TEMPO-Mediated Anodic Oxidation of Methyl Glycosides and 1-Methyl and 1-Azido Disaccharides

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Keywords: Azides / Carbohydrates / Glycosides / Oxidation / TEMPO / Uronic acids

Methyl glycosides of L-sorbopyranoside, D-fructopyranoside, D-glucosaminopyranoside, 2,3-dehydro-2,3-dideoxyglucopyranoside, cellobiose, lactose, and maltose and the 1-azido derivatives of glucose, cellobiose, lactose, and maltose have been converted into the corresponding uronic acids in moderate to excellent yields by TEMPO-mediated anodic oxidation. The anode proves to be an advantageous alternative to other cooxidants in TEMPO$^+$ oxidations of carbohydrates and is compatible with *N*-acylamino and azido groups and with double bonds. The electrolyte, a carbonate buffer, can easily be removed with a cation-exchange resin, a facile scale-up by increasing the electrode area is possible.

Introduction

The selective oxidation of carbohydrates has been intensively studied over recent decades and continues to be an area of current interest.[1−5] For oxidation to uronic acids, stoichiometrically employed reagents such as nitric acid[6] and nitrogen dioxide[6,7] have been developed, as well as catalytic methods: oxygen with noble metal catalysts[3,5,8,9] or stable organic nitroxyl radicals with cooxidants.[10−30] The sterically shielded nitrosonium ion, generated from the nitroxyl radical by one-electron oxidation, selectively converts primary hydroxy groups in the presence of secondary ones. Preparative oxidations of carbohydrates to uronic acids are usually performed at room temperature, with sodium hypochlorite as oxidant and TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) or its derivatives and sodium bromide as a double mediatory system. Under these conditions, hypochlorite or the intermediate bromine can cause side reactions with sensitive functional groups. Furthermore, the separation of the polar uronic acids from aqueous solutions of sodium halides is frequently difficult.

The use of anodic oxidation is an advantageous alternative. The electrode does not interfere with the alcohol oxidation and the electrolysis system is easy to work up and to scale up. First examples of selective anodic oxidations on preparative scale with TEMPO as mediator have been reported recently.[31,32]

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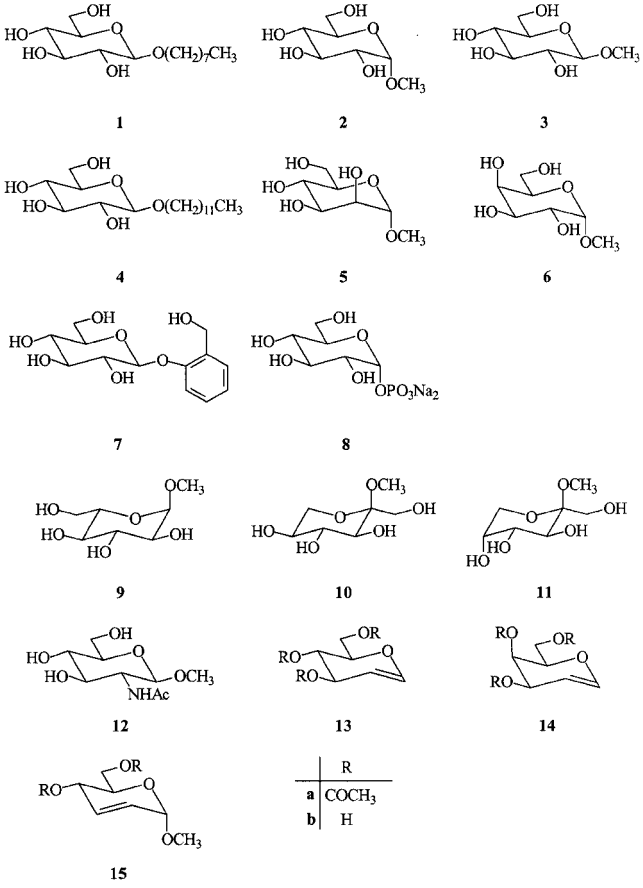
Results and Discussion

We have recently shown that the primary hydroxy groups in the monosaccharides **1**−**8** can be oxidized selectively at the anode with TEMPO as mediator to afford the corresponding uronic acids in yields between 45 and 98%.[31] To proceed in exploration of the scope of this TEMPO-mediated oxidation the methyl glycosides **9**−**15** were prepared and oxidized.

Preparation of Methyl Glycosides

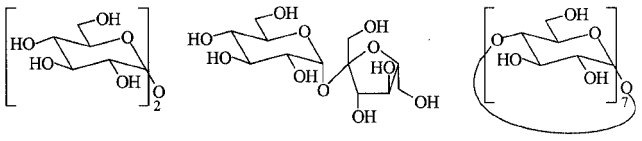
Methyl α-L-glucopyranoside (**9**) was obtained from L-glucose in 34% yield by heating the carbohydrate at reflux in methanol with a Dowex cation-exchange resin as catalyst.[33] In the ^{1}H NMR spectrum the coupling constant of $^3J_{1,2}$ = 3.6 Hz supports the assigned α configuration. The only L-sugar available in reasonable amounts is L-sorbose, because it is an intermediate in the technical production of vitamin C.[9,34] When a solution of L-sorbose was stirred in methanol with 0.1% 2 N hydrochloric acid at room temperature for 24 h, only 11% of methyl α-L-sorbopyranoside (**10**) was obtained, together with 37% of α- and β-L-sorbofuranoside. After an increase in the added 2 N hydrochloric acid to 1% and 4 d of stirring, **10** was obtained in 76% yield.[35] D-Fructose was also stirred for 4 d in methanol with 0.1% concd. hydrochloric acid. Besides two methyl furanosides, the target methyl β-D-fructopyranoside (**11**) was obtained in 48% yield after isolation by flash chromatography.[35] D-Glucosamine was converted into the pentaacetate in 66% yield with pyridine/acetic anhydride, and this was subsequently converted into a mixture of α- and β-



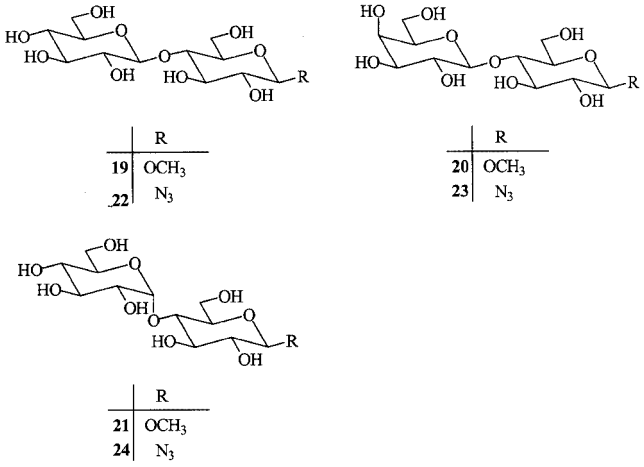
methyl glycosides (α/β = 1:1.4) by acid catalysis in methanol and deacylated with sodium methoxide to provide methyl *N*-acetylglucosaminopyranoside (**12**) in 76% yield after purification by flash chromatography.[36,37] D-Glucose was converted into the triacetylglucal **13a** in 98% yield in a one-pot reaction via the 1-bromotetraacetate and reductive elimination with zinc.[38] The glucal was then deacylated with sodium methoxide in 96% yield to afford the glucal **13b**. When the same reaction conditions were applied to galactose, the triacetylgalactal **14a** was obtained in a lower yield of 53% yield[38] and deacylated to give **14b** in 98% yield. With boron trifluoride–diethyl ether in benzene/methanol, **13a** was transformed – by S_N2' substitution of the 3-acetoxy group by the methoxy group – into **15a** in 90% yield.[39] This was subsequently deacylated with sodium methoxide to afford 96% of **15b**.

Preparation of Methyl Glycosides of Disaccharides

The nonreducing disaccharides trehalose (**16**), sucrose (**17**), and β-cyclodextrin (**18**) have been oxidized at C-6 to give the corresponding dicarboxylic acids.[31]



In these cases, interference with the oxidation at the anomeric center was precluded by acetal formation. With reducing disaccharides, such an oxidation has to be prevented by conversion of these carbohydrates into their 1-methoxy or 1-azido derivatives. For that purpose the corresponding methyl glycosides of cellobiose (**19**), lactose (**20**), and maltose (**21**) were prepared.



The synthesis of the methyl glycosides **19**–**21** involved a four-step sequence:[40–42] conversion into the octaacetate (90–98% yield), exchange of 1-acetoxy for bromide (82–89% yield), substitution of bromide for methoxy (50–98% yield), and deacylation to afford **19**–**21** (92–98% yield). In this way, **19**, **20**, and **21** were obtained in 78, 63, and 39% overall yields, respectively.

Glycosyl azides are used in carbohydrate chemistry as an entry to *N*-glycosides.[43,44] TEMPO oxidations with sodium hypochlorite as cooxidant have been described for a number of azido monosaccharides, affording the corresponding uronic acids in good yields.[13,45] The oxidation of azido disaccharides, however, has not yet been reported. The same is true for the TEMPO-catalyzed anodic oxidation of 1-azido carbohydrates.

Preparation of Glycosyl Azides

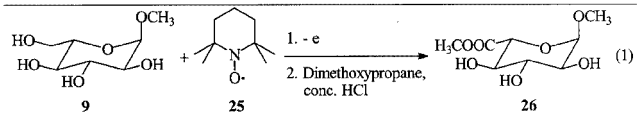
The azides **22**–**24** were prepared from cellobiose, lactose, and maltose by treatment of the corresponding per-*O*-acetylated bromides with sodium azide to afford the per-*O*-acetylated β-1-azido carbohydrates (49–95%). These were subsequently deacetoxylated with sodium methoxide in methanol (87–99%).[46] In this way the 1-azido disaccha-

ides **22**−**24** were obtained in 63, 40 and 37% overall yields, respectively.

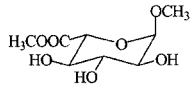
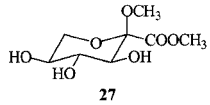
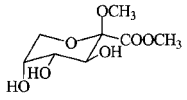
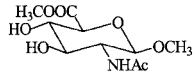
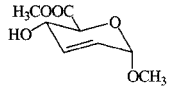
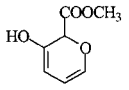
Anodic Oxidation of Mono- and Disaccharides with TEMPO (25) as Mediator and the Anode as Cooxidant

The carbohydrates were oxidized at a controlled potential of 0.53 V (versus Ag/AgCl electrode) in an undivided cell with a graphite anode and a platinum cathode, in the presence of 0.20−0.25 equiv. of TEMPO. For isolation and characterization, the uronic acids were converted into their corresponding methyl esters [Equation (1), Table 1].

Table 1. TEMPO-mediated anodic oxidation of methyl glycosides **9**−**12** and **15b** to the corresponding uronic acids



9 **25** **26**

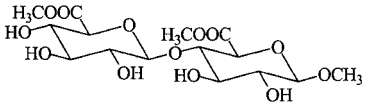
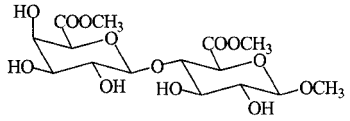
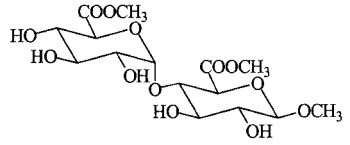
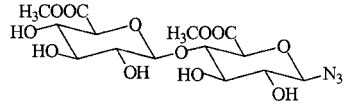
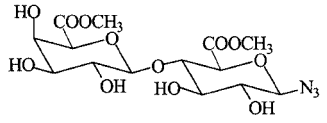
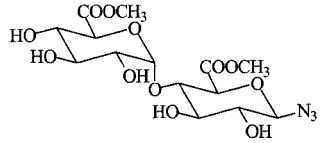
Entry	Substrate[a]	Product	Yield (%)
1	**9**	 **26**	87
2	**10**	 **27**	74
3	**11**	 **28**	54
4	**12**	 **29**	80
5	**15b**	 **30**	23
		 **31**	15

[a] Conditions as described in the Exp. Sect.

From **9** and **10**, the methyl esters of the uronic acids were obtained in good yields. The yield in the case of the conversion of **11** into **28** was only moderate, possibly due to the presence of the secondary axial 4-OH group, which is more sensitive to oxidation than the secondary equatorial hydroxy groups. The formed hydroxy ketone can subsequently undergo a retro-aldol cleavage in the alkaline medium.[8] In the oxidation of **12** to **29**, the yield of the uronic acid in the crude product was high according to HPLC analysis. However, isolation proved to be difficult. Methylation of the carboxylate with dimethyl sulfate or acidification of solutions to pH = 4−5 and treatment with diazomethane yielded only about 25% of **29**. With freshly prepared 2,2-dimethoxypropane and a drop of concd. hydrochloric acid, however, the ester **29** could be isolated in 80% yield. The oxidation of α-methyl *N*-acetylglucosaminopyranoside with oxygen and platinum oxide has been reported to proceed in 89% yield.[47]

Conversion of **15b** and acidification of the produced sodium carboxylate yielded a uronic acid that underwent fast elimination to **31**. To suppress this unwanted reaction, the labile uronic acid had to be rapidly converted into the ester. For that purpose the salt solution was concentrated to dryness, the residue was redissolved in methanol/water (2:1), and the solution was then treated with small portions of a cation-exchange resin and diazomethane. After removal of the resin and flash chromatography, 23% of **30** and 15% of **31** were isolated. Compound **30** is still very labile and decomposes into **31** within 3 d at room temperature. Oxidation of the glucals **13b** and **14b** under the same conditions afforded mixtures of many compounds in low yield. As the selectivity could not be improved, these products were not characterized.

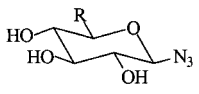
Table 2. TEMPO-mediated anodic oxidation of 1-methoxy disaccharides **19**−**21** and 1-azido disaccharides **22**−**24** to the corresponding dicarboxylic acids

Entry	Substrate[a]	Product	Yield (%)
1	**19**	 **32**	69
2	**20**	 **33**	59
3	**21**	 **34**	61
4	**22**	 **35**	63
5	**23**	 **36**	42
6	**24**	 **37**	57

[a] Conditions as described in the Exp. Sect.

TEMPO-mediated anodic oxidation of the disaccharides **19**−**21** and **22**−**24** afforded the corresponding diuronic acids **32**−**37** (Table 2).

With the 1-methoxy disacharides, good yields of the dimethyl diesters **32**−**34** could be obtained. The conversion of **21** into **34** with oxygen and platinum as catalyst has also been described, but in only 7% yield.[48] With the corresponding 1-azido derivatives **22**−**24** the yields are good, too. Only in the case of **23**, in which the axial secondary 4-OH group in the galactopyranosyl part of the disaccharide is more sensitive to oxidation (see the conversion **11** into **27** above), was the yield somewhat lower.



	R
37	CH_2OH
38	CO_2CH_3

In addition, β-D-glucopyranosyl azide (**38**), prepared analogously to **22**−**24** in 59% overall yield,[46] was anodically oxidized with TEMPO as mediator to the corresponding uronic acid, isolated as the methyl ester **39** in 82% yield. This is superior to the 74% yield obtained with TEMPO and sodium hypochlorite as cooxidant.[13]

Conclusion

In the previous paper,[31] TEMPO-mediated anodic oxidations of alkyl glucopyranosides, methyl galactopyranosides, and methyl mannopyranosides − together with those of the non-reducing di-, oligo- and polysaccharides trehalose, sucrose, β-cyclodextrin, and starch − were reported. In this contribution the scope of application has been extended and the use of indirect anodic oxidation of carbohydrates with TEMPO as mediator consolidated.

The range of convertible carbohydrates has been expanded to methyl glycosides of ketohexoses with oxidation at the 1-OH group and to a glucosaminopyranoside, demonstrating the compatibility of the amino group with the anodic reaction conditions. Unsaturated carbohydrates − with the exception of enol ethers − can be converted too, but acidic media have to be avoided during workup to prevent elimination reactions resulting in dienes.

Methyl glycosides and glycosyl azides of reducing disaccharides can be selectively oxidized at the primary hydroxy groups to provide the corresponding diuronic acids in good yield. The azido group also proved to be compatible with the anode.

With regard to the reagent, anodic oxidation has proven to be an interesting alternative to chemical cooxidants in conversions with $TEMPO^+$. The sodium carbonate used both as buffer and electrolyte can easily be removed by treatment with a cation-exchange resin. The method allows easy scale-up by increasing the electrode area, and permanent immobilization of TEMPO at the electrode surface may be achievable.[32]

Experimental Section

General Remarks: All starting chemicals are commercially available and were used without further purification. Methanol was dried and all solvents were distilled before use. Melting points were determined with a Kofler Micro hot stage and are not corrected. Solutions were concentrated in a rotary evaporator at bath temperatures < 50 °C. IR spectra were obtained with a Bruker IFS 28 FT-IR spectrometer. NMR spectra were recorded with a Bruker AMX 400 spectrometer at 400 MHz (for ^1H NMR), at 100 MHz (for ^{13}C NMR), and with a Varian Unityplus spectrometer, at 600 MHz (for ^1H NMR) and 151 MHz (for ^{13}C NMR). D_2O, $CDCl_3$, and CD_3OD were used as solvents. Chemical shifts (δ) are given in ppm and coupling constants (*J*) are given in Hz. Two-dimensional ^1H-^1H-COSY and C,H-correlation ($^1J_{C,H}$,$^{2,3}J_{C,H}$) experiments were performed for complete signal assignments wherever necessary. The measurement of GC/MS spectra was conducted with a Finnigan-MAT 312 machine (EI, 70 eV) with an HP 5 (25 m, 0.20 mm i.d., 0.33 μm film) capillary column. ESI mass spectra were recorded with a Quattro LC-Z micromass quadrupole mass spectrometer. Gas chromatography was carried out with a Hewlett−Packard HP 6890 Series plus with the HP 5 capillary column (30 m, 0.32 mm i.d., 0.25 μm film). Optical rotations were recorded at the Na D-line (589 nm, 20 °C, cell length 10 cm). Elemental analyses were obtained by the analytical laboratory of the Organisch-Chemisches Institut der Universität Münster. Preparative-scale electrolyses were carried out in an undivided or in a divided beaker-type cell with NS 14.5 joint for a reflux condenser and/or a fermentation tube. The undivided cell had an inner diameter of 4 cm and a capacity of 100 mL. It was closed with a Teflon stopper (NS 45), which had three bore holes: two for the current feeders and one for the Luggin capillary, which was connected with the reference electrode and the tip of which was positioned close to the anode. The area of the graphite anode was 8 cm^2 (electrographite, Sigri). A platinum foil (8 cm^2) on a Teflon frame was used as cathode. Both electrodes were connected to the current source through steel rods. The inner diameter of the divided beaker type cell was 2.8 cm (capacity 60 mL). The divided cell was closed with a Teflon stopper (NS 45), which had three bore holes for the anodic current feeder, the Luggin capillary, and the cathode chamber. The cathode chamber had an inner diameter of 1.5 cm and was separated from the anode chamber by a glass frit (D3). Within the cathode chamber a platinum foil cathode (1 cm^2) was fixed next to the glass frit. The tip of the Luggin capillary was placed between the glass frit and the graphite anode (4 cm^2, electrographite, Sigri). In both cases the reference electrode was Ag/AgCl/3 M KCl in water (+0.21 V vs. NHE). The current source was a Wenking ST 88.

Electrochemical Oxidation of Methyl Glycosides (General Procedure A): The stated amounts of glycoside (0.025 to 0.050 mol/L) and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, **25**, 0.005−0.010 mol/L, for details see individual procedures) were dissolved in carbonate-buffered water (42.80 g/L, 0.40 mol/L Na_2CO_3, 24.80 g/L, 0.30 mol/L $NaHCO_3$). The solution was electrolyzed at a potential of 0.53 V versus Ag/AgCl electrode (corresponding to 0.56 V versus SCE) in an undivided cell at 20 °C. After the electrolysis, a sufficient amount of acidic cation-exchange resin (80 mL, Amberlite IR 120) was added. After the mixture had been stirred for 0.5 h, the resin was filtered off and the solvent was removed at 50 °C in vacuo. For the isolation and characterization of the reaction products, the uronic acids were usually converted into their corresponding methyl esters as follows. A proportion of the crude product was dissolved in methanol (10 mL) and treated with 2,2-dimethoxypropane (1.0 mL, 8.20 mmol) and one drop of concd. aq. hydrochloric

acid (p.a., approximately 0.32 mmol, corresponding to 0.03 mol/L). After the mixture had been stirred for 1 d, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel.

Electrochemical Oxidation of Glycosyl Azides (General Procedure B): The stated amounts of glycosyl azide were electrolyzed and worked up as described in General Procedure A, with the exception that a divided cell was used.

Methyl (Methyl α-L-glucopyranoside)uronate (26): Methyl α-L-glucopyranoside (**9**, 710 mg, 3.66 mmol) and TEMPO (**25**, 110 mg, 0.72 mmol) were dissolved in 72 mL of carbonate buffer. The solution was electrolyzed according to General Procedure A. After consumption of 2120 C (6.0 F/mol), the electrolysis was stopped and the system was worked up; 790 mg of crude product was obtained, of which 171 mg was esterified. The methyl ester **26** (151 mg, 0.68 mmol, corresponding to 3.17 mmol in the crude product, 87%, current yield 58%) was isolated by flash chromatography (ethyl acetate/methanol, 3:1) as a yellow syrup. $[\alpha]_D^{20} = -95.0$ (c = 1.00, H_2O). IR (film): $\tilde{\nu}$ = 3390 (s, O−H), 1745 (s, C=O) cm^{-1}. ^1H NMR (400 MHz, D_2O): δ = 3.37 (s, 3 H, OCH_3), 3.49 (d, $^3J_{4,5}$ = 9.3 Hz, 1 H, 4-H), 3.54 (dd, $^3J_{1,2}$ = 3.1, $^3J_{2,3}$ = 9.8 Hz, 1 H, 2-H), 3.64 (t, $^3J_{2,3}$ = 9.1 Hz, 1 H, 3-H), 3.77 (s, 3 H, $COOCH_3$), 4.15 (d, 1 H, 5-H), 4.81 (d, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, D_2O): δ = 53.6 (q, $COOCH_3$), 56.1 (q, OCH_3), 71.2 (d, C-5), 71.3 (d, C-2), 71.8 (d, C-4), 73.1 (d, C-3), 100.2 (d, C-1), 172.2 (s, C-6) ppm. MS (GC/MS coupling, 70 eV, EI, silylation with MSTFA in pyridine): *m/z* (%) = 423 (5) [$M^+ - CH_3$], 391 (8) [$M^+ - CH_3 - CH_3OH$], 333 (10) [$M^+ - CH_3 - Si(CH_3)_3OH$], 317 (12) [$M^+ - OCH_3 - Si(CH_3)_3OH$], 259 (12) [$M^+ - OSi(CH_3)_3 - Si(CH_3)_3OH$], 217 (100) [$(CH_3)_3SiOCHCHCHOSi(CH_3)_3^+$], 204 (90) [$(CH_3)_3SiOCHCHOSi(CH_3)_3^+$], 159 (45) [$(CH_3)_3SiOCHCHCHOCH_3^+$], 147 (57) [$(CH_3)_3SiOSi(CH_3)_2^+$], 73 (92) [$Si(CH_3)_3^+$]. $C_8H_{14}O_7$ (222.19): calcd. C 43.24, H 6.35; found C 42.60, H 6.15. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_8H_{14}O_7 + Na^+$ 245.0637; found 245.0620.

Methyl (Methyl β-L-sorbopyranoside)uronate (27): Methyl β-L-sorbopyranoside (**10**, 730 mg, 3.76 mmol) and TEMPO (**25**, 118 mg, 0.76 mmol) were electrolyzed in 75 mL of buffer according to General Procedure A. After consumption of 2976 C (8.2 F/mol), the electrolysis was stopped and the system was worked up to provide 730 mg of crude product, of which 150 mg was esterified. The methyl ester **27** (131 mg, 0.57 mmol, corresponding to 2.86 mmol in the crude product, 76%, current yield 37%) was isolated by flash chromatography (ethyl acetate/methanol, 1:2) as a white solid. $[\alpha]_D^{20} = -25.2$ (c = 0.98, MeOH). M.p. 193 °C. IR (film): $\tilde{\nu}$= 3387 (br. s, O−H), 1746 (s, C=O) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 3.33−3.35 (m, 1 H, 6b-H), 3.37 (s, 3 H, OCH_3), 3.47 (d, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.54−3.58 (m, 2 H, 4-H, 5-H), 3.72−3.76 (m, 1 H, 6a-H), 3.79 (s, 3 H, $COOCH_3$) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 51.6 (q, OCH_3), 53.3 (q, $COOCH_3$), 65.3 (t, C-6), 71.3 (d, C-5), 75.7 (2d, C-3, C-4), 101.9 (s, C-2), 170.1 (s, C-1) ppm. MS (GC/MS coupling, 70 eV, EI, silylation with MSTFA in pyridine): *m/z* (%) = 423 (1) [$M^+ - CH_3$], 391 (2) [$M^+ - CH_3 - CH_3OH$], 379 (34) [$M^+ - CH_3 - CO_2$], 319 (3), 305 (5) [$M^+ - Si(CH_3)_3 - CH_3OH - CO$], 289 (11) [$M^+ - OSi(CH_3)_3 - CH_3OH - CO$], 257 (14) [$M^+ - OSi(CH_3)_3 - 2 \times CH_3OH - CO$], 217 (20) [$(CH_3)_3SiOCHCHCHOSi(CH_3)_3^+$], 204 (63) [$(CH_3)_3SiOCHCHOSi(CH_3)_3^+$], 191 (15), 189 (15), 159 (4) [$(CH_3)_3SiOCHCHCHOCH_3^+$], 147 (35) [$(CH_3)_3SiOSi(CH_3)_2^+$], 133 (18), 89 (12) [$OSi(CH_3)_3^+$], 73 (100) [$Si(CH_3)_3^+$]. $C_8H_{14}O_7$ (222.19): calcd. C 43.24, H 6.35; found C 42.60, H 6.15. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_8H_{14}O_7 + Na^+$ 245.0637; found 245.0669.

Methyl (Methyl β-D-fructopyranoside)uronate (28): Methyl β-D-fructopyranoside (**11**, 730 mg, 3.76 mmol) and TEMPO (**25**, 118 mg, 0.75 mmol) were electrolyzed in carbonate-buffered water (75 mL) and, after a charge of 2945 C (8.1 F/mol) had been consumed, worked up according to General Procedure A. A proportion (152 mg) of the crude product (771 mg) was esterified. Product **28** (92 mg, 0.41 mmol, corresponding to 2.11 mmol in the crude product, 56%, current yield 28%) was isolated as a colorless syrup by flash chromatography (ethyl acetate/methanol, 3:1). $[\alpha]_D^{20} = -90.9$ (c = 1.00, MeOH). IR (film): $\tilde{\nu}$ = 3395 (br. s, O−H), 1742 (s, C=O) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 3.38 (s, 3 H, OCH_3), 3.70 (dd, $^3J_{5,6b}$ = 1.4, $^2J_{6a,6b}$ = 12.4 Hz, 1 H, 6b-H), 3.77 (m, 5 H, 5-H, 6a-H, $COOCH_3$), 3.91−3.94 (m, 2 H, 4-H, 3-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 51.8 (q, OCH_3), 53.1 (q, $COOCH_3$), 66.5 (t, C-6), 70.7 (d, C-4), 71.3 (d, C-5), 72.1 (d, C-3), 102.3 (s, C-2), 170.0 (s, C-1) ppm. MS (GC/MS coupling, 70 eV, EI, silylation with MSTFA in pyridine): *m/z* (%) = 379 (12) [$M^+ - CH_3 - CO_2$], 319 (2), 305 (8) [$M^+ - Si(CH_3)_3 - CH_3OH - CO$], 289 (20) [$M^+ - OSi(CH_3)_3 - CH_3OH - CO$], 257 (32) [$M^+ - OSi(CH_3)_3 - 2 \times CH_3OH - CO$], 217 (28) [$(CH_3)_3SiOCHCHCHOSi(CH_3)_3^+$], 204 (35) [$(CH_3)_3SiOCHCHOSi(CH_3)_3^+$], 191 (10), 189 (8), 159 (3) [$(CH_3)_3SiOCHCHCHOCH_3^+$], 147 (30) [$(CH_3)_3SiOSi(CH_3)_2^+$], 133 (15), 89 (14) [$OSi(CH_3)_3^+$], 73 (100) [$Si(CH_3)_3^+$], 45 (8). $C_8H_{14}O_7$ (222.19): calcd. C 43.24, H 6.35; found C 42.65, H 6.08. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_8H_{14}O_7 + Na^+$ 245.0637; found 245.0621.

Methyl (Methyl *N*-acetyl-D-glucosaminopyranoside)uronate (29): Methyl *N*-acetyl-D-glucosaminopyranoside (**12**, 941 mg, 4.00 mmol, α/β = 1:1.4 by NMR) was electrolyzed with TEMPO (156 mg, 1.00 mmol) in 80 mL of carbonate buffer according to General Procedure A until 3214 C (8.3 F/mol) of charge had been consumed. A proportion (249 mg) of the crude product (1.11 g) was esterified. Subsequent isolation of the ester by flash chromatography (ethyl acetate/methanol, 6:1, stained with 1.0% bromocresol green in ethanol) afforded the methyl ester **29** (188 mg, 0.71 mmol, corresponding to 3.80 mmol in the crude product, 80%, current yield 39%) as a colorless syrup. $[\alpha]_D^{20} = +58.0$ (c = 1.00, MeOH). IR (film): $\tilde{\nu}$ = 3351 (s, br. O−H), 1785 (s, C=O), 1742 (s, C=O) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 1.96 (s, 3 H, CH_3), 3.37 (s, 3 H, OCH_3), 3.56−3.65 (m, 2 H, 3-H, 4-H), 3.76 (s, 3 H, $COOCH_3$), 3.93 (dd, $^3J_{2,3}$ = 10.0 Hz, 1 H, 2-H), 4.01 (d, $^3J_{4,5}$ = 9.3 Hz, 1 H, 5-H), 4.68 (d. $^3J_{1,2}$ = 3.4 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100-MHz, CD_3OD): δ = 22.8 (q, CH_3), 53.1 (q, $COOCH_3$), 55.3 (d, C-2), 56.3 (q, OCH_3), 72.7 (d, C-3), 73.2 (d, C-5), 74.0 (d, C-4), 100.7 (d, C-1), 172.0 (s, C-6), 174.0 (s, $COOCH_3$) ppm. MS (ESI/MS coupling, ES+): *m/z* (%) = 264 (25) [$M + H^+$], 246 (5) [$M + H^+ - H_2O$], 232 (100) [$M + H^+ - CH_3OH$], 214 (32) [$232 - H_2O$], 196 (5) [$323 - 2 \times H_2O$], 172 (7) [$232 - CH_3OH - CO$], 154 (12) [$214 - CH_3OH - CO$], 126 (35). $C_{10}H_{17}NO_7$ (263.25): calcd. C 45.63, H 6.51, N 5.32; found C 45.46, H 6.57, N 5.00.

Methyl (Methyl 2,3-dehydro-2,3-dideoxy-α-glucopyranoside)uronate (30) and (2*S*)-3-Hydroxy-2-methoxycarbonyl-2*H*-pyran (31): Methyl 2,3-dehydro-2,3-dideoxy-α-glucopyranoside (**15b**, 499 mg, 3.10 mmol) and TEMPO (**25**, 87 mg, 0.62 mmol) were dissolved in 65 mL of carbonate buffer. The solution was electrolyzed according to General Procedure A. After consumption of 1836 C (6.1 F/mol), the electrolysis was stopped and the mixture was worked up. For half of the electrolyte, the solvent was evaporated under vacuum and the crude product was dissolved in 45 mL of methanol/water, 2:1. Diazomethane in diethyl ether (0.5 M, 60 mL) and acidic cation-exchange resin were added alternately until gas evolution ceased. After 1 h, the resin was filtered off and the solvent was evaporated. Flash chromatography (petroleum ether/diethyl ether, 2:1) provided the labile methyl ester **30** (66 mg, 0.35 mmol, corresponding to 0.70 mmol in the crude product, 23%, current yield 15%) as a colorless syrup. Additionally, the methyl ester **31** (37 mg, 0.23 mmol, corresponding to 0.47 mmol in the crude product, 15%, current yield 10%) was isolated as a white solid. Compound **30** decomposed into **31** within 3 d at room temperature.

Methyl Ester 30: ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.48 (s, 3 H, OCH_3), 3.86 (s, 3 H, $COOCH_3$), 4.24 (d, $^3J_{4,5}$ = 9.5 Hz, 1 H, 5-H), 4.37−4.42 (m, 1 H, 4-H), 4.97 (d, $^3J_{1,2}$ = 1.8 Hz, 1 H, 1-H), 5.75−5.79 (m, 1 H, 3-H), 5.96−5.99 (m, 1 H, 2-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.6 (q, $COOCH_3$), 56.1 (q, OCH_3), 65.0 (d, C-4), 66.8 (d, C-5), 95.7 (d, C-1), 125.9 (d, C-3), 131.9 (d, C-2), 171.5 (s, $COOCH_3$) ppm. MS (ESI/MS coupling, ES+): *m*/*z* (%) = 211 (55) [M + Na^+], 193 (3) [M + Na^+ − H_2O], 179 (7) [M + Na^+ − CH_3OH], 161 (3) [193 − CH_3OH], 147 (7) [179 − CH_3OH], 133 (7) [161 − CO], 111 (100) [M + Na^+ − $HO(CH)_4OCH_3$, retro-Diels−Alder reaction], 23 (45) [Na^+].

Methyl Ester 31: $[\alpha]_D^{20}$ = +106.3 (*c* = 1.05, MeOH). M.p. 43 °C. IR (film): ṽ = 3441 (br. s, O−H), 1745 (s, C=O) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, $COOCH_3$), 5.21 (s, 1 H, 5-H), 6.36−6.39 (m, 2 H, 2-H, 3-H), 7.40 (d, $^3J_{1,2}$ = 0.9 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.2 (q, OCH_3), 66.8 (d, C-5), 108.7 (d, C-3), 110.5 (d, C-2), 143.0 (d, C-1), 150.7 (d, C-4), 171.9 (s, $COOCH_3$) ppm. MS (ESI/MS coupling, ES+): *m*/*z* (%) = 174 (75) [M + NH_4^+], 157 (20) [M + NH_4^+ − NH_3], 156 (25) [M + NH_4^+ − H_2O], 139 (100) [M + NH_4^+ − NH_3 − H_2O], 124 (10) [156 − CH_3OH], 118 (8), 18 (10) [NH_4^+]. $C_7H_8O_4$ (156.14) calcd. C 53.85, H 5.16; found C 54.00, H 5.31.

Methyl [Methyl 4-*O*-(methyl β-D-glucopyranosyluronate)-β-D-glucopyranoside]uronate (32): Methyl 4-*O*-(β-D-glucopyranosyl)-β-D-glucopyranoside (**19**, 660 mg, 1.85 mmol) and TEMPO (**25**, 58 mg, 0.37 mmol) were electrolyzed in 75 mL of buffer according to General Procedure A. After consumption of 1999 C (11.2 F/mol), the electrolysis was stopped and the mixture was worked up to provide 720 mg of crude product, of which 185 mg was esterified. The dimethyl ester **32** (135 mg, 0.33 mmol, corresponding to 1.30 mmol in the crude product, 69%, current yield 49%) was isolated by flash chromatography (ethyl acetate/methanol, 3:1) as a white solid. $[\alpha]_D^{20}$ = −37.9 (*c* = 1.08, MeOH). M.p. 95 °C. IR (film): ṽ = 3422 (br. s, O−H), 1742 (s, C=O) cm^{-1}. ^{1}H NMR (600 MHz, D_2O): δ = 3.19−3.23 (m, 2 H, 2′-H, 2-H), 3.36−3.46 (m, 5 H, OCH_3, 4′-H, 3′-H), 3.32−3.37 (m, 2 H, 3′-H, 5′-H), 3.54 (t, $^3J_{3,4}$ = 8.6 Hz, 1 H, 3-H), 3.68−3.69 (m, 7 H, 2× $COOCH_3$, 4-H), 3.93 (d, $^3J_{4',5'}$ = 10.0 Hz, 1 H, 5′-H), 4.07 (d, $^3J_{4,5}$ = 9.3 Hz, 1 H, 5-H), 4.32−4.34 (m, 2 H, 1′-H, 1-H) ppm. ^{13}C NMR (151 MHz, D_2O): δ = 53.1, 53.2 (2q, $COOCH_3$), 58.1 (q, OCH_3), 70.0 (d, C-4′), 72.3 (d, C-2′), 72.4 (d, C-2), 73.1 (d, C-5), 73.5 (d, C-3), 74.2 (d, C-5′), 74.7 (d, C-3′), 79.8 (d, C-4), 102.4 (d, C-1′), 103.4 (d, C-1), 170.0 (s, C-6), 170.7 (s, C-6′) ppm. MS (ESI/MS coupling, ES+): *m*/*z* (%) = 430 (15) [M + NH_4^+], 413 (7) [M + NH_4^+ − NH_3], 395 (10) [413 − H_2O], 381 (40) [413 − CH_3OH], 363 (15) [381 − H_2O], 345 (15) [381 − 2 × H_2O], 223 (65) [$H_3COOC-C_6H_{11}O_5$ + H^+, β-cleavage], 205 (40) [223 − H_2O], 191 (100) [223 − CH_3OH], 173 (35) [191 − H_2O], 155 (20) [191 − 2 × H_2O]. $C_{15}H_{24}O_{13}$ (412.34): calcd. C 43.69, H 5.87; found C 42.66, H 6.10. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_{15}H_{24}O_{13}$ + Na^+ 435.1115; found 435.1089.

Methyl [Methyl 4-*O*-(methyl β-D-galactopyranosyluronate)-β-D-glucopyranoside]uronate (33): Methyl 4-*O*-(β-D-galactopyranosyl)-β-D-glucopyranoside (**20**, 676 mg, 1.90 mmol) and TEMPO (**25**, 58 mg, 0.38 mmol) were dissolved in 75 mL of carbonate buffer. The solution was electrolyzed according to General Procedure A. After consumption of 1868 C (10.2 F/mol), the electrolysis was stopped and the system was worked up. Of the crude product obtained (706 mg), 185 mg was esterified. Flash chromatography (ethyl acetate/methanol, 3:1) provided the dimethyl ester **33** (121 mg, 0.29 mmol, corresponding to 1.12 mmol in the crude product, 59%, current yield 46%) as a yellow syrup. $[\alpha]_D^{20}$ = −23.3 (*c* = 0.98, MeOH). IR (film): ṽ = 3418 (br. s, O−H), 1743 (s, C=O) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 3.28 (m, 1 H, 2-H), 3.50−3.54 (m, 5 H, 2′-H, 3′-H, OCH_3), 3.59 (t, $^3J_{3,4}$ = 8.9 Hz, 1 H, 3-H), 3.72−3.77 (m, 7 H, 2× $COOCH_3$, 4-H), 4.03 (d, $^3J_{4,5}$ = 9.7 Hz, 1 H, 5-H), 4.14 (dd, $^3J_{4',5'}$ = 1.5 Hz, 1 H, 4′-H), 4.28 (d, $^3J_{1,2}$ = 8.2 Hz, 1 H, 1 H), 4.30 (d, $^3J_{1',2'}$ = 7.2 Hz, 1 H, 1′-H), 4.37 (d, 1 H, 5′-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 53.1, 53.4 (2q, $COOCH_3$), 57.9 (q, OCH_3), 71.4 (d, C-4′), 71.9 (d, C-2′), 74.3 (d, C-3′), 74.7 (d, C-2), 75.2 (d, C-5), 75.8 (d, C-5′), 76.1 (d, C-3), 83.3 (d, C-4), 105.3 (d, C-1′), 105.9 (d, C-1), 170.4 (s, C-6′), 170.8 (s, C-6) ppm. MS (ESI/MS coupling, ES+): *m*/*z* (%) = 435 (24) [M + Na^+], 245 (45) [$H_3COOC-C_6H_{11}O_5$ + Na^+, β-cleavage], 186 (20), 159 (12), 157 (8), 127 (8), 23 (100) [Na^+]. $C_{15}H_{24}O_{13}$ (412.34): calcd. C 43.69, H 5.87; found C 42.92, H 6.12. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_{15}H_{24}O_{13}$ + Na^+ 435.1115; found 435.1086.

Methyl [Methyl 4-*O*-(methyl α-D-glucopyranosyluronate)-β-D-glucopyranoside]uronate (34): Methyl 4-*O*-(α-D-glucopyranosyl)-β-D-glucopyranoside (**21**, 499 mg, 1.40 mmol) was electrolyzed with TEMPO (**25**, 44 mg, 0.28 mmol) in 55 mL of carbonate buffer according to General Procedure A until 1572 C (11.6 F/mol) of charge had been consumed. A proportion (186 mg) of the crude product (541 mg) was esterified. Subsequent isolation by flash chromatography (ethyl acetate/methanol, 3:1) afforded the dimethyl ester **34** (121 mg, 0.29 mmol, corresponding to 0.85 mmol in the crude product, 61%, current yield 42%) as a colorless syrup. $[\alpha]_D^{20}$ = +59.7 (*c* = 1.03, MeOH). IR (film): ṽ = 3375 (br. s, O−H), 1746 (s, C=O) cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD): δ = 3.25 (dd, 1 H, 2-H), 3.43−3.47 (m, 2 H, 2′-H, 4′-H), 3.49 (s, 3 H, OCH_3), 3.57 (t, $^3J_{2',3'}$ = 9.7 Hz, 1 H, 3′-H), 3.63 (t, $^3J_{2,3}$ = 9.2 Hz, 1 H, 3-H), 3.69−3.74 (m, 4 H, $COOCH_3$, 4-H), 3.98 (d, $^3J_{4,5}$ = 8.9 Hz, 1 H, 5-H), 4.01 (d, $^3J_{4',5'}$ = 10.4 Hz, 1 H, 5′-H), 4.25 (d, $^3J_{1,2}$ = 8.0 Hz, 1 H, 1-H), 5.16 (d, $^3J_{1',2'}$ = 3.2 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 53.0, 53.5 (2q, $COOCH_3$), 57.9 (q, OCH_3), 73.5 (d, C-4′), 73.8 (d, C-2′), 74.1 (d, C-5′), 74.6 (d2, C-2, C-3′), 76.1 (d, C-5), 77.3 (d, C-3), 82.8 (d, C-4), 103.0 (d, C-1′), 104.0 (d, C-1), 170.8 (s, C-6), 172.2 (s, C-6′) ppm. MS (ESI/MS coupling, ES+): *m*/*z* (%) = 435 (35) [M + Na^+], 245 (30) [$H_3COOC-C_6H_{11}O_5$ + Na^+, α-cleavage], 186 (13), 159 (8), 157

(5), 127 (4), 23 (100) [Na^+]. $C_{15}H_{24}O_{13}$ (412.34): calcd. C 43.69, H 5.87; found C 42.86, H 6.21. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_{15}H_{24}O_{13} + Na^+$ 435.1115; found 435.1108.

Methyl [4-*O*-(Methyl β-D-glucopyranosyluronate)-β-D-glucopyranosyl azide]uronate (35): 4-*O*-(β-D-Glucopyranosyl)-β-D-glucopyranosyl azide (**22**, 455 mg, 1.25 mmol) and TEMPO (**25**, 39 mg, 0.25 mmol) were dissolved in 40 mL of carbonate buffer. The solution was electrolyzed according to General Procedure B. After consumption of 1822 C (15.1 F/mol), the electrolysis was stopped and the system was worked up. A proportion (119 mg) of crude product (482 mg) was esterified. Flash chromatography (ethyl acetate/methanol, 6:1) provided the dimethyl ester **35** (68 mg, 0.16 mmol, corresponding to 0.79 mmol in the crude product, 63%, current yield 33%) as a white solid. $[\alpha]_D^{20} = -39.9$ (c = 1.00, MeOH). M.p. 81 °C. IR (film): $\tilde{\nu}$ (cm^{-1}) = 3389 (br. s, O−H), 2122 (s, N_3), 1741 (s, C=O). ^1H NMR (600 MHz, CD_3OD): δ = 3.27−3.32 (m, 2 H, 2-H, 2′-H), 3.42 (s, 6 H, $COOCH_3$), 3.44 (t, $^3J_{3',4'}$ = 8.9 Hz, 1 H, 3′-H), 3.63 (t, $^3J_{3,4}$ = 9.0 Hz, 1 H, 3-H), 3.75 (t, 1 H, 4′-H), 3.83−3.86 (m, 1 H, 4-H), 4.00 (d, $^3J_{4',5'}$ = 9.9 Hz, 1 H, 5′-H), 4.20 (d, $^3J_{4,5}$ = 10.2 Hz, 1 H, 5-H), 4.47 (d, $^3J_{1',2'}$ = 7.6 Hz, 1 H, 1′-H), 4.70 (d, $^3J_{1,2}$ = 8.7 Hz, 1 H, 1-H) ppm. ^{13}C NMR (151 MHz, CD_3OD): δ = 50.2, 53.5 (2q, $COOCH_3$), 73.2 (d, C-4′), 74.3 (d, C-2), 74.4 (d, C-2′), 75.9 (d, C-3), 76.7 (d, C-5′), 76.9 (d, C-5), 77.3 (d, C-3′), 81.7 (d, C-4), 92.3 (d, C-1), 104.8 (d, C-1′), 170.2 (s, C-6), 171.2 (s, C-6′) ppm. MS (ESI/MS coupling, ES+): *m/z* (%) = 446 (20) [M + Na^+], 418 (2) [M + Na^+ − N_2], 392 (3) [M + Na^+ − $NaOCH_3$], 315 (100) [M + Na^+ − HN_3 − CH_3OH − 2 × CO], 231 (40) [$H_3COOC-C_5H_9O_5 + Na^+$, β-cleavage], 213 (22) [231 − H_2O], 210 (5), 164 (8), 151 (10), 112 (12), 23 (35) [Na^+]. $C_{14}H_{21}N_3O_{12}$ (423.33): calcd. C 39.72, H 5.00, N 9.93; found C 39.04, H 5.12, N 7.08. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_{14}H_{21}N_3O_{12} + Na^+$ 446.1023; found 446.1032.

Methyl [4-*O*-(Methyl β-D-galactopyranosyluronate)-β-D-glucopyranosyl azide]uronate (36): 4-*O*-(β-D-Galactopyranosyl)-β-D-glucopyranosyl azide (**23**, 455 mg, 1.25 mmol) and TEMPO (**25**, 39 mg, 0.25 mmol) were electrolyzed in carbonate-buffered water (40 mL) until 1026 C (8.6 F/mol) had been consumed, and the system was worked up according to General Procedure B. A proportion (141 mg) of the crude product (426 mg) was esterified. The dimethyl ester **35** (74 mg, 0.18 mmol, corresponding to 0.53 mmol in the crude product, 42%, current yield 39%) was isolated as a white solid by flash chromatography (ethyl acetate/methanol, 6:1). $[\alpha]_D^{20}$ = −32.8 (c = 1.00, MeOH). M.p. 78 °C. IR (film): $\tilde{\nu}$ = 3408 (br. s, O−H), 2122 (s, N_3), 1743 (s, C=O) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 3.34 (t, $^3J_{1,2}$ = 8.4 Hz, 1 H, 2-H), 3.58−3.66 (m, 2 H, 2′-H, 3′-H), 3.70 (t, $^3J_{2,3}$ = 8.8 Hz, 1 H, 3-H), 3.84 (t, $^3J_{3,4}$ = 9.1 Hz, 1 H, 4-H), 3.86 (s, 3 H, $COOCH_3$), 3.87 (s, 3 H, $COOCH_3$), 4.22−4.25 (m, 2 H, 5-H, 4′-H), 4.38 (d, $^3J_{1',2'}$ = 6.8 Hz, 1 H, 1′-H), 4.47 (d, $^3J_{4',5'}$ = 1.1 Hz, 1 H, 5′-H), 4.73 (d, $^3J_{1,2}$ = 8.4 Hz, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 53.1, 53.6 (2q, $COOCH_3$), 71.3 (d, C-4′), 71.8 (d, C-2′), 74.2 (d, C-3′), 74.4 (d, C-2), 75.8 (d, C-5′), 76.1 (d, C-3), 76.7 (d, C-5), 82.8 (d, C-4), 92.3 (d, C-1), 105.2 (d, C-1′), 170.2 (s, C-6), 170.4 (s, C-6′) ppm. MS (ESI/MS coupling, ES+): *m/z* (%) = 446 (18) [M + Na^+], 418 (4) [M + Na^+ − N_2], 392 (2) [M + Na^+ − $NaOCH_3$], 315 (100) [M + Na^+ − HN_3 − CH_3OH − 2 × CO], 231 (75) [$H_3COOC-C_5H_9O_5 + Na^+$, β-cleavage], 213 (25) [231 − H_2O], 210 (2), 164 (5), 151 (4), 113 (10), 23 (15) [Na^+]. $C_{14}H_{21}N_3O_{12}$ (423.33): calcd. C 39.72, H 5.00, N 9.93; found C 39.61, H 5.32, N 7.95. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_{14}H_{21}N_3O_{12} + Na^+$ 446.1023; found 446.1066.

Methyl [4-*O*-(Methyl α-D-glucopyranosyluronate)-β-D-glucopyranosyl azide]uronate (37): 4-*O*-(α-D-Glucopyranosyl)-β-D-glucopyranosyl azide (**24**, 455 mg, 1.25 mmol) was electrolyzed with TEMPO (**25**, 39 mg, 0.25 mmol) in 40 mL of carbonate buffer according to General Procedure B until 1592 C (13.3 F/mol) of charge had been consumed. A proportion (183 mg) of the crude product (510 mg) was esterified. Subsequent isolation of the ester by flash chromatography (ethyl acetate/methanol, 8:1) afforded the dimethyl ester **37** (107 mg, 0.25 mmol, corresponding to 0.71 mmol in the crude product, 57%, current yield 34%) as a colorless syrup. $[\alpha]_D^{20}$ = +56.4 (c = 1.00, MeOH). IR (film): $\tilde{\nu}$ (cm^{-1}) = 3366 (br. s, O−H), 2122 (s, N_3), 1746 (s, C=O). ^1H NMR (400 MHz, CD_3OD): δ = 3.14−3.22 (m, 1 H, 2-H), 3.38−3.45 (m, 2 H, 2′-H, 4′-H), 3.55 (t, $^3J_{3',4'}$ = 9.6 Hz, 1 H, 3′-H), 3.60−3.65 (m, 1 H, 3-H), 3.71−3.74 (m, 7 H, 2× $COOCH_3$, 4-H), 3.98 (d, $^3J_{4',5'}$ = 9.8 Hz, 1 H, 5′-H), 4.06 (d, $^3J_{4,5}$ = 9.9 Hz, 1 H, 5-H), 4.59 (d, $^3J_{1,2}$ = 8.6 Hz, 1 H, 1-H), 5.15 (d, $^3J_{1',2'}$ = 3.4 Hz, 1 H, 1′-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 53.0, 53.6 (2q, $COOCH_3$), 73.5 (d, C-4′), 73.8 (d, C-2′), 74.1 (d, C-5′), 74.2 (d, C-2), 74.6 (d, C-3′), 77.4 (d, C-3), 77.6 (d, C-5), 82.2 (d, C-4), 92.4 (d, C-1), 103.0 (d, C-1′), 170.2 (s, C-6), 172.2 (s, C-6′) ppm. MS (ESI/MS coupling, ES+): *m/z* (%) = 446 (98) [M + Na^+], 418 (10) [M + Na^+ − N_2], 392 (5) [M + Na^+ − $NaOCH_3$], 315 (100) [M + Na^+ − HN_3 − CH_3OH − 2× CO], 231 (55) [$H_3COOC-C_5H_9O_5 + Na^+$, α-cleavage], 213 (23) [231 − H_2O], 210 (20), 164 (15), 151 (13), 112 (12), 23 (42) [Na^+]. $C_{14}H_{21}N_3O_{12}$ (423.33): calcd. C 39.72, H 5.00, N 9.93; found C 39.75, H 5.82, N 7.77. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high-resolution MS (HRMS). HRMS (ESI): calcd. for $C_{14}H_{21}N_3O_{12} + Na^+$ 446.1023; found 446.1023.

Methyl (β-D-Glucopyranosyl azide)uronate (39): β-D-Glucopyranosyl azide (**38**, 419 mg, 2.00 mmol) was electrolyzed with TEMPO (63 mg, 0.40 mmol) in 40 mL of carbonate buffer according to General Procedure B until 1026 C (5.3 F/mol) of charge had been consumed. A proportion (100 mg) of the crude product (407 mg) was esterified. Subsequent isolation of the ester by flash chromatography (cyclohexane/ethyl acetate, 1:4) afforded the methyl ester **39** (94 mg, 0.44 mmol, corresponding to 1.64 mmol in the crude product, 82%, current yield 62%) as a white solid. $[\alpha]_D^{20}$ = −54.3 (c = 1.50, MeOH). M.p. 102 °C. IR (film): $\tilde{\nu}$ = 3389 (br. s, O−H), 2123 (s, N_3), 1740 (s, C=O) cm^{-1}. ^1H NMR (400 MHz, CD_3OD): δ = 3.17 (t, $^3J_{1,2}$ = 8.5, $^3J_{2,3}$ = 9.1 Hz, 1 H, 2-H), 3.40 (t, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 3.54 (t, $^3J_{4,5}$ = 9.7 Hz, 1H 4-H), 3.78 (s, 3 H, $COOCH_3$), 3.94 (d, 1 H, 5-H), 4.58 (d, 1 H, 1-H) ppm. ^{13}C NMR (100 MHz, CD_3OD): δ = 53.2 (q, $COOCH_3$), 73.0 (d, C-4), 74.6 (d, C-2), 77.6 (d, C-3), 78.7 (d, C-5), 92.4 (d, C-1), 170.9 (s, C-6) ppm. MS (ESI/MS coupling, ES+): *m/z* (%) = 256 (45) [M + Na^+], 224 (3) [M + Na^+ − CH_3OH], 68 (8), 23 (100) [Na^+]. $C_7H_{11}N_3O_6$ (233.18) calcd. C 36.06, H 4.75, N 18.02; found C 35.90, H 4.53, N 16.63. The analyses were affected by residual methanol that could not be removed after drying for 2 d at room temperature and 0.1 Torr. The elemental composition is additionally supported by high resolution MS (HRMS). HRMS (ESI): calcd. for $C_7H_{11}N_3O_6 + Na^+$ 256.0546; found 256.0576.

Acknowledgments

This work was supported through the Arbeitsgemeinschaft Industrieller Forschungsvereinigungen (AIF-project No. 11621N/1) by the Bundeswirtschaftsminister.

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Received July 22, 2002
[O02414]