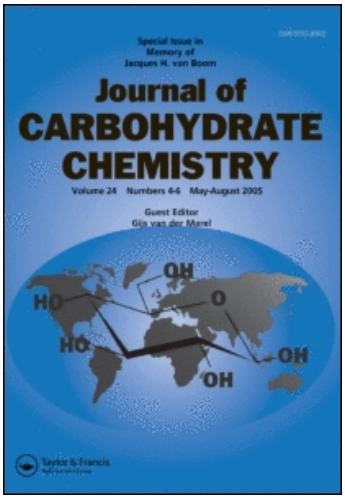

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The Alkylation of Mono- and Disaccharides Via an Initialising Electrochemical Step

Carl Heinz Hamann[a]; Susanne Fischer[a]; Herbert Polligkeit[a]; Peter Wolf[a]
[a] Fachbereich Chemie, AG Angewandte Physikalische Chemie Universität Oldenburg, Oldenburg/Oldb

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THE ALKYLATION OF MONO - AND DISACCHARIDES VIA AN INITIALISING ELECTROCHEMICAL STEP

Carl Heinz Hamann*, Susanne Fischer, Herbert Polligkeit, Peter Wolf

Fachbereich Chemie, AG Angewandte Physikalische Chemie
Universität Oldenburg, Postfach 2503, 2900 Oldenburg/Oldb.

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ABSTRACT

A new approach to the formation of ether derivatives of some mono- and disaccharides by an initialising electrochemical step is described. With the exception of the nonreducing sucrose all compounds are protected at the anomeric center. In contrast to the general procedure we replaced the common bases by platinum as an electrode material with a small hydrogen overvoltage in aprotic media, such as DMF. In this way the hydroxyl groups are transformed to alcoholate anions with the generation of hydrogen. The reaction of these electrochemically generated anions with alkylating reagents such as allyl bromide, benzyl bromide and methyl iodide results in the formation of ether derivatives.

INTRODUCTION

One field of activity in our research group is the electroreductive generation of alcoholate anions of simple alcohols such as methanol or ethanol in a membrane electrolysis cell.[1] This technique is of interest for industrial application. We have extended our method to carbohydrates, which can be regarded as polyalcohols. In preparative carbohydrate chemistry the use of protecting groups is very significant with ether derivatives of simple mono- and disaccharides playing an important role. Using alkyl halides such as benzyl bromide or methyl iodide opens a convenient route for the preparation of these common derivatives. In most of the alkylation procedures the alkyl halides are used together with strong bases such as sodium hy-

droxide, silver oxide or methylsulfinyl anions.[2] This is demonstrated in an immense number of articles and reviews.

In recent studies we focused on the electrochemical behaviour of simple mono - and disaccharides (**Fig.** 1), which are protected only at the anomeric center. The hydroxyl groups of the saccharides are transformed to polyalcoholate anions (Scheme 1) by an electroreductive step on platinum with generation of hydrogen.

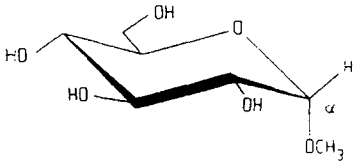
Concerning sufficient electrochemical stability of the supporting electrolyte, the system DMF/LiBr proved to be useful. Both DMF and lithium cations are not electroactive at the working potential we used in electrolysis. We assume a single electron transfer from the electrode to the substrate which implies a direct deprotonation of the hydroxyl groups.[3,4,5] After electrolyses, electrophiles are added to the electrolyte solution in a second step (ex-situ). A similar procedure is used in the electrochemical alkylation of thiols, where electroreductively generated thiolates reacted with various organohalides to yield substituted sulfides.[6] It is our intention to replace common bases and organometallic compounds in a chemical reaction by a simple platinum electrode, to achieve different regioselectivities. We report the electrochemical behaviour of some mono- and disaccharides and the substitution patterns of the resulting ether derivatives.

RESULTS AND DISCUSSION

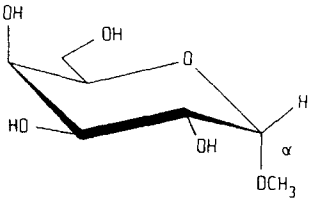
The electrochemical reactivities of mono- and disaccharides were examined by cyclic voltammograms, as illustrated in earlier publications.[3,4] The current-potential dependencies of methyl α-D-glucopyranoside and other model compounds, monosaccharides as well as disaccharides, are similar. All cyclic voltammograms exhibit a broad cathodic current peak in the potential region of -2 V. It is therefore not possible to distinguish between the deprotonation of single hydroxyl groups.

During electrolysis the electrochemically generated anions are stabilized by lithium as the counterion. Due to the high electrochemical reactivity of the alkyl halides at potentials of -2 V, the reaction with the sugar anions was carried out after electrolysis. Tables 1 and 2 illustrate the substitution pattern and the current yields of the preferably monosubstituted saccharides.

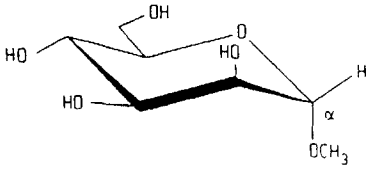
The substitution pattern of methyl α-D-glucopyranoside and sucrose did not exhibit a dependency on solvent or supporting electrolyte. An alternative application



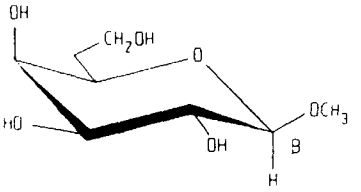
methyl α - D - glucoside



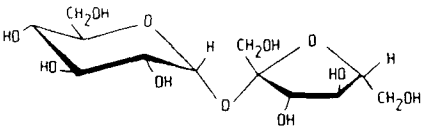
methyl α - D - galactoside



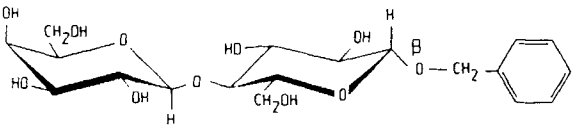
methyl α - D - mannoside



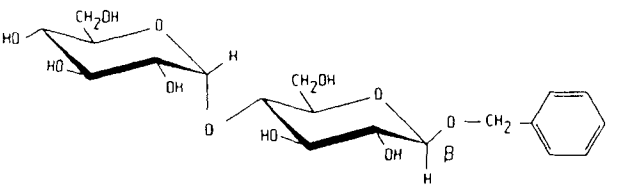
methyl β - D - galactoside



sucrose



benzyl β - lactoside



benzyl β - maltoside

FIG. 1. Model mono- and disaccharides for alkylation via an initialising electrochemical step

$$R\text{-}OH + e^- \longrightarrow R\text{-}O^- + \tfrac{1}{2}H_2$$

SCHEME 1

of NMP, DMSO and CH_3CN or $LiClO_4$ as supporting electrolyte decreased the current yield but the substitution pattern remained unchanged. If monovalent lithium is substituted by bivalent magnesium or zinc, the deprotonation of hydroxyl groups does not occur due to the positive reduction potential of magnesium and zinc and inhibition of the electrode surface. Variation of the potential of the electrolysis in the range of -1.8 and -2.3 V did not show any effects. The same is true for substitution of electrode material by graphite. This shows that neither the electrolyte system, nor the electrode material are determining the substitution pattern.

The selective protection of carbohydrates with alkyl halides is influenced by the acidity of the hydroxyl groups as well as by inter- and intramolecular hydrogen bonding, configuration and sterical aspects of the saccharides.[7] The size of the alkyl halides also plays an important role.

An initial electrochemical step in connection with a specific adsorption configuration of the substrate on the electrode surface should also show an influence on regioselectivity of the reaction. The monosaccharides exhibited a broader spectrum of substituted products than the disaccharides. The HO-2 position of *gluco*- and *manno*-residues was preferentially substituted, whereas in the *galacto*-residue the HO-3 position is favoured preferentially due to the neighboring axial HO-4 group. The order of substitution of the hydroxyl groups was $2 > 6 > 4 \gg 3$ for the glucoside, $2 > 4 > 3 > 6$ for the mannoside and $3 > 6 \gg 2 = 4$ in the case of galactoside.

The HO-2 position of mannoside and glucoside is the most acidic one.[8,9] The reactivity of sucrose revealed a high selectivity in order of decreasing reactivity at HO-2, HO-1' and HO-3', which is probably due to the high acidity of the hydroxyl groups in these positions,[10] due to strong intramolecular hydrogen bonding between these hydroxyl groups. The high degree of substitution at HO-2 of sucrose is in agreement with the substitution in HO-2 of the glucose residue.

In contrast to the results mentioned above, the ionization and subsequent reaction of benzyl β-derivatives of maltose and lactose with alkyl halides led to remarkably

TABLE 1. Substitution patterns and current yields[a] of benzyl-, methyl- and allyl ethers of monosaccharides

educt	alkyl halide	product distribution at C-positions in %									current yield in %
		2	3	4	6	2,3	2,4	2,6	4,6	3,6	
methyl α-D-gluco-pyranoside	benzyl bromide	43	3	8	13	2,5	7,5	14	5	4	50
methyl α-D-gluco-pyranoside	methyl iodide	36	9	13	10	-----32---------					51
methyl α-D-gluco-pyranoside	allyl bromide	60	11	/	17	/	12	/	/	/	40
methyl α-D-manno-pyranoside	benzyl bromide	76	13	/	3	----- 8----------					65
methyl α-D-manno-pyranoside	methyl iodide	42	26	/	7	-----25----------					35
methyl α-D-manno-pyranoside	allyl bromide	55	23	/	22	/	/	/	/	/	40
methyl α-D-galacto-pyranoside	benzyl bromide	28	31,5	/	25	----6----------				9,5	30
methyl β-D-galacto-pyranoside	benzyl bromide	5	49	/	30	-----5,5----------				10,5	34

a. Current yield of isolated products. The yield determining partner is the electron, which is transferred from the electrode to the substrate. The current of a batch wise electrolysis decreases with consumption of substrate. This means the electrolysis has to be stopped long before the substrate is consumed in total. In the present case this was done after times up to 6 hours , corresponding to a consumption of 40 to 50 % of the substrate. For this reason we noted current yields and no product yields. Diethers were not separated in all cases.

different substitution patterns. Only one hydroxyl group of the glycosyl residues of these saccharides was transformed into an ether derivative. This was HO-3' of lactose and HO-2' of maltose, with the current yield ranging from 75 up to 100 %. This corresponds to the high reactivity of the HO-2 and HO-3 groups in

TABLE 2. Substitution pattern and current yields of benzyl-, methyl- and allyl ethers of disaccharides

educt	alkyl halide	product distribution at C-positions in %					current yield in %
		2	6	1'	2'	3'	
sucrose	benzyl bromide	48	/	39	/	13	48
sucrose	methyl iodide	54	/	27	/	19	63
sucrose	allyl bromide	39	/	61	/	/	28
benzyl β-lactoside	benzyl bromide	25	/	/	/	75	40
benzyl β-lactoside	methyl iodide	10	/	/	/	90	26
benzyl β-lactoside	allyl bromide	mixture of 2 and 3'					41
benzyl β-maltoside	benzyl bromide	20	/	/	80	/	34
benzyl β-maltoside	methyl iodide	/	/	/	100	/	38

methyl α-D-glucoside and -galactoside, respectively. The HO-2 group of the aglycon only reacted to a small extent. The evident preference of the non-reducing residue in both saccharides might be caused by the anomeric benzyl group and the resulting adsorption configuration on the electrode surface. The aromatic system renders adsorption of the aglycon residue on the electrode surface unfavorable due to repulsive interactions of the electronic system of the arene and the electrode caused by the highly negative potential. This would explain the surprising regioselectivity. The influence of the anomeric benzyl group on adsorption will be investigated.

Disaccharides as well as monosaccharides exhibited a high preference for the substitution of secondary hydroxyl groups. The reason for this could be a direct electron transfer from the electrode to the specific hydroxyl groups, if migration of hydrogen due to intramolecular hydrogen bondings is excluded. The monosaccharides show a preferred monosubstitution, but nevertheless give a high number of

isomers. The smaller monosaccharides may have several adsorption configurations on the electrode, which would explain the broader spectrum of products. An alternative explanation might be that the smaller monosaccharides may more easily undergo intermolecular hydrogen transfer than the large benzyl β-protected disaccharides.

There are only few data in the literature which may be compared to our model compounds. The selective equimolar benzylation of methyl α-D-galactoside with sodium hydride and benzyl bromide in DMF leads to a yield of 50 % monoethers.[11] The order of reactivity of the hydroxyl groups is 6 > 4 > 2 > 3. In the case of the β-anomer it is 6 > 3 > 2 without benzylation in the HO-4 position. These results reveal a different reactivity of the hydroxyl groups caused by use of different cations,[12] in comparison to our results. The methylation of methyl α-D-glucoside with sodium hydroxide and methyl iodide in *tert*-butyl alcohol results in the formation of mono-, di- and triethers. The order of reactivity is 2 > 6 > 3 ≈ 4.[13] There is no significant influence on the substitution pattern when using sodium or lithium.[14]

A correlation of the electrostatic surface potential distribution of these sugar molecules with the substitution pattern will be discussed elsewhere.[15] Ester compounds could be obtained by the same method with acyl halides as trapping agents.[3,4]

EXPERIMENTAL

Electrolysis

Electrolysis was carried out in a three compartment cell with a working volume of 40 mL (**Fig. 2**). The working electrode as well as the counter electrode were platinized platinum sheets with an area of 6 cm^2. All potentials are referred to the Ag/0.01 M Ag^+ system in acetonitrile. Catholyte and anolyte compartments were separated by a fine porosity glass frit G 3 (monosaccharides) or a cation exchange membrane Nafion^R 417 (disaccharides).[16] In all experiments DMF/0.5 M LiBr was used as the electrolyte system (< 500 ppm H_2O).

Substrate concentrations were 0.5 M (methyl α-D-glucopyranoside, methyl α-D-mannoside), 0.4 M (sucrose) and 0.2 M (methyl α-D-galactoside, methyl β-D-galactoside, benzyl β-lactoside and benzyl β-maltoside). During electrolysis argon was bubbled through the catholyte.

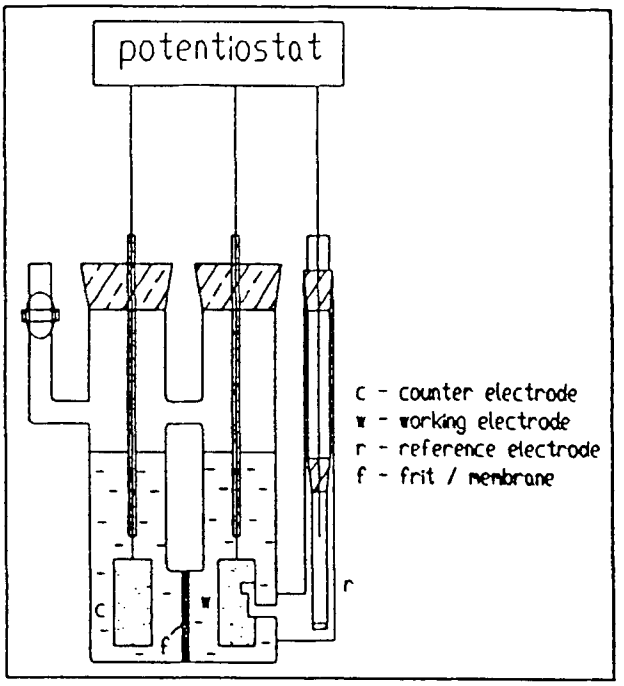


FIG. 2. Three compartment cell for electrolysis. Both electrodes are platinized platinum sheets. The reference system is a silver wire in a 0.01 M $AgNO_3$ solution in acetonitrile.

Solvents and reagents

DMF was refluxed over CaH_2, distilled in vacuum and stored over molecular sieve 4 Å. LiBr and the saccharides were dried under high vacuum at 100 °C. Monosaccharides (Cerestar) as well as sucrose (Janssen), lactose and maltose (Fluka) were purchased. Benzyl β-disaccharides were synthesized as outlined in the literature.[17,18,19]

Instrumentation

Electrolyses were performed with a potentiostatic set up (BANK POS 73). HPLC was performed on a Shimadzu LC-4A instrument equipped with silica gel columns (Polygosil 60-5, Macherey-Nagel) and LiChrosorb columns (RP 18-60/5) on

analytical (250 x 4 mm) and preparative scales (250 x 16 mm). NMR spectra were recorded with a Bruker AM 300 MHz instrument, using TMS as internal standard. If necessary, chemical shift assignments were confirmed by decoupling. Optical rotations were recorded with a Perkin-Elmer polarimeter MC 241. TLC was performed on silica gel (Merck 60 F_{254}).

General procedures

After electrolysis the electrophiles were added in 1.1 equivalent of the current consumed in the electrolysis and left to react for about 12 hours. In the case of monosaccharides, the solvent was removed and most of the educt was recrystallized from acetone. The conducting electrolyte was separated via cation and anion exchange columns (Amberlite IR 120 and IRA 400). The crude mixture of products was separated by reversed-phase chromatography (gradient elution: MeOH/H_2O). Disaccharides were acetylated in pyridine/acetic anhydride. The crude products were dissolved in chloroform, washed with water and dried (Na_2SO_4). Subsequently the solvent was evaporated. Traces of pyridine were removed by co-evaporation with toluene. Preparative column chromatography was performed using silica gel KG 60. If necessary, subsequent separation was performed using HPLC. In this case hexane/ethyl acetate in the ratio 1:1 or 2:1 was used as the eluent.

^{1}H NMR Data

Methyl 2-*O*-Benzyl-α-D-glucopyranoside. mp 118 °C, $[\alpha]_D$ 86 (*c* 1.0, $CHCl_3$), Lit.[20]: mp 120 °C, $[\alpha]_D^{23}$ 86.8, ^{1}H NMR ($CDCl_3$) δ 3.28 (s, 3 H, OCH_3), 4.54 (d, $J_{1,2}$ = 3.6 Hz, H-1), 4.58 (d, 1 H, $J_{PhCHa,PhCHb}$ = 12.2 Hz, PhCHa), 4.7 (d, 1 H, PhCHb), Lit: ^{1}H NMR[21], ^{13}C NMR[21,22]

Methyl 3-*O*-Benzyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 89 (*c* 0.5, $CHCl_3$), Lit.[20]: mp 89-90 °C, $[\alpha]_D^{23}$ 90.3, ^{1}H NMR ($CDCl_3$) δ 3.44 (s, 3 H, OCH_3), 4.52 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11.6 Hz, PhCHa), 4.75 (d, $J_{1,2}$ = 3.5 Hz, H-1), 5.02 (d, 1 H, PhCHb), Lit.: ^{1}H NMR , ^{13}C NMR

Methyl 4-*O*-Benzyl-α-D-glucopyranoside. mp 127 °C, $[\alpha]_D$ 152 (*c* 1.0, $CHCl_3$) Lit.[20]: mp 126-127 °C, $[\alpha]_D^{23}$148.9, see also Lit.[23,24], ^{1}H NMR ($CDCl_3$), δ 3.36 (s, 3 H, OCH_3), 4.67 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11.8 Hz, PhCHa), 4.70 (d, 1 H, $J_{1,2}$ = 3.3 Hz, H-1), 4.88 (d, 1 H, PhCHb)

Methyl 6-*O*-Benzyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 105 (*c* 0.93, $CHCl_3$), Lit.[21]: mp 64-65 °C, $[\alpha]_D^{23}$ 106.4, see also Lit.[24,25,26] ^1H NMR ($CDCl_3$) δ 3.37 (s, 3 H, OCH_3), 4.57 (t, 2 H, $J_{PhCHa,PhCHb}$ = 12 Hz, PhCHa, PhCHb), 4.73 ($J_{1,2}$ = 3.7 Hz, H-1), Lit.: ^1H NMR[28]

Methyl 2,4-Di-*O*-benzyl-α-D-glucopyranoside. mp 74 °C, $[\alpha]_D$ 87 (*c* 0.7, $CHCl_3$), Lit.[21]: mp 75 °C, $[\alpha]_D^{23}$ 87, ^1H NMR ($CDCl_3$) δ 3.33 (s, 3 H, OCH_3), 4.61 (d, 1 H, $J_{1,2}$ = 3.6 Hz, H-1), 4.66 (d, 1 H, $J_{PhCH1a,PhCH1b}$ = 12.1 Hz, PhCH1a), 4.7 (d, 1 H, PhCH1b), 4.73 (d, 1 H, $J_{PhCH2a,PhCH2b}$ = 11.6 Hz, PhCH2a), 4.91 (d, 1 H, PhCH2b), Lit.: ^1H NMR[12]

Methyl 2,6-Di-*O*-benzyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 57 (*c* 0.8, $CHCl_3$), Lit.[20]: mp 81 °C, $[\alpha]_D^{23}$ 62.6, ^1H NMR ($CDCl_3$) δ 3.34 (s, 3 H, OCH_3), 4.56 (d, 1 H, $J_{PhCH1a,PhCH1b}$ = 12.2 Hz, PhCH1a), 4.61 (d, 1 H, PhCH1b), 4.64 (d, $J_{1,2}$ = 3.5 Hz, H-1) 4.66 (d, 1 H, $J_{PhCH2a,PhCH2b}$ = 12 Hz, PhCH2a), 4.69 (d, 1 H, PhCH2b), Lit.: ^{13}C NMR[22]

Methyl 3,6-Di-*O*-benzyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 74 (*c* 0.5, $CHCl_3$), Lit.[20]: syrup, $[\alpha]_D^{23}$ 69.2, see also Lit.[23], ^1H NMR ($CDCl_3$), δ 3.38 (s, 3 H, OCH_3), δ 4.5 (d, 1 H, $J_{PhCH1a,PhCH1b}$ = 11.3 Hz, PhCH1a), 4.55 (d, 1 H, $J_{PhCH2a,PhCH2b}$ = 12.1 Hz, PhCH2a), 4.62 (d, 1 H, PhCH2b), 4.76 (d, $J_{1,2}$ = 3.8 Hz, H-1), 4.8 (d, 1 H, PhCH1b)

Methyl 4,6-Di-*O*-benzyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 113 (*c* 0.5, $CHCl_3$), Lit.[20]: mp 77 °C, $[\alpha]_D^{23}$ 119.1, see also Lit.[25], ^1H NMR ($CDCl_3$) δ 3.41 (s, 3 H, OCH_3), 4.66 (d, 1 H, $J_{PhCH1a,PhCH1b}$ = 11.0 Hz, PhCH1a), 4.75 (d, $J_{1,2}$ = 3.8 Hz, H-1), 4.84-4.94 (m, 3 H, $J_{PhCH2a,PhCH2b}$ = 11.4 Hz, PhCH1b, PhCH2a, PhCH2b), Lit.: ^1H NMR[12], ^{13}C NMR[12]

Methyl 2-*O*-Methyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 46 (*c* 0.7, $CHCl_3$), Lit.[28]: syrup, $[\alpha]_D$ 48, ^1H NMR (D_2O) δ 3.28 (s, 3 H, OCH_3), 3.43 (s, 3 H, OCH_3), 4.93 (d, $J_{1,2}$ = 3.6 Hz, H-1), Lit.: ^{13}C NMR[21,29,30,31]

Methyl 3-*O*-Methyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 52 (*c* 0.6, $CHCl_3$), Lit.[32]: mp 118 °C, $[\alpha]_D$ 81.1, see also Lit.[28,33], ^1H NMR (D_2O) δ 3.33 (s, 3 H, OCH_3), 3.50 (s, 3 H, OCH_3), 4.69 (d, $J_{1,2}$ = 3.9 Hz, H-1), Lit.: ^{13}C NMR[21,29]

Methyl 4-*O*-Methyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 136 (*c* 0.5, $CHCl_3$), Lit.[34]: mp 94 °C, $[\alpha]_D$ 164, see also Lit.[35], ^1H NMR (D_2O) δ 3.29 (s, 3 H, OCH_3), 3.44 (s, 3 H, OCH_3), 4.68 (d, $J_{1,2}$ = 3.8 Hz, H-1), Lit.: ^{13}C NMR[29,36]

Methyl 6-*O*-Methyl-α-D-glucopyranoside. syrup, $[\alpha]_D$ 104 (*c* 0.9, $CHCl_3$), Lit.[37]: syrup, $[\alpha]_D$ 127.9 (H_2O), ^1H NMR (D_2O) δ 3.29 (s, 3 H, OCH_3), 3.30 (s, 3 H, OCH_3), 4.68 (d, $J_{1,2}$ = 3.6 Hz, H-1), Lit.: ^{13}C NMR[29,36]

Methyl 3,4,6-Tri-*O*-acetyl-2-*O*-allyl-α-D-glucopyranoside. only analysed by ^1H NMR ($CDCl_3$), δ 1.95-2.02 (3 s, 9 H, CH_3CO), 3.4 (s, 3 H, OCH_3), 3.47 (dd, $J_{2,3}$ = 10.0 Hz, H-2), 3.9 (o, $J_{5,6}$ = 2.3 Hz, $J_{5,6'}$ = 4.6 Hz, H-5), 3.97-4.05 (m, 3 H, H-6, methylene protons), 4.21 (dd, 1 H, $J_{6,6'}$ = 12.3 Hz, H-6'), 4.78 (d, $J_{1,2}$ = 3.5 Hz, H-1), 4.91 (t, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 10.0 Hz, H-4), 5.11-5.23 (m, 2 H, vinyl protons), 5.33 (t, H-3) 5.7-5.85 (m, 1 H, vinylene proton)

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-allyl-α-D-glucopyranoside. only analysed by ^1H NMR ($CDCl_3$) δ 2.01-2.09 (3 s, 9 H, CH_3CO), 3.4 (s, 3 H, OCH_3), 3.49 (dd, $J_{5,6}$ = 4,8 Hz, $J_{6,6'}$ = 10.8 Hz, H-6), 3.54 (dd, $J_{5,6'}$ = 3.1 Hz, H-6'), 3.93 (o, H-5), 3.98-4.02 (m, 2 H, methylene protons), 4.89 (dd, $J_{2,3}$ = 10.1 Hz, H-2), 4.94 (d, $J_{1,2}$ = 3.6 Hz, H-1), 5.09 (dd, $J_{4,5}$ = 10.1 Hz, H-4), 5.15-5.3 (m, 2 H, vinyl protons), 5.48 (dd, $J_{3,4}$ = 9.4 Hz, H-3), 5.8-5.94 (m, 1 H, vinylene proton)

Methyl 3,6-Di-*O*-acetyl-2,4-di-*O*-allyl-α-D-glucopyranoside. only analysed by ^1H NMR ($CDCl_3$) δ 2.1, 2.12 (2 s, 6 H, 2 CH_3CO), 3.38 (s, 3 H, OCH_3), 3.41 (dd, $J_{2,3}$ = 10.1 Hz, H-2), 3.45 (t, H-4), 3.79 (o, $J_{4,5}$ = 10.0 Hz, H-5), 4.0-4.17 (m, 4 H, methylene protons), 4.2 (dd, $J_{5,6}$ = 5.1 Hz, H-6), 4.31 (dd, $J_{5,6'}$ = 2.3 Hz, H-6'), 4.8 (d, $J_{1,2}$ = 3.5 Hz, H-1), 5.1-5.29 (m, 4 H, vinyl protons), 5.43 (t, $J_{3,4}$ = 9.6 Hz, H-3), 5.67-5.9 (m, 2 H, vinylene protons)

Methyl 2-*O*-Benzyl-α-D-mannopyranoside. mp 95°C, $[\alpha]_D$ 22 (*c* 2, $CHCl_3$), ^1H NMR ($CDCl_3$) δ 3.32 (s, 3 H, OCH_3), 4.69 (d, 1 H, $J_{PhCHa,PhCHb}$ = 12 Hz, PhCHa), 4.71 (d, 1 H, PhCHb), 4.77 (d, $J_{1,2}$ = 2.2 Hz, H-1), Lit.: ^1H NMR and ^{13}C NMR[21]

Methyl 3-*O*-Benzyl-α-D-mannopyranoside. syrup, ^1H NMR ($CDCl_3$) δ 3.29 (s, 3 H, OCH_3), 4.58 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11.5 Hz, PhCHa), 4.66 (d, 1 H, PhCHb), 4.77 (d, $J_{1,2}$ = 1 Hz, H-1), 2,4,6-tri-*O*-acetyl ester, ^1H NMR ($CDCl_3$) δ 1.98-2.05 (3 s, 9 H, 3 CH_3CO), 3.40 (s, 3 H, OCH_3), 4.08 (dd, $J_{5,6}$ = 2.7 Hz, $J_{6,6'}$ = 12.0 Hz, H-6), 4.17 (dd, $J_{5,6'}$ = 5.9 Hz, H-6'), 4.74 (d, $J_{1,2}$ =

1.7 Hz, H-1), 5.16 (t, $J_{3,4}$ = 9.6 Hz, $J_{4,5}$ = 9.8 Hz, H-4), 5.32 (d, $J_{2,3}$ = 3.4 Hz, H-2), Lit.: ^{1}H NMR and ^{13}C NMR[21]

Methyl 6-*O*-Benzyl-α-D-mannopyranoside. syrup, ^{1}H NMR ($CDCl_3$) δ 3.32 (s, 3 H, OCH_3), 4.57 (t, 2 H, $J_{PhCHa,PhCHb}$ = 12.1 Hz, PhCHa, PhCHb), 4.74 (d, $J_{1,2}$ = 1 Hz, H-1), 2,3,4-tri-*O*-acetyl ester, ^{1}H NMR ($CDCl_3$) δ 1.93-2.08 (3 s, 9 H, 3 CH_3CO), 3.42 (s, 3 H, OCH_3), 4.74 (d, $J_{1,2}$ = 1.9 Hz, H-1), 5.20 (dd, $J_{2,3}$ = 3.1 Hz, H-2), 5.22 (dd, H-3), 5.31 (t, $J_{3,4}$ = 9.9 Hz, $J_{4,5}$ = 9.4 Hz, H-4)

Methyl 2,6-Di-*O*-benzyl-α-D-mannopyranoside. syrup, $[\alpha]_D$ -3 (*c* 0.7, $CHCl_3$), Lit.[38]: syrup, $[\alpha]_D^{26}$ -4.9, ^{1}H NMR ($CDCl_3$) δ 3.36 (s, 3 H, OCH_3), 4.55 (d, 1 H, $J_{PhCH1a,PhCH1b}$ = 11.6 Hz, PhCH1a), 4.59 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11.8 Hz, PhCH2a), 4.63 (d, 1 H, PhCH2b), 4.74 (d, 1 H, PhCH1b), 4.81 (d, $J_{1,2}$ = 1.2 Hz, H-1)

Methyl 2-*O*-Methyl-α-D-mannopyranoside. syrup, $[\alpha]_D$ 51 (*c* 1.0, $CHCl_3$), Lit.[39]: syrup, $[\alpha]_D$ 51, see also Lit.[40], ^{1}H NMR ($CDCl_3$) δ 3.28 (s, 3 H, OCH_3), 3.34 (s, 3 H, OCH_3), 4.79 (d, $J_{1,2}$ = 1.5 Hz, H-1), Lit.: ^{1}H NMR[41,42]

Methyl 3-*O*-Methyl-α-D-mannopyranoside. syrup, $[\alpha]_D$ 60 (*c* 0.4, $CHCl_3$), Lit.[41]: syrup, $[\alpha]_D^{25}$ 59.6, ^{1}H NMR ($CDCl_3$) δ 3.26 (s, 3 H, OCH_3), 3.28 (s, 3 H, OCH_3), 4.6 (d, $J_{1,2}$ < 1 Hz, H-1), Lit.: ^{1}H NMR and ^{13}C NMR[43]

Methyl 6-*O*-Methyl-α-D-mannopyranoside. syrup, $[\alpha]_D$ 79 (*c* 0.5, $CHCl_3$), Lit.[44]: syrup, $[\alpha]_D^{25}$ 78.8, see also Lit.[45], ^{1}H NMR (acetone) δ 3.31 (s, 3 H, OCH_3), 3.33 (s, 3 H, OCH_3), 4.61 (d, $J_{1,2}$ = 1.0 Hz, H-1)

Methyl 3,4,6-Tri-*O*-acetyl-2-*O*-allyl-α-D-mannopyranoside. only analysed by ^{1}H NMR ($CDCl_3$) δ 1.9-2.0 (3 s, 9 H, CH_3CO), 3.4 (s, 3 H, OCH_3), 3.75 (dd, $J_{1,2}$ = 1.8 Hz, $J_{2,3}$ = 3.2 Hz, H-2), 3.85 (o, $J_{4,5}$ = 9.9 Hz, $J_{5,6}$ = 2.4 Hz, $J_{5,6'}$ = 5.2 Hz, H-5), 4.0-4.1 (m, 3 H, H-6, methylene protons), 4.2 (dd, $J_{6,6'}$ = 12.1 Hz, H-6'), 4.7 (d, H-1), 5.1-5.22 (m, 3 H, $J_{3,4}$ = 10.0 Hz, H-3, vinyl protons), 5.3 (t, H-4), 5.75-5.9 (m, 1 H, vinylene proton)

Methyl 2,3,4-Tri-*O*-acetyl-6-*O*-allyl-α-D-mannopyranoside. only analysed by ^{1}H NMR ($CDCl_3$) δ 1.96-2.07 (3 s, 9 H, CH_3CO), 3.31 (s, 3 H, OCH_3), 3.47 (d, 2 H, H-6, H-6'), 3.83 (q, $J_{5,6}$ = $J_{5,6'}$ = 5.7 Hz, H-5), 3.98-4.05 (m, 2 H, methylene protons), 4.64 (d, $J_{1,2}$ = 1.5 Hz, H-1), 5.1-5.2 (m, 3 H, H-2, vinyl protons), 5.2-5.27 (m, 2 H, $J_{3,4}$ = 9.8 Hz, H-3, H-4), 5.65-579 (m, 1 H, vinylene proton)

Methyl 2-*O*-Benzyl-α-D-galactopyranoside. mp 120 °C, $[\alpha]_D$ 113 (*c* 1.0, $CHCl_3$), Lit.[45]: mp 122 °C, $[\alpha]_D$ 114.5, ^1H NMR ($CDCl_3$) δ 3.43 (s, 3 H, OCH_3), 4.71 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11.8 Hz, PhCHa), 4.73 (d, 1 H, PhCHb), 4.85 (d, $J_{1,2}$ = 3.9 Hz, H-1) Lit.: ^1H NMR[45]

Methyl 3-*O*-Benzyl-α-D-galactopyranoside. syrup, $[\alpha]_D$ 97 (*c* 0.5, $CHCl_3$), Lit.[45]: syrup, $[\alpha]_D$ 95, ^1H NMR ($CDCl_3$) δ 3.32 (s, 3 H, OCH_3), 4.61 (d, 1 H, $J_{PhCHa,PhCHb}$ = 12 Hz, PhCHa), 4.68 (d, 1 H, PhCHb), 4.69 (d, $J_{1,2}$ = 3.5 Hz, H-1), Lit.: ^1H NMR[21]

Methyl 6-*O*-Benzyl-α-D-galactopyranoside. mp 143 °C, $[\alpha]_D$ 116 (*c* 0.4, $CHCl_3$), Lit.[45]: mp 145 °C, $[\alpha]_D$ 117.5, ^1H NMR ($CDCl_3$) δ 3.41 (s, 3 H, OCH_3), 4.6 (t, 2 H, $J_{PhCHa,PhCHb}$ = 12.3 Hz, PhCHa, PhCHb), 4.83 (d, $J_{1,2}$ = 3.7 Hz, H-1)

Methyl 2,6-Di-*O*-benzyl-α-D-galactopyranoside. syrup, $[\alpha]_D$ 73 (*c* 0.4, $CHCl_3$), Lit.[46]: syrup, $[\alpha]_D^{22}$ 74.9, see also Lit.[14], ^1H NMR ($CDCl_3$) δ 3.35 (s, 3 H, OCH_3), 4.58 (s, 2 H, PhCH1a, PhCH1b), 4.66 (d, 1 H, $J_{PhCH2a,PhCH2b}$ = 12.1 Hz, PhCH2a), 4.7 (d, 1 H, PhCH2b), 4.72 (d, $J_{1,2}$ = 3.4 Hz, H-1)

Methyl 3,6-Di-*O*-benzyl-α-D-galactopyranoside. syrup, $[\alpha]_D$ 112 (*c* 0.5, $CHCl_3$), Lit.[14]: syrup, $[\alpha]_D$ 109, ^1H NMR ($CDCl_3$) δ 3.43 (s, 3 H, OCH_3), 4.57 (d, 1 H, $J_{PhCH1a,PhCH1b}$ = 11.9 Hz, PhCH1a), 4.62 (d, 1 H, PhCH1b), 4.73 (s, 2 H, PhCH2a, PhCH2b), 4,85 (d, $J_{1,2}$ = 3.9 Hz, H-1)

Methyl 2-*O*-Benzyl-β-D-galactopyranoside. mp 145 °C, $[\alpha]_D$ 11 (*c* 1.0, $CHCl_3$), Lit.[45]: mp 146 °C, $[\alpha]_D$ 13, ^1H NMR ($CHCl_3$) δ 3.59 (s, 3 H, OCH_3), 4.31 (d, $J_{1,2}$ = 7.6 Hz, H-1), 4.66 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11.5 Hz, PhCHa), 4.95 (d, 1 H, PhCHb)

Methyl 3-*O*-Benzyl-β-D-galactopyranoside. mp 135 °C, $[\alpha]_D$ -2 (*c* 1.0, ($CHCl_3$), Lit.[45]: mp 136 °C, $[\alpha]_D$ 0.0, ^1H NMR (D_2O) δ 3.39 (s, 3 H, OCH_3), (4.16 d, $J_{1,2}$ = 7.5 Hz, H-1), 4.50 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11.7 Hz, PhCHa), 4.61 (d, 1 H, PhCHb), Lit.: ^1H NMR and ^{13}C NMR[19]

Methyl 6-*O*-Benzyl-β-D-galactopyranoside. mp 99 °C, $[\alpha]_D$ -28 (*c* 0.6, $CHCl_3$), Lit.[45]: mp 101 °C, $[\alpha]_D$ -33, see also Lit.[24], ^1H NMR ($CDCl_3$) δ 3.49 (s, 3 H, OCH_3), 4.13 (d, $J_{1,2}$ = 7.5 Hz, H-1), 4.54 (t, 1 H, $J_{PhCHa,PhCHb}$ = 12.2 Hz, PhCHa, PhCHb)

Methyl 3,6-Di-*O*-benzyl-β-D-galactopyranoside. syrup, $[\alpha]_D$ -3 (*c* 0.4, $CHCl_3$), Lit.[25]: syrup, $[\alpha]_D$ -1.9, see also Lit.[14], ^1H NMR ($CDCl_3$) δ 3.42 (s,

3 H, OCH_3), 4.17 (d, $J_{1,2}$ = 7.7 Hz, H-1), 4.59 (s, 2 H, PhCHa, PhCHb), 4.7 (d, 1 H, $J_{PhCHa,PhCHb}$ = 11, 8 Hz, PhCHa), 4. 77 (d, 1 H, PhCHb)

3,4,6,1',3',4',6'-Hepta-*O*-acetyl-2-*O*-benzylsucrose. syrup, $[\alpha]_D$ 53 (*c* 1.05, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 1.93 - 2.20 (7s, 21H, CH_3CO), 3.58 (dd, $J_{1,2}$ = 3.6Hz, $J_{2,3}$ = 10.1 Hz, H-2), 5.56 (d, $J_{1,2}$ = 3.6 Hz, H-1) 7.23 - 7.43 (m, 5 H, aromatic protons)

Anal. Calcd for $C_{33}H_{42}O_{18}$ (726.7): C, 54.54; H, 5.79. Found: C, 54.30; H, 5.90.

2,3,4,6,3',4',6'-Hepta-*O*-acetyl-1'-*O*-benzylsucrose. syrup, $[\alpha]_D$ 56 (*c* 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 1.93 - 2.17 (7s, 21H, CH_3CO), 3.41 (d, 1 H $J_{1'CHa,\ 1'CHb}$ = 10.6Hz, 1'-CHb), 3.59 (d, 1 H, $J_{1'CHb,\ 1'CHa}$ = 10.6Hz, 1'-CHa), 7.26 - 7.38 (m, 5 H, aromatic protons)

Anal. Calcd for $C_{33}H_{42}O_{18}$ (726.7): C, 54.54; H 5.79. Found: C, 53.31; H, 5.84.

2,3,4,6,1',4',6'-Hepta-*O*-acetyl-3'-*O*-benzylsucrose. syrup, $[\alpha]_D$ 75 (*c* 2.0, $CHCl_3$), ^{1} H NMR ($CDCl_3$) δ 2.00 — 2.20 (7s, 21H, CH_3CO), 4.20 (d, $J_{3',4'}$ = 7.5Hz, H-3'), 7.24 - 7.43 (m, 5H, aromatic protons)

Anal. Calcd for $C_{33}H_{42}O_{18}$ (726.7): C, 54.54; H, 5.79. Found: C, 54.55; H, 5.91.

3,4,6,1',3',4',6'-Hepta-*O*-acetyl-2-*O*-methylsucrose. syrup, $[\alpha]_D$ 45 (*c* 2.0, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ 1.95 - 2.19 (7s, 21 H, CH_3CO), 3.36 (dd, $J_{1,2}$ = 3.7 Hz, $J_{2,3}$ = 10.3 Hz, H-2), 3.40 (s, 3H, OCH_3), 5.62 (d, $J_{1,2}$ = 3.7 Hz, H-1)

Anal. Calcd for $C_{27}H_{38}O_{18}$ (650.58): C, 49.85; H, 5.89. Found: C, 49.11; H, 5.69.

2,3,4,6,3',4',6'-Hepta-*O*-acetyl-1'-*O*-methylsucrose. syrup, $[\alpha]_D$ 49 (*c* 2.0, $CHCl_3$), ^{1}H-NMR ($CDCl_3$) δ 1.95 - 2.20 (7s, 21 H, CH_3CO), 3.4 (d, $J_{1'CHa,\ 1'CHb}$ = 10.8 Hz, 1 H, 1'-CHb), 3.42 (s, 3 H, OCH_3), 3.65 (d, $J_{1'CHb,\ 1'CHa}$ = 10.8 Hz, 1 H, 1'-CHa)

$C_{27}H_{38}O_{18}$ (650.58) : Found C 49.57 H 5.58, Calc. C 49.85 H 5.89

2,3,4,6,1',4',6'-Hepta-*O*-acetyl-3'-*O*-methylsucrose. syrup, $[\alpha]_D$ 6.4 (*c* 2.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 1.98 - 2.18 (7s, 21 H, CH_3CO), 3.48 (s, 3 H, OCH_3), 4.30 (d, $J_{3',4'}$ = 6.7 Hz, H-3')

Anal. Calcd for $C_{27}H_{38}O_{18}$ (650.58): H, 5.55; C, 49.85. Found: C, 49.60; H, 5.89.

3,4,6,1',3',4',6'-Hepta-*O*-acetyl-2-*O*-allylsucrose. only analysed by ^{1}H NMR ($CDCl_3$) δ 2.00 - 2.20 (7s, 21 H, CH_3CO), 3.50 (dd, $J_{1,2}$ = 3.4 Hz, $J_{2,3}$ = 10.0 Hz, H-2), 5.0 (t, $J_{3,4}$ = 9.6 Hz, H-4), 5.20 - 5.30 (m, 2 H, vinyl protons), 5.35 (t, $J_{2,3}$ = 9.7 Hz, H-3), 5.4 (t, $J_{3',4'}$ = 6.5 Hz, H-4'), 5.5 (t, H-3'), 5.55 (d, $J_{1,2}$ = 3.5 Hz, H-1), 5.55 (d, $J_{1,2}$ = 3.4 Hz, H-1), 5.70 - 5.90 (m, 1 H, vinylene proton)

2,3,4,6,3',4',6'-Hepta-*O*-acetyl-1'-*O*-allylsucrose. only analysed by ^{1}H NMR ($CDCl_3$) δ 2.00 - 2.20 (7s, 21H, CH_3CO), 3.40 (d, $J_{1'CHa,\ 1'CHb}$ = 10.6 Hz, 1 H, 1'-CHb), 3.6 (d, $J_{1'CHb,\ 1'CHa}$ = 10.6 Hz, 1 H, 1'-CHa)

Benzyl (2,3,6,2',4',6'-Hexa-*O*-acetyl-3'-*O*-benzyl) β-D-lactoside. $[\alpha]_D$ 144 (*c* 1.1, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 1.94 - 2.16 (6 s, 18 H, CH_3CO), 3.48 (dd, $J_{3',2'}$ = 10.1 Hz, $J_{3',4'}$ = 3.4 Hz, H-3'), 4.58 (d, $J_{PhCHa,PhCHb}$ = 12.3 Hz, 1 H, PhCHb Aglycon), 4.85 (d, $J_{PhCHb,PhCHa}$ = 12.3 Hz, 1 H, PhCHa,Aglycon), 7.20 - 7.39 (m, 10 H, aromatic protons)

Anal. Calcd for $C_{38}H_{46}O_{17}$ (774.77): C, 58.91; H, 5.98. Found: C, 60.06; H, 6.13.

Benzyl (3,6,2',3',4',6'-Hexa-*O*-acetyl-2-*O*-benzyl) β-D-lactoside. $[\alpha]_D$ -18.2 (*c* 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 1.94 - 2.15 (6s, 18 H, CH_3CO), 3.39 (dd, $J_{1,2}$ = 8.1 Hz, $J_{2,3}$ = 9.6 Hz, H-2), 7.21 - 7.40 (m, 10 H, aromatic protons)

Anal. Calcd for $C_{38}H_{46}O_{17}$ (774.77): C, 58.91; H, 5.98. Found: C, 58.36; H, 5.91.

Benzyl (3,6,2',3',4',6'-Hexa-*O*-acetyl-3'-*O*-methyl) β-D-lactoside. syrup, $[\alpha]_D$ -10.8 (*c* 1.0, $CHCl_3$), H NMR ($CDCl_3$) δ 1.95 - 2.17 (6s, 18 H, CH_3CO), .27 (dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 3.3 Hz, H-3'), 3.33 (s, 3 H, OCH_3), d, ($J_{1',2'}$ = 8.0 Hz, H-1'), 4.51 (d, $J_{1,2}$ = 7.9 Hz, H-1), 4.59 (d, $J_{PhCHa,PhCHb}$ 1= 2.3 Hz, PhCHb Aglycon), 4.86 (d, $J_{PhCHb,PhCHa}$ = 12.3 Hz, PhCHa Aglycon), 7.23 - 7.38 (aromatic protons)

Anal. Calcd for $C_{32}H_{42}O_{17}$ (698.67): C, 55.01; H, 6.01. Found: C, 54.95; H, 5.91.

Benzyl (3,6,2',3',4',6'-Hexa-*O*-acetyl-2-*O*-methyl) β-D-lactoside. syrup, ^{1}H NMR ($CDCl_3$) δ 1.92 - 2.19 (6s, 18 H, CH_3CO), 3.35 (s, 3 H, OCH_3),

3.42 (dd, $J_{1,2}$ = 7.9 Hz, $J_{2,3}$ = 10.1 Hz, H-2), 7.21 - 7.40 (5 H, aromatic protons)

Benzyl (3,6,2',3',4',6'-Hexa-*O*-acetyl-2-*O*-allyl) β-D-lactoside. syrup, ^{1}H NMR ($CDCl_3$) δ 1.96 - 2.15 (6 s, 18 H, CH_3CO), 3.31 (dd, $J_{1,2}$ = 7.7 Hz $J_{2,3}$ = 9.4 Hz, H-2), 5.80 (m, 1 H, CH_2CHCH_2), 7.24 - 7.38 (5 H, aromatic protons)

Benzyl (2,3,6,2',4',6'-Hexa-*O*-acetyl-3'-*O*-allyl) β-D-lactoside. syrup, ^{1}H NMR ($CDCl_3$) δ 1.93 - 2.14 (6 s, 18 H, CH_3CO), 3.44 (dd, $J_{2',3'}$ = 10.0 Hz, $J_{3',4'}$ = 3.4 Hz, H-3'), 5.84 (m, 1 H, vinylene proton), 7.20 - 7.33 (5 H, aromatic protons)

Benzyl (2,3,6,3',4',6'-Hexa-*O*-acetyl-2'-*O*-benzyl) β-D-maltoside. syrup, $[\alpha]_D$ 39 (*c* 1.0, $CHCl_3$), ^{1}H NMR ($CDCl_3$) δ 1.89 - 2.08 (6s, 18 H, CH_3CO),3.49 (dd, $J_{1',2'}$ = 3.5 Hz, $J_{2',3'}$ = 10.0 Hz, H-2'), 4.51 - 4.64 (m, 5 H, 6'-CH_a, H-1, PhCHb Aglycon, $PhCH_2$), 4.85 (d, J $_{PhCHa,PhCHb}$ = 12.1 Hz, PhCHa Aglycon), 7.24 - 7.39 (10 H, aromatic protons)

Anal. Calcd for $C_{38}H_{46}O_{17}$ (774.77): C, 58.91; H, 5.98. Found: C, 58.95; H, 6.15.

Benzyl (3,6,2',3',4',6'-Hexa-*O*-acetyl-2-*O*-benzyl) β-D-maltoside. syrup, ^{1}H NMR ($CDCl_3$) δ 1.90 - 2.18 (6s, 18 H, CH_3CO), 3.37 (dd, $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 9.4 Hz, H-2), 7.15 - 7.38 (10 H, aromatic protons)

Benzyl (2,3,6,3',4',6'-Hexa-*O*-acetyl-2'-*O*-methyl) β-D-maltoside. syrup, $[\alpha]_D$ -28 (*c* 2.0, $CHCl_3$),^{1}H NMR ($CDCl_3$) δ 1.97 - 2.15 (6s, 18 H, CH_3CO), 4.56 (d, $J_{1,2}$ = 7.8 Hz, H-1), 5.17 (d, $J_{1',2'}$ = 3.7 Hz, H-1'),

Anal. Calcd for $C_{32}H_{42}O_{17}$ (698.67): C, 55.01; H, 6.01. Found: C, 54.88; H, 5.85.

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