



Syntheses and Characterization of New 3-*O*-Allyl Ether Chloralose Derivatives

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The new 3-*O*-allyl ether derivatives of sugar were synthesized with high yield and mild reaction conditions. The synthesis of 3-*O*-acetylchloralose derivatives (**5-8**) and 3-*O*-allyl ether chloralose derivatives (**9-12**) were carried out. These new 3-*O*-allyl ether of chloralose derivatives are potential monomers for the synthesis of new glycopolymers.

Keywords: Allyl ethers, Chloralose, Furano sugars, Glycomonomers.

INTRODUCTION

The allyl group is widely used in carbohydrate chemistry. It survives a variety of reaction conditions (acidic or basic) that permits orthogonal protection strategies and can be selectively removed¹. Fedorynski *et al.*² and Jarosz & Szewczyk³ protected the primary position by selective monoallylation and were used in preparation of 6-*O*-allyl-3-*O*-benzyl-1,2-isopropylidene- α -D-allofuranose. Sugar-carrying allylic ethers such as 3-*O*-allyl-1,2,5,6-di-*O*-iso-propylidene- α -D-glucopyranose has already been reported⁴. Sugar-derived allylic ethers were also converted into new glyco-substances having isoxazolidine ring systems through intramolecular nitron addition reactions⁵. Furthermore, the allylic double bond can be polymerized by free radical polymerization.

Allyl glycosides are often used as intermediate products in the synthesis of oligosaccharides, in which the allyl group may serve as an orthogonal protection group for the anomeric center^{6,7}. For example, Liu *et al.*⁸ and Khamsi *et al.*⁹ reported some allyl glycosides form peracetylated glycosyl donors with high yields¹⁰. The double bond of allyl glycosides has also been utilized as a handle to functionalize carbohydrates for generating glycoconjugates¹¹. Additionally, the allylic double bond can be modified by radical addition of thiols which allows for further functionalization and derivization at the amino or hydroxyl group^{12,13}.

Recently, the basic raw materials used for polymers have expanded by including sugar such as glucose, galactose, fructose and sucrose. Chemically containing sugar moieties onto synthetic polymers are individual method for functionalization of synthetic polymers. Owing to this method, the polymer is not only functionalized, but also other desirable properties such

as biodegradability, biocompatibility and biorenewability can be achieved¹⁴ and so this could be available alternative for developing environmental friendly products. Some applications of sugar-carrying polymers are drug delivery systems, dental medicine, bioimplants, contact lenses, tissue engineering and many medicinal applications¹⁵. Additionally, they have the advantage of being potentially biodegradable. For example, sugar-containing vinyl monomers were synthesized from isopropylidene¹⁶ and other protected sugars^{14,17}.

EXPERIMENTAL

NMR spectra were recorded at 400 MHz (¹H) and at 100.57 (¹³C) on a Varian Mercury FT NMR spectrometer at 300 K. FTIR spectra were recorded on a Varian 670-IR spectrometer. Chemical shift values (δ) are reported in ppm downfield from TMS as an international standard: J values are given Hz. Elemental analyses (C,H) were performed with a Perkin-Elmer series II 2400 analyser. Optical rotations were determined using a Rudolph Research Analytical Autopol I automatic polarimeter. TLC and column chromatography were performed on pre-coated aluminium plates (Merck 5554) and silica gel G-60 (Merck 7734), respectively. Allyl alcohol, acetic anhydride (Ac₂O) and all the solvents were commercially obtained as chemical pure reagents and used without purification. All solvents were dried over molecular sieves, for at least 2 h prior to use. When dry conditions were required, the reaction was performed under an argon atmosphere. All solvent removals were carried out under reduced pressure. Light petroleum refers to the fraction with b.pt. 40-70 °C. Petroleum ether : EtOAc (7:3) was used for TLC. The spots on the TLC were visualized using ethanolic solution of H₂SO₄ (5 %) followed by heating at 110 °C for 5 min.

General procedure for acetylation reaction: Firstly, a solution of 1,2-*O*-isopropylidene chloralose derivatives (**1-4**) (3.50 g, 0.01 mol), Ac₂O (6.6 mL, 0.07 mol) and 4-dimethylaminopyridine (DMAP) (0.12 g, 0.001 mol) in dry pyridine: EtOAc (1:10) (8:80 mL) was stirred for 24 h at room temperature under argon gas. A solution of reaction mixture was extracted with 5% HCl solution (3 × 50 mL). Then the water phase was extracted with EtOAc (3 × 100 mL). Organic phase was dried over anhydrous Na₂SO₄, filtered off and evaporated under reducing pressure. The residue was purified by column chromatography with eluting solvent (light petroleum: EtOAc) (6:4) to give pure 3-*O*-acetyl-1,2-*O*-isopropylidene chloralose derivatives (**5-8**).

3-*O*-Acetyl-5,6-*O*-isopropylidene-1,2-*O*-(*R*)-trichloroethylidene- α -D-glucofuranose (5**):** The title product was synthesized, yield 85 % (3.32 g). [α]_D²⁰ -22.0 (*c* 1, CH₂Cl₂). FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2983-2895 (C-H), 1710 (C=O), 1148 (COC), 797 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 6.10 (d, 1H, *J*_{1,2} 3.6 Hz, H-1), 5.31 (s, 1H, HCCl₃), 4.75 (d, 1H, H-2), 4.60 (ddd, 1H, H-5), 4.44 (dd, 1H, *J*_{4,5} 2.8 Hz, H-4), 4.30 (d, 1H, *J*_{3,4} 3.2 Hz, H-3), 4.16 (dd, 1H, *J*_{6a,6b} 8.8, *J*_{5,6a} 6.4 Hz, H-6a), 3.96 (dd, *J*_{5,6b} 5.2 Hz, H-6b), 2.01 (s, 3H, OAc), 1.40 (s, 3H, CH₃-isop.), 1.35 (s, 3H, CH₃-isop.). ¹³C NMR: 169.5 (C=O), 115.7 (C_{isop.}), 109.7, 107.7 (HC-CCL₃, C-1), 97.4 (HC-CCL₃), 83.9, 83.4, 82.4 (C-2, C-3, C-4), 74.2 (C-5), 64.3 (C-6), 28.2, 27.5, 23.0 (Me groups). Anal. Calcd for C₁₃H₁₇O₇Cl₃: C, 39.87; H, 4.38; found: C, 39.92; H, 4.04.

3-*O*-Acetyl-5,6-*O*-isopropylidene-1,2-*O*-(*S*)-trichloroethylidene- α -D-glucofuranose (6**):** The title product was synthesized, yield 80 % (3.13 g). [α]_D²¹ -18.0 (*c* 0.96, CH₂Cl₂). FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2985-2892 (C-H), 1711 (C=O), 1150 (COC), 798 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 6.17 (d, 1H, *J*_{1,2} = 3.9 Hz, H-1), 5.90 (s, 1H, HCCl₃), 4.72 (d, 1H, H-2), 4.24 (ddd, 1H, H-5), 4.10 (d, 1H, *J*_{3,4} = 6.6 Hz, H-3), 4.08 (dd, 1H, *J*_{4,5} = 2.7 Hz, H-4), 3.95 (dd, 1H, *J*_{6a,6b} = 9.7, *J*_{5,6a} = 6.4 Hz, H-6a), 3.80 (dd, 1H, *J*_{5,6b} = 5.9 Hz, H-6b), 1.99 (s, 3H, OAc), 1.35 (s, 3H, CH₃-isopropylidene), 1.21 (s, 3H, CH₃-isopropylidene.). ¹³C NMR: 169.2 (C=O), 115.3 (C_{isop.}), 110.0, 107.6 (HC-CCL₃, C-1), 99.4 (HC-CCL₃), 85.8, 82.7, 78.4 (C-2, C-3, C-4), 75.6 (C-5), 67.2 (C-6), 28.7, 27.6, 23.1 (Me groups). Anal. Calcd for C₁₃H₁₇O₇Cl₃: C, 39.87; H, 4.38; found: C, 39.62; H, 4.15.

3-*O*-Acetyl-5,6-*O*-isopropylidene-1,2-*O*-(*S*)-trichloroethylidene- α -D-galactofuranose (7**):** The title product was synthesized, yield 84 % (3.30 g). [α]_D²⁰ -26.0 (*c* 1, CH₂Cl₂). FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2980-2891 (C-H), 1710 (C=O), 1153 (COC), 796 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 6.21 (d, 1H, *J*_{1,2} 4.0 Hz, H-1), 5.66 (s, 1H, HCCl₃), 4.96 (d, 1H, H-2), 4.48 (dd, 1H, *J*_{4,5} 2.8 Hz, H-4), 4.30 (d, 1H, *J*_{3,4} 3.2 Hz, H-3), 4.18 (m, 1H, H-5), 4.10 (dd, 1H, *J*_{6a,6b} 8.0, *J*_{5,6a} 6.0 Hz, H-6a), 3.96 (dd, *J*_{5,6b} 5.0 Hz, H-6b), 2.05 (s, 3H, OAc), 1.37 (s, 3H, CH₃-isop.), 1.29 (s, 3H, CH₃-isop.). ¹³C NMR: 169.3 (C=O), 115.1 (C_{isop.}), 109.8, 107.6 (HC-CCL₃, C-1), 98.4 (HC-CCL₃), 84.8, 83.5, 82.7 (C-2, C-3, C-4), 79.8 (C-5), 67.3 (C-6), 25.5, 23.7, 21.0 (Me groups). Anal. Calcd for C₁₃H₁₇O₇Cl₃: C, 39.87; H, 4.38; found: C, 39.90; H, 4.14.

3-*O*-Acetyl-5,6-*O*-isopropylidene-1,2-*O*-(*R*)-trichloroethylidene- β -D-mannofuranose (8**):** The title product was synthesized, yield 78 % (3.05 g). [α]_D²⁰ -32.0 (*c* 1, CH₂Cl₂).

FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2984-2891 (C-H), 1709 (C=O), 1151 (COC), 798 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 5.94 (d, 1H, *J*_{1,2} 4.0 Hz, H-1), 5.64 (s, 1H, HCCl₃), 5.10 (d, 1H, H-2), 4.12 (dd, 1H, *J*_{4,5} 2.8 Hz, H-4), 4.43 (m, 1H, H-5), 4.28 (d, 1H, *J*_{3,4} 3.2 Hz, H-3), 4.12 (dd, 1H, *J*_{6a,6b} 8.0, *J*_{5,6a} 6.0 Hz, H-6a), 3.94 (dd, *J*_{5,6b} 5.6 Hz, H-6b), 2.09 (s, 3H, OAc), 1.41 (s, 3H, CH₃-isop.), 1.37 (s, 3H, CH₃-isop.). ¹³C NMR: 169.5 (C=O), 115.7 (C_{isop.}), 107.7, 106.7 (HC-CCL₃, C-1), 97.4 (HC-CCL₃), 83.9, 83.4, 82.4 (C-2, C-3, C-4), 74.3 (C-5), 69.3 (C-6), 28.2, 27.5, 22.5. (Me groups). Anal. Calcd for C₁₃H₁₇O₇Cl₃: C, 39.87; H, 4.38; found: C, 40.08; H, 4.19.

General procedure for etherification reaction: Firstly, a solution of 3-*O*-acetyl-1,2-*O*-isopropylidene chloralose derivatives (**5-8**) (3.92 g, 0.01 mol), allyl alcohol (0.82 mL, 0.012 mol) and boron trifluoride diethyl etherate (BF₃·OEt₂) (4.73 mL, 0.05 mol) in dry acetonitrile (100 mL) was stirred for 2 to 5 h at 0 °C under argon gas. A solution was neutralized with saturated solution of Na₂CO₃ and the solvent at 50 °C. Then the water phase was extracted with EtOAc (3 × 100 mL). Organic phase was dried over anhydrous Na₂SO₄, filtered off and evaporated under reducing pressure. The residue was purified by column chromatography with eluting solvent (light petroleum: EtOAc) (9:1) to give pure 3-*O*-allyl-1,2-*O*-isopropylidene chloralose derivatives (**9-12**).

3-*O*-Allyl-5,6-*O*-isopropylidene-1,2-*O*-(*R*)-trichloroethylidene- α -D-glucofuranose (9**):** The title product was synthesized, yield 74 % (2.90 g). [α]_D²¹ -19.0 (*c* 1, CH₂Cl₂). FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2984-2895 (C-H), 1617 (C=C), 1152 (COC), 797 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 6.05 (d, 1H, *J*_{1,2} 3.6 Hz, H-1), 5.82 (m, 1H, CH₂CH=CH₂), 5.60 (s, 1H, HCCl₃), 5.25 (dd, 1H, CH₂CH=CH₂, *J* = 17.0, 1.4 Hz), 5.20 (dd, 1H, CH₂CH=CH₂, *J* = 10.3, 1.5 Hz), 4.73 (d, 1H, H-2), 4.65 (m, 1H, H-5), 4.47 (dd, 1H, *J*_{4,5} 1.8 Hz, H-4), 4.25 (d, 1H, *J*_{3,4} 3.2 Hz, H-3), 4.20 (m, 2H, OCH₂CH=CH₂), 4.14 (dd, 1H, *J*_{6a,6b} 9.0, *J*_{5,6a} 6.4 Hz, H-6a), 3.98 (dd, *J*_{5,6b} 5.2 Hz, H-6b), 1.39 (s, 3H, CH₃-isop.), 1.33 (s, 3H, CH₃-isop.); ¹³C NMR: 133.3, 117.7 (CH=CH₂), 115.1 (C_{isop.}), 108.1, 105.3 (HC-CCL₃, C-1), 99.3 (HC-CCL₃), 86.1, 83.4, 79.4 (C-2, C-3, C-4), 71.9 (C-5), 68.5 (C-6), 29.2, 27.5, 22.9 (Me groups). Anal. Calcd for C₁₄H₁₉O₆Cl₃: C, 43.12; H, 4.88; found: C, 42.72; H, 4.90.

3-*O*-Allyl-5,6-*O*-isopropylidene-1,2-*O*-(*S*)-trichloroethylidene- α -D-glucofuranose (10**):** The title product was synthesized, yield 68 % (2.65 g). [α]_D¹⁹ -12.0 (*c* 1.0, CH₂Cl₂). FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2980-2895 (C-H), 1611 (C=C), 1150 (COC), 796 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 6.19 (d, 1H, *J*_{1,2} = 3.6 Hz, H-1), 5.91 (s, 1H, HCCl₃), 5.80 (m, 1H, CH₂CH=CH₂), 5.40 (dd, 1H, CH₂CH=CH₂, *J* = 17.2, 1.5 Hz), 5.27 (dd, 1H, CH₂CH=CH₂, *J* = 10.5, 1.3 Hz), 5.22 (d, 1H, CH₂CH=CH₂), 4.70 (d, 1H, H-2), 4.31 (m, 1H, H-5), 4.10 (d, 1H, *J*_{3,4} = 6.0 Hz, H-3), 4.08 (dd, 1H, *J*_{4,5} = 2.7 Hz, H-4), 4.02 (m, 2H, OCH₂CH=CH₂), 3.95 (dd, 1H, *J*_{6a,6b} = 9.6, *J*_{5,6a} = 6.4 Hz, H-6a), 3.80 (dd, 1H, *J*_{5,6b} = 5.9 Hz, H-6b), 1.43 (s, 3H, CH₃-isopropylidene), 1.35 (s, 3H, CH₃-isopropylidene). ¹³C NMR: 133.4, 117.6 (CH=CH₂), 115.2 (C_{isop.}), 110.0, 107.6 (HC-CCL₃, C-1), 99.4 (HC-CCL₃), 88.4, 84.3, 75.4 (C-2, C-3, C-4), 72.4 (C-5), 68.8 (C-6), 27.3, 23.1, 20.5 (Me groups). Anal. Calcd for C₁₄H₁₉O₆Cl₃: C, 43.12; H, 4.88; found: C, 42.88; H, 4.95.

3-*O*-Allyl-5,6-*O*-isopropylidene-1,2-*O*-(*S*)-trichloroethylidene- α -D-galactofuranose (11**):** The title product was

synthesized, yield 64 % (2.50 g). $[\alpha]_D^{21}$ -16.0 (*c* 1, CH₂Cl₂). FTIR (KBr, $\nu_{\max}$, cm⁻¹): 2986-2890 (C-H), 1620 (C=C), 1149 (COC), 796 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 6.21 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 5.88 (m, 1H, CH₂CH=CH₂), 5.66 (s, 1H, HCCl₃), 5.22 (dd, 1H, CH₂CH=CH₂, J = 17.1, 1.4 Hz), 5.12 (dd, 1H, CH₂CH=CH₂, J = 10.4, 1.3 Hz), 4.96 (d, 1H, H-2), 4.48 (dd, 1H, $J_{4,5}$ 2.8 Hz, H-4), 4.30 (d, 1H, $J_{3,4}$ 3.2 Hz, H-3), 4.18 (m, 1H, H-5), 4.15 (m, 2H, OCH₂CH=CH₂), 4.10 (dd, 1H, $J_{6a,6b}$ 8.0, $J_{5,6a}$ 6.0 Hz, H-6a), 3.96 (dd, $J_{5,6b}$ 5.0 Hz, H-6b), 2.05 (s, 3H, OAc), 1.37 (s, 3H, CH₃-isop.), 1.30 (s, 3H, CH₃-isop.). ¹³C NMR: 135.4, 117.6 (CH=CH₂), 115.7 (C_{isop.}), 110.6, 109.5 (HC-CCl₃, C-1), 99.6 (HC-CCl₃), 87.4, 85.0, 78.6 (C-2, C-3, C-4), 75.8 (C-5), 72.3 (C-6), 26.6, 25.8, 21.3 (Me groups). Anal. Calcd for C₁₄H₁₉O₆Cl₃: C, 43.12; H, 4.88; found: C, 43.22; H, 4.70.

3-*O*-Allyl-5,6-*O*-isopropylidene-1,2-*O*-(*R*)-trichloroethylidene- β -D-mannofuranose (12): The title product was synthesized, yield 60 % (2.35 g). $[\alpha]_D^{21}$ -23.0 (*c* 1, CH₂Cl₂). (KBr, $\nu_{\max}$, cm⁻¹): 2983-2897 (C-H), 1619 (C=C), 1153 (COC), 798 (CH-Cl). ¹H NMR (CDCl₃, 400 MHz): δ 5.94 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1), 5.82 (m, 1H, CH₂CH=CH₂), 5.74 (s, 1H, HCCl₃), 5.30 (dd, 1H, CH₂CH=CH₂, J = 17.3, 1.3 Hz), 5.16 (dd, 1H, CH₂CH=CH₂, J = 10.2, 1.4 Hz), 5.10 (d, 1H, H-2), 4.52 (dd, 1H, $J_{4,5}$ 2.8 Hz, H-4), 4.43 (m, 1H, H-5), 4.28 (d, 1H, $J_{3,4}$ 3.2 Hz, H-3), 4.19 (m, 2H, OCH₂CH=CH₂), 4.12 (dd, 1H, $J_{6a,6b}$ 8.6, $J_{5,6a}$ 6.3 Hz, H-6a), 3.94 (dd, $J_{5,6b}$ 5.6 Hz, H-6b), 2.09 (s, 3H, OAc), 1.41 (s, 3H, CH₃-isop.), 1.37 (s, 3H, CH₃-isop.). ¹³C NMR: 134.9, 116.5 (CH=CH₂), 117.9 (C_{isop.}), 107.6, 102.5 (HC-CCl₃, C-1), 99.1 (HC-CCl₃), 86.4, 82.5, 76.3 (C-2, C-3, C-4), 74.3 (C-5), 72.3 (C-6), 24.6, 21.2, 20.9 (Me groups). Anal. Calcd for C₁₄H₁₉O₆Cl₃: C, 43.12; H, 4.88; found: C, 43.07; H, 4.79.

RESULTS AND DISCUSSION

The object of this study to prepare isopropylidene protected allyl saccharides (**9-12**) in this context. These compounds were

obtained from trichloroethylidene acetal of D-glucose¹⁸, D-galactose¹⁹ and D-mannose²⁰. Monosaccharides mostly react in their furanose forms with chloral to give trichloroethylidene acetals. 1,2-*O*-(*R*)-trichloro-ethylidene- α -D-glucofuranose is also known α -chloralose which is commercially available compound. It is used as an anesthetic for animals²¹. Furthermore, trichloroethylidene acetals are suitable protecting groups for the synthesis of some biologically important compounds²² and antimicrobial chloralose derivatives are also known²³. Trichloroethylidene acetal derivatives (**1-4**) were further acetalized with 2,2-dimethoxypropane (2,2-DMP) to give the 5,6-*O*-isopropylidene derivatives (**5-8**)^{21,24,25}. Then, 5,6-*O*-isopropylidene derivatives (**5-8**) reacted with acetic anhydride and catalytic amount of DMAP in pyridine/EtOAc (1/10) at room temperature to give 3-*O*-acetylchloralose derivatives (**5-8**). Finally, this 3-*O*-acetylchloralose derivatives (**5-8**) reacted with allyl alcohol and Lewis acid (BF₃·OEt₂) in dry acetonitrile at 0 °C under argon to give 3-*O*-allyl ether chloralose derivatives (**9-12**) (Figs. 1-3). All compounds were structurally characterized by using FTIR, ¹H and ¹³C NMR.

In the FTIR spectrum of the acetyl derivatives (**5-8**), the characteristic absorptions for C=O (carbonyl), COC (ether) and CH-Cl (acetal) groups were observed approximately at 1710, 1150 and 797 cm⁻¹, respectively. In the ¹H NMR spectrum of the 3-*O*-acetyl-5,6-*O*-isopropylidene of chloralose derivatives (**5-8**), the methyl protons (3H, OAc) appeared as a singlet approximately at 2 ppm, unlike the ¹H NMR spectrum of the 5,6-*O*-isopropylidene of chloralose derivatives (**1-4**). Also, in the ¹³C NMR spectrum of the 3-*O*-acetyl-5,6-*O*-isopropylidene of chloralose derivatives (**5-8**) were observed the peak of the carbonyl carbon of the acetyl group at approximately 170 ppm.

In the FTIR spectrum of the 3-*O*-allyl ether chloralose derivatives (**9-12**), the characteristic absorptions for C=C (allyl), COC (ether) and CH-Cl (acetal) groups were observed approximately 1620, 1148 and 798 cm⁻¹, respectively. In the ¹H NMR spectrum of the 3-*O*-allyl-5,6-*O*-isopropylidene of

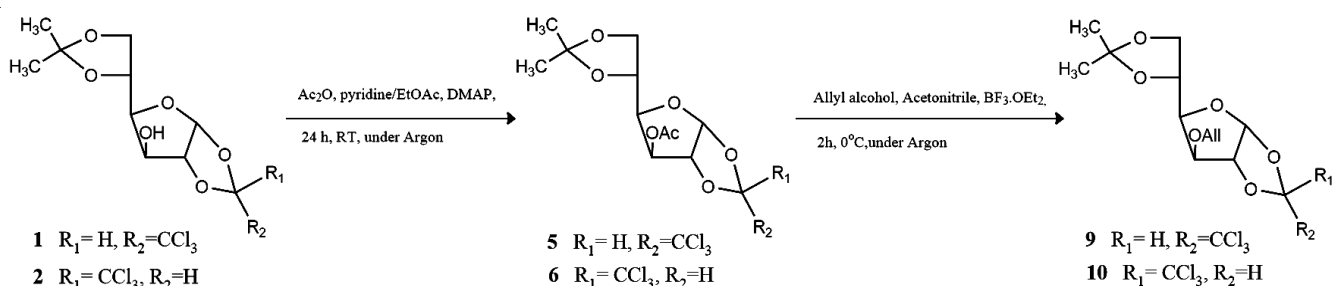


Fig. 1. Synthesis of 3-*O*-allyl ether derivatives of α -chloralose (**9**) and β -chloralose (**10**)

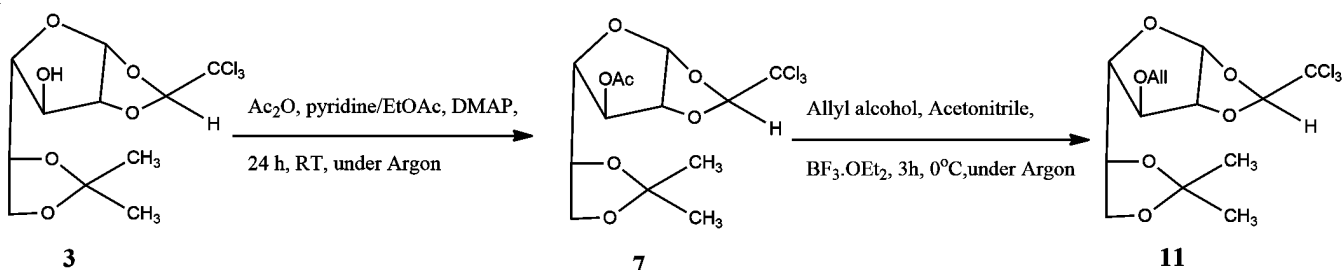
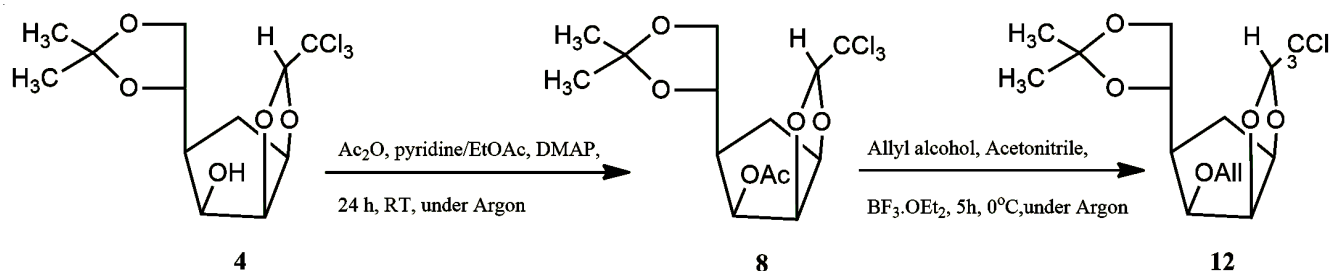


Fig. 2. Synthesis of 3-*O*-allyl ether derivatives of galactochloralose (**11**)

Fig. 3. Synthesis of 3-*O*-allyl ether derivatives of mannochloralose (**12**)

chloralose derivatives (**9-12**) appeared the specific double bond protons at 5.80-5.10 ppm and allylic methylene protons between 4.20 and 4.00 ppm. Furthermore, in the ^{13}C NMR spectrum of the 3-*O*-allyl-5,6-*O*-isopropylidene of chloralose derivatives (**9-12**) were observed the peaks of the double bond carbons at approximately 135 and 117 ppm.

Conclusion

The new 3-*O*-allyl ether derivatives of sugar (**9-12**) were synthesized from the 3-*O*-acetylchloralose derivatives (**5-8**) with high yield and mild reaction conditions. All new compounds were characterized by NMR and FTIR spectroscopic methods. These new 3-*O*-allyl ether of chloralose derivatives can be used as intermediates in synthetic carbohydrate chemistry and are also potential monomers for the synthesis of new glycopolymers.

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