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An electrochemical synthesis of methyl α-isomaltoside

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Abstract

A novel approach has been developed for the synthesis of methyl α-isomaltoside (**10**), comprising, as the first step, electrochemical conversion of the hydroxyl groups of methyl α-D-glucopyranoside into the corresponding anions. The anions subsequently react with tetra-*O*-acetyl-α-D-glucopyranosyl bromide to give methyl 2′,3′,4′,6′-tetra-*O*-acetyl-α-isomaltoside (**8**) as the main product, *O*-deacetylation of which affords **10**. The glycosidation proceeds under complete stereochemical control.

Keywords: Isomaltoside, methyl α-; Disaccharides; Electrochemical synthesis; Structure

1. Introduction

Previously [1] a method has been described, involving one electrochemical step, for the esterification and etherification of glycosides of mono- and di-saccharides. In this way products containing partially protected OH groups could be obtained. The first electrochemical step consisted of the transformation of the hydroxyl groups into the corresponding anions ($R\text{-}OH \rightarrow R\text{-}O^-$). The second chemical step involved reactions of the anions with electrophilic reagents ($R\text{-}O^- + R'\text{-}X \rightarrow R\text{-}O\text{-}R' + X^-$, where X is a halogen and R′ is an acyl or an alkyl group).

We now report an application of this method to the synthesis of a disaccharide. Although there are numerous efficient and stereoselective methods for the synthesis of oligosaccharides [2], new methods are still of interest in view of the crucial biological function of oligosaccharides.

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As starting reagents, methyl α-D-glucopyranoside (R-OH) and tetra-*O*-acetyl-α-D-glucopyranosyl bromide (R′-X) were chosen, because similar reagents were used in the Koenigs–Knorr method [3]. Thus, a comparison of the two methods is possible.

2. Results and discussion

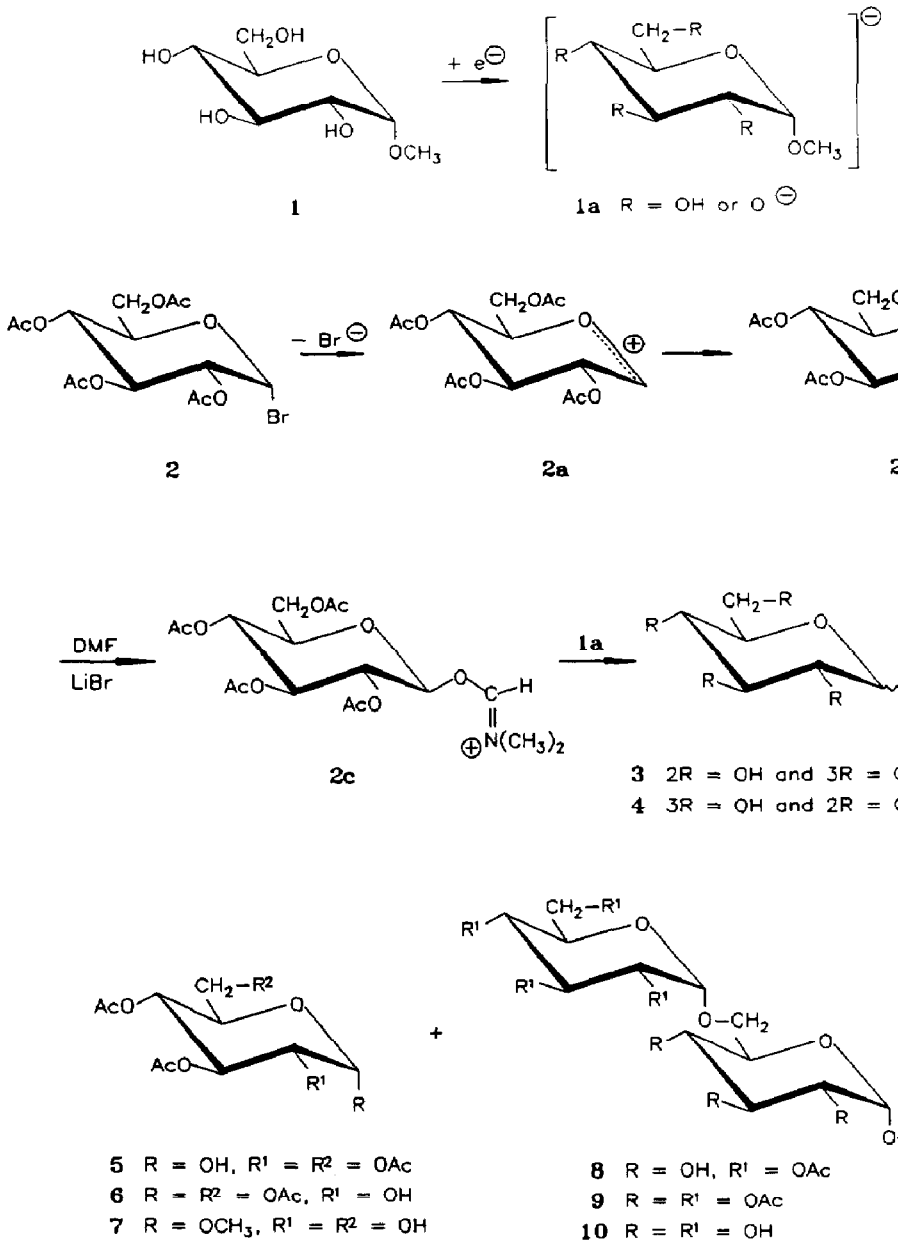
Methyl α-D-glucopyranoside (**1**) after electrochemical transformation[1] to the corresponding anion (**1a**) reacted with tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**2**) in *N*,*N*-dimethylformamide (DMF) in the presence of LiBr at 20°C for 12 h to give a mixture of products whose chromatographic separation gave compounds **1** and **3–8**. The ratios of compounds **3–8** were ca. 2:4:1:1:4.5:11, the major product being methyl 2′,3′,4′,6′-tetra-*O*-acetyl-α-isomaltoside (**8**). Its structure was based on mass spectrometry (*m*/*z* 524 $M^{+\cdot}$), elemental analysis, optical rotation, IR spectroscopy, and ^{1}H NMR data ($J_{1,2} = J_{1',2'} = 4$ Hz, signals of four OAc groups, and the values of the chemical shifts for the signals of H-1′–H-6′ being higher than for H-1–H-6). The structure of **8** was further supported by chemical reactions. Thus, on oxidation of **8** with periodate, ~2 mol of oxidant were consumed and ~1 mol of formic acid was released. This result confirmed the presence of free hydroxyl groups at C-2, 3, and 4. Acetylation of **8** yielded the heptaacetate **9** (^{1}H NMR, signals of seven OAc groups, *m*/*z* 650 $M^{+\cdot}$). *O*-Deacetylation of **8** with triethylamine in aqueous methanol gave methyl 6-*O*-α-D-glucopyranosyl-α-D-glucopyranoside (methyl α-isomaltoside) (**10**), its structure being based on $[\alpha]_D$, elemental analysis, mass spectrometry, and ^{13}C NMR data. The high positive optical rotation suggests the α configuration of C-1′ as well as at C-1, but it should be noted that our value does not agree with that cited in the literature [4] for this compound (see Experimental). The ^{13}C NMR spectrum of **10** indicated the presence of two glycosyl residues (δ 100.2, C-1; 99.25, C-1′; 67.3, C-6; and 61.8, C-6′), and the value for the C-6 signal showed that the glycosidic link involved O-6.

Compounds **5** and **6** were identified as 2,3,4,6-tetra-*O*-acetyl- [5–9] and 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose [7,9–11], respectively. Acetylation of both **5** and **6** gave the known 1,2,3,4,6-penta-*O*-acetyl-α-D-glucopyranose [12,13]. The latter compound also arose from acetylation of **3** and **4**. This finding, together with the ^{1}H NMR and mass spectral evidence, led us to conclude that **3** and **4** were di-*O*-acetyl- and tri-*O*-acetyl-D-glucoses, respectively.

The structure of **7** was supported by its elemental analysis, mass spectrum (*m*/*z* 278 $M^{+\cdot}$), and ^{1}H NMR spectrum. The latter contained signals for OCH_3 and two OAc groups. The presence of OAc groups at C-3 and C-4 is evident from the downfield shifts of H-3 and H-4 (δ 5.08 and 5.31, respectively) compared to that of H-2 (δ 3.68). Acetylation of **7** gave methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside [14].

From the type of products obtained it would appear that the anion **1a** reacts not only with the anomeric carbon atom of **2** but also with carbonyl carbons of the acetyl groups of this compound. It appears that disaccharide **8** is formed first and that this is the main process. A second reaction yields deesterification products **3** and **4** and the transesterification product

[1] It was earlier established [1] that, after electrolysis, only about 50% of the substrate undergoes transformation into its anionic form.



7, in low yields. It is noteworthy, however, that the main reaction is both regio- and stereoselective since the formation of the glycosidic sugar–sugar link involves exclusively the anion at C-6 of compound **1a** to give the product with an α configuration. Such a configuration of the glycosidic linkage was unexpected since it seemed probable that the structure of compound **2** (α configuration plus the 2-*O*-acetyl group) and a possible Koenigs–Knorr type mechanism would ensure the formation of the β-product.

At present we cannot give a convincing explanation for the observed exclusive reaction of **1** at O-6. It is probable that steric factors are decisive, because reaction of anion **1a** with less bulky electrophiles is not so stereoselective [1]. With regard to the observed stereo-

selectivity, it is useful to consider literature reports on the influence of positively charged leaving groups on glycosidations using glycosyl halides [15–22], and the following mechanism is suggested.

In the first step, an intermediate **2c** arises from the reaction of compound **2** via **2a** and **2b** with DMF. The β configuration at the anomeric centre of **2c** is an outcome of equatorial attack of DMF on the anomeric carbon atom of the intermediate **2b** and it can be argued that **2c** is stabilized by the reverse anomeric effect [15,18,22]. In a subsequent step, an axial attack of the anion **1a** on the anomeric carbon of **2c** takes place to form the α-glycosidic linkage. Participation of the ion **2a** in this process is suggested by the presence of compounds **5** and **6** which can arise from this ion.

3. Experimental

General methods and materials.—Melting points are uncorrected. Optical rotations were measured on a Hilger–Watt polarimeter. Silica Gel G Sheets (Merck) were used for TLC with *A*, 1:1 hexane–EtOAc and *B*, 9:3:1 $CHCl_3$–MeOH–H_2O. MN-Kieselgel (<0.08 mm) was used for column chromatography. HPLC was performed on a Shimadzu LC-4A apparatus equipped with Silica Gel columns (Polygosil$^{(R)}$ 60-5) and LiChrosorb columns (RP 18-60/15) in analytical (250×4 mm) and preparative scale (250×16 mm), respectively. ^{1}H NMR spectra were recorded with a Bruker AM 300 MHz instrument for solutions in $CDCl_3$ (internal Me_4Si) or D_2O (external Me_4Si). ^{13}C NMR spectra were recorded with a Tesla BS 567A (25.142 MHz) spectrometer for D_2O solutions (external Me_4Si standard). Field-desorption (FD) mass spectra were recorded on a MAT 711 mass spectrometer.

Electrochemical measurements were performed with a potentiostatic setup (BANK, POS 73) according to the literature procedure [1].

Electrolysis was carried out at a potential of -2 V and a current density within the range 20–40 mA · cm^{-2} in a three-compartment cell with a working volume of 40 mL. The working electrode as well as the counter electrode were platinized platinum sheets of 6 cm^2 surface. All potentials are referred to a 0.01 M Ag/Ag^+ system in MeCN. Catholyte and anolyte chambers were separated by a fine porosity glass frit G3. The supporting electrolyte was DMF (50 mL)/LiBr (0.5 M). During electrolysis Ar was bubbled through the solution.

DMF was dried and distilled using standard methods [23]. LiBr and methyl α-D-glucopyranoside (**1**) were dried under high vacuum at 100°C. Tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**2**) had mp 87–89°C, $[\alpha]_D^{20}$ +189° (*c* 0.5, $CHCl_3$); lit. [24] mp 88–89°C, $[\alpha]_D^{20}$ +198° ($CHCl_3$).

General procedure.—The electrolysis of **1** (1.94 g, 0.01 mol) was carried out in DMF (50 mL) containing LiBr (2.17 g, 0.025 mol) at 20°C for 7 h, then the electrolysis was stopped and **2** (3.2 g, 0.0078 mol) in DMF (25 mL) was added. After 14 h at 20°C, the solution was concentrated to ~50 mL under diminished pressure and passed through an anion (Amberlite IRA-400; AcO^- ionic form or Amberlite IRA-93) and cation (Amberlite IR-120; $TRIZAH^+$ ionic form or Amberlite IRP-64) exchange column, then the solvent was removed under reduced pressure to give 3.5 g of light-yellow syrup. HPLC chromatography (solvent *A*) for analytical and preparative scale and column chromatography (solvent *B*) for preparative scale of the crude mixture gave first tri-*O*-acetyl-D-glucose (**3**;

0.18 g, 7.5%, syrup; R_f (solvent *B*) 0.70; ν_{max} 3450 (OH) and 1760 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$): δ 2.01, 2.07 and 2.10 (3 s, 9 H, 3 Ac). Mass spectrum (FD): *m/z* 306 ($M^{+\cdot}$).

Eluted second was di-*O*-acetyl-D-glucose (**4**; 0.290 g, 14%, syrup), R_f (solvent *B*) 0.68; ν_{max} 3430 (OH) and 1765 cm^{-1} (ester CO); ^1H NMR ($CDCl_3$): δ 2.01, 2.08, (2 s, 6 H, 2 Ac). Mass spectrum (FD): *m/z* 264 ($M^{+\cdot}$).

Eluted third was 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (**5**; 0.095 g, 3.5%), mp 104–106°C; $[\alpha]_D^{20}$ +126 → 82° (*c* 0.2, $CHCl_3$); lit. [5] mp 100°C, $[\alpha]_D^{20}$ +135.6° ($CDCl_3$), +142.2 → 80.5° (EtOH); lit. [6] α anomer, mp 99–100°C, $[\alpha]_D^{20}$ +135.1° ($CHCl_3$), $[\alpha]_D^{20}$ +139.4° → +80.3° (95% EtOH); R_f (solvent *B*) 0.62; ν_{max} 3430 (OH) and 1755 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$): δ 2.02, 2.05, 2.07 and 2.10 (4 s, 12 H, 4 Ac), 4.12 (m, 2 H, H-5 and H-6a), 4.25 (m, 1 H, H-6b), 4.87 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.08 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.50 (d, 1 H, $J_{1,2}$ 3.0 Hz, H-1) and 5.56 (dd, $J_{3,4}$ 10 Hz, H-3). Mass spectrum (FD): *m/z* 348 ($M^{+\cdot}$). Anal. Calcd for $C_{14}H_{20}O_{10}$: C, 48.28; H, 5.79. Found: C, 48.31; H, 5.83.

Eluted fourth was 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (**6**; 0.110 g, 4%), mp 101–102°C, $[\alpha]_D^{22}$ +140° (*c* 0.2, $CHCl_3$); lit. [10] mp 97–98°C, $[\alpha]_D$ +145° ($CHCl_3$); lit. [11] mp 98–100°C, $[\alpha]_D$ +141.1° ($CHCl_3$); R_f (solvent *B*) 0.55; ν_{max} 3445 (OH) and 1760 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$): δ 2.05, 2.07, 2.10, and 2.20 (4 s, 12 H, 4 Ac), 2.91 (d, 1 H, O-H), 3.88 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.04 (m, 2 H, H-6a and H-5), 4.28 (m, 1 H, H-6b), 5.14 (dd, 1 H, $J_{3,4}$ 10 Hz, H-4), 5.26 (dd, 1 H, $J_{4,5}$ 10 Hz, H-3), and 6.25 (d, 1 H, $J_{1,2}$ 2.5 Hz, H-1); lit. [9] 2.02 (s, 3 H, 1 Ac), 2.08 (s, 6 H, 2 Ac), 2.18 (s, 3 H, 1 Ac), 3.23 (d, 1 H, O-H), 3.70–4.30 (m, 4 H, H-2, H-5, 2 H-6), 6.23 (d, 1 H, $J_{1,2}$ 3.7 Hz, H-1). Mass spectrum (FD): *m/z* 348 ($M^{+\cdot}$). Anal. Calcd for $C_{14}H_{20}O_{10}$: C, 48.28; H, 5.79. Found: C, 48.33; H, 5.82.

Conventional treatment of **5** as well as **6** with Ac_2O–pyridine and crystallization of the crude product from MeOH afforded penta-*O*-acetyl-α-D-glucopyranose, mp 111–113°C, $[\alpha]_D^{21}$ +104° (*c* 0.5, $CHCl_3$); lit. [13] mp 112–114°C, $[\alpha]_D^{20}$ +102° ($CHCl_3$); ^1H NMR ($CDCl_3$): δ 2.01, 2.02, 2.05, 2.08 and 2.18 (5 s, 15 H, 5 Ac), 4.05 (m, 1 H, H-6a), 4.10 (m, 1 H, H-5), 4.20 (m, 1 H, H-6b), 5.10 (4 dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 5.15 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 5.46 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), and 6.32 (d, 1 H, $J_{1,2}$ 3 Hz, H-1), in agreement with published data [12].

Eluted fifth was methyl 3,4-di-*O*-acetyl-α-D-glucopyranoside (**7**; 0.340 g, 15.7%, syrup), $[\alpha]_D^{22}$ +128° (*c* 0.5, $CHCl_3$); R_f (solvent *B*) 0.3; ν_{max} 3455 (OH) and 1765 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$): δ 2.06 and 2.12 (2 s, 6 H, 2 Ac), 3.45 (s, 3 H, OCH_3), 3.68 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 4.14 (m, 1 H, H-5), 4.24 (m, 2 H, H-6a,b), 5.08 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 5.37 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), and 5.36 (dd, 1 H, $J_{1,2}$ 3 Hz, H-1). Mass spectrum (FD): *m/z* 278 ($M^{+\cdot}$). Anal. Calcd for $C_{11}H_{18}O_8$: C, 47.48; H, 6.52. Found: C, 47.55; H, 6.47.

Acetylation of **7** with Ac_2O–pyridine gave methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside, mp 100–103°C, $[\alpha]_D^{20}$ +127° (*c* 0.5, $CHCl_3$); lit. [14] mp 100°C, $[\alpha]_D^{20}$ +131° ($CHCl_3$).

Eluted sixth was methyl 6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucopyranoside (**8**) isolated as a syrup (1.56 g, 38%), $[\alpha]_D^{22}$ +138° (*c* 0.5, $CHCl_3$); R_f (solvent *B*) 0.3; ν_{max} 3500 (OH) and 1760 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$): δ 2.01, 2.08, 2.12,

2.14 (4 s, 12 H, 4 Ac), 3.38 (s, 3 H, OCH_3), 3.43 (m, 1 H, H-5), 3.71 (dd, 1 H, $J_{2,3}$ 10 Hz, H-2), 3.78 (m, 1 H, H-5′), 3.98 (dd, 1 H, $J_{4,5}$ 10 Hz, H-4), 4.12 (dd, 1 H, $J_{3,4}$ 10 Hz, H-3), 4.14 (m, 1 H, H-6′a), 4.21 (m, 2 H, H-6a,b), 4.52 (m, 1 H, H-6′b), 4.70 (dd, 1 H, $J_{2',3'}$ 10 Hz, H-2′), 4.91 (d, 1 H, $J_{1,2}$ 4 Hz, H-1), 5.02 (dd, 1 H, $J_{4',5'}$ 10 Hz, H-4′), 5.29 (dd, 1 H, $J_{3',4'}$ 10 Hz, H-3′) and 5.32 (d, 1 H, $J_{1',2'}$ 4 Hz, H-1′). Mass spectrum (FD): *m/z* 524 ($M^{+\cdot}$). Anal. Calcd for $C_{21}H_{32}O_{15}$: C, 48.09; H, 6.15. Found: C, 48.20; H, 6.17.

Oxidation of **8** (26.2 mg, 0.05 mmol) with $NaIO_4$ (42.8 mg, 0.2 mmol) was carried out in 4:1 MeOH–H_2O using the method of Jackson and Hudson [25]. Based on 1 mol of **8**, 2.02 mol of oxidant were reduced and ~1 mol of formic acid was formed.

The triol **8** was treated with Ac_2O–pyridine. Crystallization of the crude product from MeOH afforded methyl 2,3,4-tri-*O*-acetyl-6-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-glucopyranoside (**9**), mp 158°C, $[\alpha]_D^{22}$ +168° (*c* 0.2, $CHCl_3$); ν_{max} 1760 cm^{-1} (CO ester); ^1H NMR ($CDCl_3$): δ 1.98, 2.02, 2.05, 2.07, 2.09, 2.12, and 2.15 (7 s, 21 H, 7 Ac). Mass spectrum (FD): *m/z* 650 ($M^{+\cdot}$). Anal. Calcd for $C_{27}H_{38}O_{18}$: C, 49.84; H, 5.89. Found: C, 49.75; H, 5.85.

A solution of **8** (0.100 g, 0.2 mmol) in 10:1 MeOH–H_2O (30 mL) containing triethylamine (2 mL) was kept at 20°C for 18 h. TLC (solvent *B*) showed the complete conversion of **8** into one product. Solvent removal left a syrup, which was lyophilized to give pure methyl 6-*O*-α-D-glucopyranosyl-α-D-glucopyranoside as an amorphous solid (**10**; 54 mg, 80%), $[\alpha]_D^{23}$ +107° (*c* 0.15, EtOH); lit. [4] for the methyl α-glycoside, $[\alpha]_D^{24}$ +50° (H_2O); lit. for the methyl β-glycoside, $[\alpha]_D^{24}$ +50° (H_2O) [26], and $[\alpha]_D^{20}$ +53.2° (H_2O) [27]; ν_{max} 3360 cm^{-1} (OH); ^{13}C NMR (D_2O): δ 100.2 (C-1), 99.25 (C-1′), 75.00 (C-3), 74.20 (C-3′), 73.30 (C-2), 73.20 (C-2′), 72.4 (C-5′), 71.4 (C-5), 70.7 (C-4 and C-4′), 67.3 (C-6), 61.8 (C-6′), and 54.9 (OCH_3). The ^{13}C chemical shifts of **10** were assigned by reference to assignments for methyl α-D-glucopyranoside [28], 6-*O*-methyl-α-D-glucopyranose [28], methyl 6-*O*-methyl-α-D-glucopyranoside [29], and α-isomaltose [28,29]. Mass spectrum (FD): *m/z* 356 ($M^{+\cdot}$). Anal. Calcd for $C_{13}H_{24}O_{11}$: C, 43.82; H, 6.79. Found: C, 43.90; H, 6.84.

Eluted seventh was methyl α-D-glucopyranoside (**1**, 0.870 g).

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