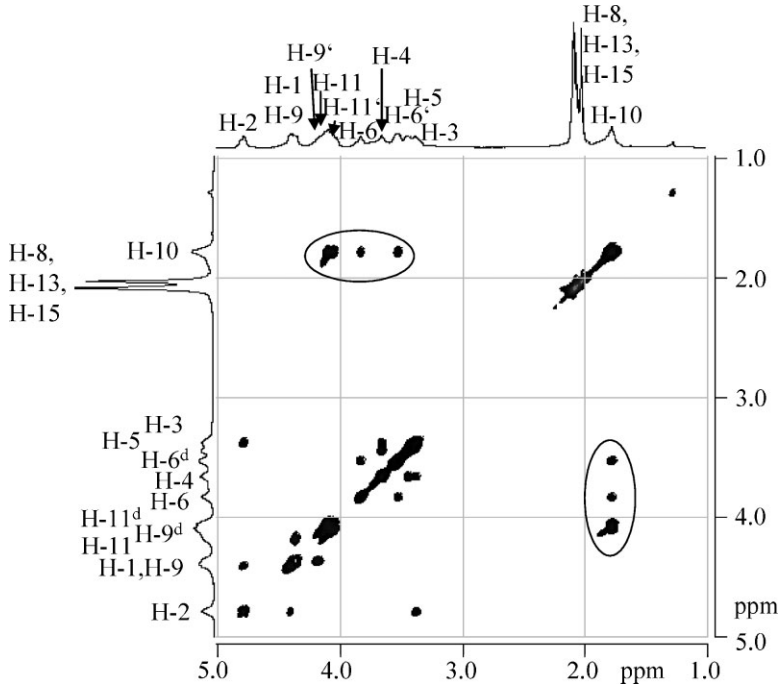


Figure 4.
$^{1}H/^{1}H$ TOCSY NMR spectrum of 2,6-di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose **6** ($CDCl_3$).

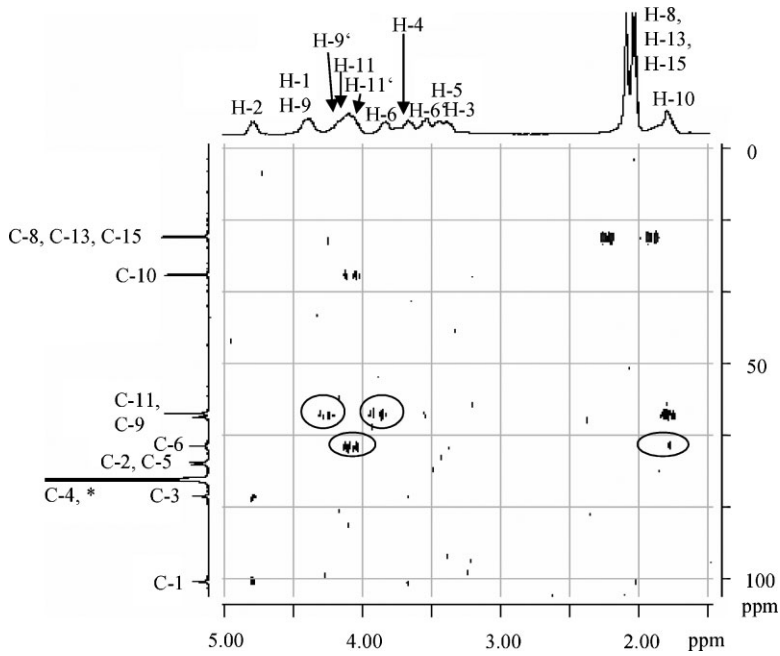


Figure 5.
$^{1}H/^{13}C$ HMBC DEPT NMR spectrum of 2,6-di-*O*-acetyl-3-mono-*O*-(propyl-3′-acetyl) cellulose **6** ($CDCl_3$).

possessing 3′-hydroxypropyl moieties at position 2, which can be determined by signals at 3.19–2.96 (repeating unit with substituent at position 2 only) and at 5.02 ppm (repeating unit with substituents at position 2 and 3, Figure 3).

Surprisingly, the $^{1}H/^{1}H$ TOCSY NMR- and $^{1}H/^{13}C$ HSQC DEPT NMR spectra show rather intensive cross peaks that indicate a coupling between the propyl-3′-acetyl group and the carbon atom 6 of the repeating unit. However, according to our broad experiences in the field of protecting group with cellulose, a reaction (i. e., allylation) of position 6 can be completely excluded. Two-dimensional spectra do not allow a statement about the concentration, but the intensity of these peaks indicates a comparably high concentration of the assumed structures. Furthermore, couplings in TOCSY NMR spectra between two spin systems can be determined only if very high coupling constants occur. Therefore, it may be assumed that the novel cellulose derivatives forms a special supramolecular structure by electron interfering spin-spin-coupling that force a convergence of orbitals based on a steric compression.[12] It leads to simulated magnetic information. It might be that there are more simulated peaks, which superpose with signals of the AGU (anhydroglucose unit), H-8, H-10, H-13 or H-15.

Conclusion

A novel cellulose ether, namely 3-mono-*O*-(3′-hydroxypropyl) cellulose was synthesized from 3-mono-*O*-allyl-2,6-di-*O*-TDMS cellulose via hydroboration with 9-borabicyclo[3.3.1]nonane and subsequent alkaline oxidation. In contrast to commercially available hydroxypropyl moieties containing cellulose ethers, a product functionalized at position 3 and with primary hydroxyl groups only was designed. The structure was clearly evaluated by spectroscopic techniques. Moreover, two-dimensional NMR spectroscopic measurements of the peracetylated sample indicate the presence of substructures, although to a low extent. The 3-mono-*O*-(3′-hydroxypropyl) cellulose will be included in studies on structure-property-relationships of cellulose ethers.

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