Electroorganic Synthesis 66:[1] Selective Anodic Oxidation of Carbohydrates Mediated by TEMPO

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Dedicated to Prof. Dr. B. Krebs on the occasion of his 60th birthday

Abstract: The carbohydrates **4–15** are anodically oxidized with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) as mediator. Selective and complete reaction at the primary hydroxyl groups affords the corresponding carboxylic acids **16–32** in moderate to excellent yield. Methyl α-D-glucopyranoside is converted in 98% yield to the uronic acid **16**. Cyclic voltammetry shows that the oxydation is base-catalyzed and the oxidation of the hydroxy group with TEMPO$^+$ (**2**) is rate determining.

Key words: anodic oxidation, carbohydrates, TEMPO, cyclic voltammetry, uronic acids

Introduction

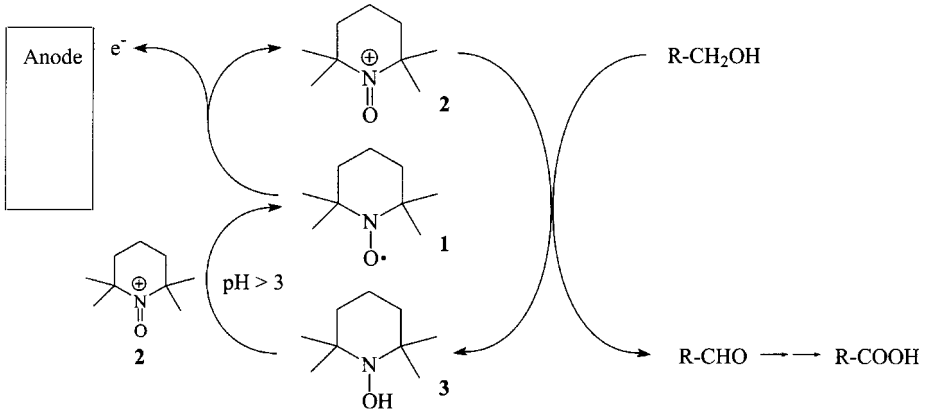
The selective oxidation of carbohydrates has been intensively studied in the last decades and continues to be an area of timely interest.[2–6] This holds especially for the conversion to uronic acids. Direct oxidations with stoichiometrically employed reagents like nitric acid[7] and nitrogen dioxide[8] as well as catalytic methods, e.g. oxygen with noble metal catalysts,[4,6,9] have been applied.

Recently catalytic methods using stable organic nitroxyl radicals like 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, **1**) as mediator have been developed.[10–28] The actual oxidation reagent is the nitrosonium ion **2** which is obtained by oxidation of **1** (Scheme 1). In the oxidation of alcohols the nitrosonium ion **2** is reduced to the hydroxylamine **3**. At pH values higher than 3, the hydroxylamine **3** symproportionates with **2** to the radical **1**.

Reactions with TEMPO and its derivatives are of industrial interest. Substituted nitroxyl radicals are prepared in larger amounts in high yields starting from the inexpensive basic chemicals acetone and ammonia.[29] Additionally the mediator TEMPO can be easily recovered in quantitative yield after the oxidation of polysaccharides.[27]

Several oxidants have been applied for the continuous regeneration of **2** in the oxidation of alcohols.[10,30,31] However, preparative oxidations of carbohydrates to uronic acids were usually performed with sodium hypochlorite as regenerating agent and TEMPO/NaBr as double mediatory system. Under these conditions hypochlorite or the intermediate bromine can cause side reactions with sensitive functional groups and the separation of polar products from concentrated aqueous solutions of sodium bromide is difficult or often impossible.[15]

In the following paper a method for the selective oxidation of carbohydrates with electrochemically regenerated **2** is presented. The mediated electrochemical oxidation has the advantage that the electrode does not interfere with the alcohol oxidation and that the electrolysis is easy to work up and to scale up. Thus far anodic oxidations of carbohydrates to uronic acids with TEMPO as mediator have been performed for analytical purposes only.[12,32,33]



Scheme 1

Cyclic Voltammetry

At first the mediated anodic oxidation of methyl α-D-glucopyranoside (**4**) with TEMPO as mediator was examined by cyclic voltammetry. 2,2,6,6-Tetramethylpiperidin-1-oxyl (**1**) is oxidized chemically reversible (Figure 1) with an anodic to cathodic peak current ratio of 1.0. This is an important requirement for a mediator, because it indicates that it can be completely recovered from an oxidation-reduction cycle.

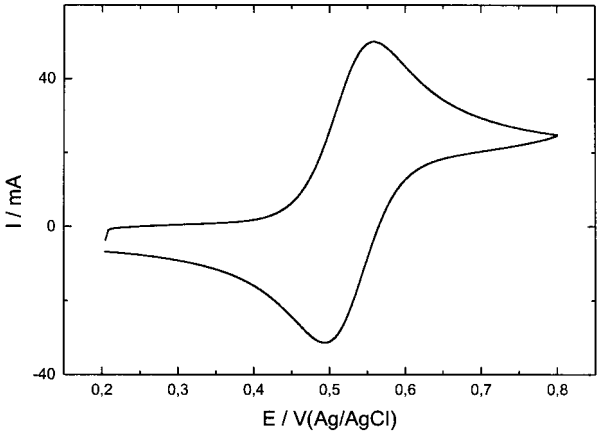


Figure 1 Cyclic voltammogram of TEMPO (0.009 mol/L) in water (0.2 mol/L $NaClO_4$, Na_2CO_3 buffer, pH 10, 10 mV/s)

Figure 2 shows cyclic voltammograms of 9 mmol/L TEMPO and 100 mmol/L methyl α-D-glucopyranoside **(4)**. Compared to pure TEMPO, the oxidation peak increased significantly at slow scan rates and the reduction peak disappeared (Figure 2). This is the typical behaviour for a mediator assisted oxidation and indicates that the oxydized form of TEMPO reacts with the alcohol and therefore cannot be reduced in the second part of the cycle. Additionally the catalytic effect of TEMPO is shown by the fact that methyl α-D-glucopyranoside **(4)** alone is not oxidized at potentials less than 1.0 V.

In contrast to the behaviour of TEMPO and methyl α D-glucopyranoside **(4)** at low scan rates, no catalytic reaction was observed at high scan rates. This indicates that the reaction of oxidized TEMPO with **4** is slow compared with the scan rate and the anodic oxidation of TEMPO.

Figure 3 shows a significant increase of the catalytic efficiency of the mediator with the pH of the solution. The

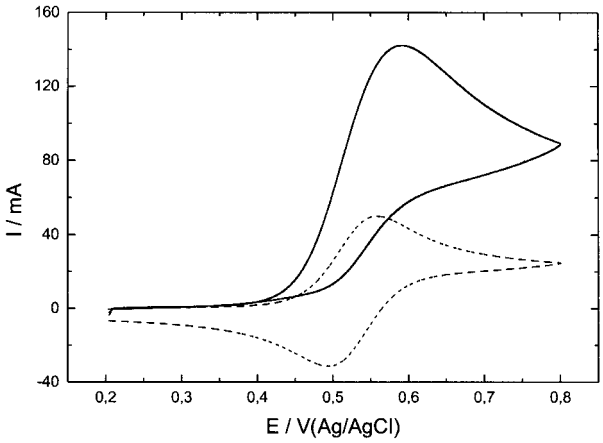


Figure 2 Cyclic voltammogram of TEMPO (0.009 mol/L) with (solid line) and without (dashed line) methyl a-D-glucopyranoside (**4**) (0.1 mol/L) in water (0.2 mol/L $NaClO_4$, Na_2CO_3 buffer, pH 10, 10 mV/s)

catalytic efficiency is the ratio of catalytic current to diffusion current of TEMPO alone. This indicates that the anodic oxidation of **4** catalyzed by TEMPO is base catalyzed. This finding supports the mechanism for the oxidation of alcohols with **2** under basic conditions as proposed by van Bekkum et al.[10,17] (Scheme 2). The alcohol first adds to the nitroso group of **2**. Subsequent deprotonation of the OH group and intramolecular β-elimination affords the hydroxylamine **3** and the aldehyde, whose hydrate is further oxidized to the corresponding carboxylic acid.

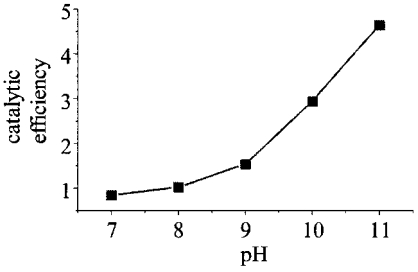
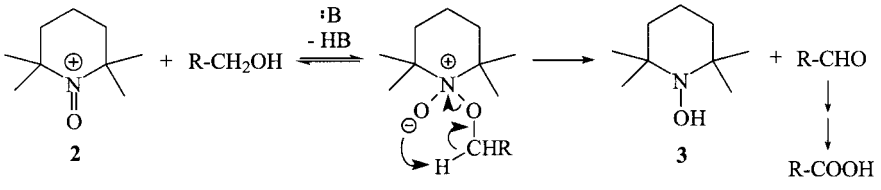
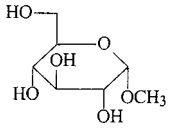
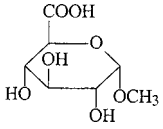
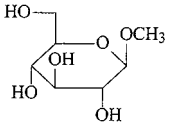
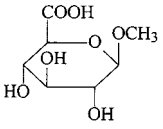
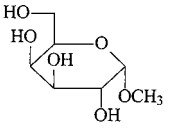
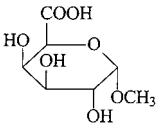
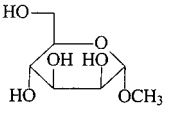
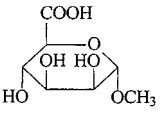
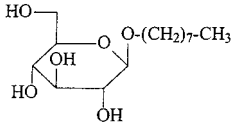
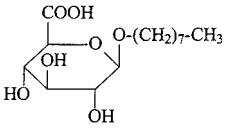
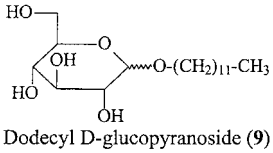
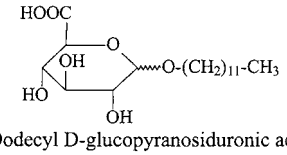
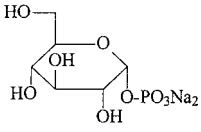
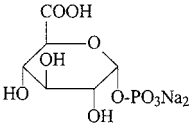
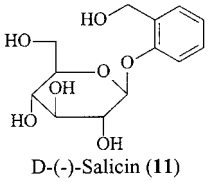
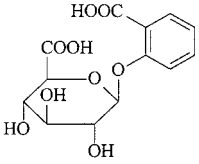


Figure 3 Catalytic efficiency [i_{pa} (TEMPO + substrate)] of the Tempo-catalyzed oxidation of **4** versus pH (0.009 mol/L TEMPO, 0.1 mol/L **4**, 0.2 mol/L $NaClO_4$, phosphate or carbonate buffer, pH 7–11, 10 mV/s)



Scheme 2

Table 1 TEMPO Mediated Anodic Oxidation of Monosaccharides

Entry	Substrate[a]	Product	Yield [%]
1	 Methyl α-D-glucopyranoside (**4**)	 Methyl α-D-glucopyranosiduronic acid (**16**)	96[b] (98[c])
2	 Methyl β-D-glucopyranoside (**5**)	 Methyl β-D-glucopyranosiduronic acid (**17**)	96[b]
3	 Methyl α-D-galactopyranoside (**6**)	 Methyl α-D-galactopyranosiduronic acid (**18**)	59[b]
4	 Methyl α-D-mannopyranoside (**7**)	 Methyl α-D-mannopyranosiduronic acid (**19**)	45[b,d]
5	 Octyl β-D-glucopyranoside (**8**)	 Octyl β-D-glucopyranosiduronic acid (**20**)	63[b]
6	 Dodecyl D-glucopyranoside (**9**)	 Dodecyl D-glucopyranosiduronic acid (**21**)	89[b]
7	 α-D-Glucopyranoside 1-(disodium phosphate) (**10**)	 α-D-Glucopyranosiduronic acid 1-(disodium phosphate) (**22**)	52[e]
8	 D-(-)-Salicin (**11**)	 2-Carboxyphenyl β-D-glucopyranosiduronic acid (**23**)	45[f]

[a] Conditions as described in the experimental section.
[b] Isolated as methyl ester.
[c] Determined by calibrated GC with tetradecanoic acid methyl ester as internal standard.
[d] 12% of **7** was recovered.
[e] Isolated as trisodium salt.
[f] Isolated as dimethyl ester.

Preparative Scale Electrolyses of 4–15

As the results of cyclic voltammetry looked promising, methyl α-D-glucopyranoside (**4**) and the monosaccharides **5–11** were oxidized in a preparative scale (Table 1). In general 20 mol% (9–16 wt%) of TEMPO were used at conditions described in the experimental section.

In all substrates the primary hydroxyl group is oxidized to the carboxylic acid. The selectivity of primary versus secondary alcohol oxidation and of carboxylic acid versus aldehyde formation is in general high, which also holds for the product yield.

Methyl α-D-glucopyranoside (**4**) is oxidized rapidly to the corresponding uronic acid **16** (Table 1, Entry 1) in a yield of 98% (calibrated GC) or 96% (isolated as methyl ester). No side product could be detected by GC analysis or NMR spectroscopy. The oxidation of **4** described here gave the highest yield of the product reported so far to our knowledge (except in one publication, however, without experimental details).[34] The oxidation of **4** with TEMPO and NaOCl/NaBr as chemical oxidant has been described, but **4** is not isolated in these cases.[15–18] After the reaction, the mediator TEMPO could be very easily recovered in 78% yield by extraction of the aqueous solution with diethyl ether. Taking into consideration that TEMPO is quite volatile, this recovery is very good.

Besides the use of TEMPO as mediator methyl α-D-glucopyranoside (**4**) was electrolyzed with 4-acetamido-TEMPO[10] under the same conditions. As the product uronic acid was isolated in 95% yield as its methyl ester after methylation, the substituent in the 4-position of the mediator seems to have no effect on the selectivity of the carbohydrate oxidation. However, the oxidation with TEMPO appears more favourable because only 20% of the 4-acetamido-TEMPO could be recovered. Probably the 4-acetamido-TEMPO is partially decomposed by oxidation at the acetamido group.

Methyl β-D-glucopyranoside (**5**) is converted to uronic acid **17** in a yield of 96% indicating that the configuration at the anomeric center does not influence the selectivity of the C-6-oxidation (Table 1, Entry 2). The reaction rate is slightly lower than the one observed for methyl α-D-glucopyranoside (**4**). With chemically regenerated **2** in a two phase system a yield of only 55% is obtained.[13]

Methyl α-D-galactopyranoside (**6**) and methyl α-D-mannopyranoside (**7**) are oxidized in good to moderate yields to the corresponding uronic acids (Table 1, Entries 3 and 4). The lower selectivity compared with the oxidation of methyl α-D-glucopyranoside (**4**) is probably due to the equatorial CH-bonds (at C-4 in **6** or at C-2 in **7**) that are accessible easier than the axial ones and therefore can be attacked more easily. This leads to ketones as undesired side products that can undergo base catalyzed reactions.

Carbohydrates **8** and **9** are nonionic surfactants from the class of alkyl polyglucosides. The conversion of these compounds into the carboxylic acids allows the transformation of nonionic surfactants into anionic surfactants.[35,36] By electrochemical oxidation the carboxylic acids **20** and **21** were obtained in good yields of 63 and 89%, respectively (Table 1, Entries 5 and 6). With TEMPO/NaBr as a double mediatory system and NaOCl as chemical oxidant in a two phase system **8** was oxidized to **20** in 67% yield.[13]

α-D-Glucopyranoside 1-disodiumphosphate (**10**) is oxidized to the corresponding uronic acid **22** in 52% yield (Table 1, Entry 7). As **10** is easily obtained from starch and **22** can be hydrolyzed to glucuronic acid in good yields, the reaction might be an interesting key step in the production of glucuronic acid from starch.[37] In this context it is important to note that the synthesis of D-glucuronic acid by acid hydrolysis of polyglucuronic acid proceeds slowly and leads to undesired side products.[38] Glucuronic acid is an interesting intermediate for fine chemicals like L-ascorbic acid or D-glucaric acid.[3]

By anodic oxidation with TEMPO as mediator, D-(–)-salicin (**11**), a natural compound occuring up to 7% in the bark of willow-trees and poplars, is converted to the dicarboxylic acid **23** in a moderate yield of 45% (Table 1, Entry 8).

Besides monosaccharides the di-, oligo- and polysaccharides **12–15** were also converted to the corresponding carboxylic acids in good to moderate yields (Table 2). From α,α-trehalose (**12**) the dicarboxylic acid **24** was obtained in 61% yield (Table 2, Entry 1). The high selectivity is remarkable considering that no reaction at the six secondary hydroxyl groups is detectable. Compound **24** is a key intermediate for the synthesis of glycolipids with antitumor properties.[39]

Sucrose (**13**) contains three primary hydroxyl groups that should be oxidizable with TEMPO as mediator. Results with oxygen over platinum as oxidant[34,40–43] showed that the 6- and the 6'-OH function are easier oxidized than the 1-hydroxyl group. The same result was obtained with electrochemically regenerated **2**. In an electrolysis with 4.8 F/mol consumption of charge (the oxidation of a primary OH group to a carboxylic acid needs 4.0 F/mol) the monocarboxylic acids **25**, **26** and **27** were formed in a ratio of 17:40:43 with a total yield of 22% (determined by GC, 27% based on conversion of 83% of sucrose, Table 2, Entry 2). As side products, 14% of glucaric acid and smaller amounts of other monosaccharide acids were found which indicates that the low yield for the sucrose monocarboxylic acids is mainly due to disaccharide cleavage. Experiments directed towards the increase of the selectivity of formation of **25**, **26** and **27** by means of extraction of formed carboxylic acids by electrodialysis[34,42,43] did not lead to higher yields of sucrose monocarboxylic acids.

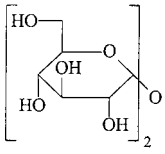
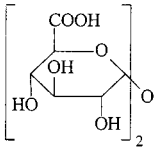
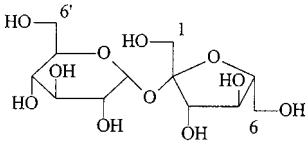
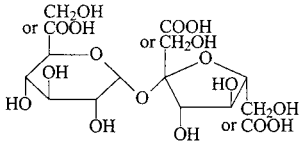
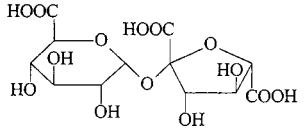
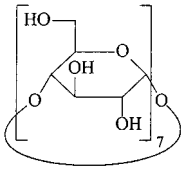
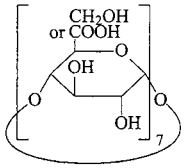
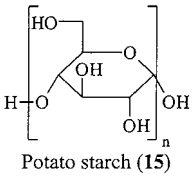
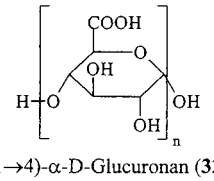
Sucrose tricarboxylic acid (**28**) is interesting as complexing agent, food additive and starting compound for the preparation of fine chemicals.[43,44] Nevertheless, the yield for the oxidation of **13** to **28** is reported only once. By platinum-catalyzed oxidation of **13** with oxygen 29% of **28** was obtained as determined by uncalibrated GC analy-

sis.[44] In order to prepare sucrose tricarboxylic acid (**28**) with TEMPO as mediator sucrose (**13**) was electrolyzed until a charge of 19.7 F/mol was consumed. Compound **28** was obtained in 39% yield (isolated as nonahydrate of the trisodium salt, Table 2, Entry 3). Although the yield of **28** is only moderate, this is a significant improvement compared to the yield described before. The reaction could be of industrial interest as sucrose is the most abundant and highly pure organic compound of low molecular weight available commercially.[45]

β-Cyclodextrin (**14**) was converted to a mixture of tri-, tetra- and pentauronic acids **29**, **30** and **31** in a ratio of about 1:2:1 in 74% yield by anodic oxidation with TEMPO as mediator (Table 2, Entry 4). ESI/MS and NMR analyses showed less than 10% side products from nonselective oxydations. The carboxylic acid groups in **29–31** can possibly be used to covalently attach (immobilize) the cyclodextrin at a support. Otherwise selective oxidations with β-cyclodextrin are rare.[7,16,46–49] The diuronic acid is accessible, however in only 14% yield, by a two step oxidation sequence starting from the ditosylate of β-cyclodextrin.[46] The oxidation of β-cyclodextrin with NaOCl, NaBr and TEMPO is reported in a patent,[16] however details on the product are not described.

Potato starch (**15**) is very selectively oxidized at the primary hydroxyl groups in 6-position. After electrolysis

Table 2 TEMPO Mediated Anodic Oxidation of Di-, Oligo- and Polysaccharides

Entry	Substrate[a]	Product	Yield (%)
1	 α,α-Trehalose (**12**)	 α,α-Trehalose-dicarboxylic acid (**24**)	61[b]
2	 Sucrose (**13**)	 1-, 6- and 6'-Sucrose-monocarboxylic acid (**25**, **26**, **27**)	22[c]
3		 1,6,6'-Sucrose-tricarboxylic acid (**28**)	39[d]
4	 β-Cyclodextrin (**14**)	 β-Cyclodextrin-tri-, tetra- and pentauronic acid (**29**, **30**, **31**)	74[e]
5	 Potato starch (**15**)	 (1→4)-α-D-Glucuronan (**32**)	63[f]

[a] Conditions as described in the experimental section.
[b] Isolated as dimethyl ester.
[c] Determined by calibrated GC with methyl α D-galactopyranoside as internal standard, 27% based on conversion of 83% of starting material, ratio **25**:**26**:**27** = 17:40:43 determined by HPLC.
[d] Isolated as trisodium salt.
[e] Obtained as crude product (113%) containing H_2O (27%) and minor side products (<10%, determined by NMR and ESI-MS), ratio 1:2:1 (determined by ESI-MS).
[f] Obtained as crude product as sodium salt (70%) containing less than 10% of side products (determined by NMR), 93% carboxylate content (measured by NMR).

with TEMPO as mediator 63% of the corresponding polyuronic acid was isolated as crude product with a 93% conversion of the primary alcohol groups (determined by NMR, Table 2, Entry 5). van Bekkum et al.[15,16,18] describe a selectivity of >95% and a crude product yield of 98% for the reaction with chemically (NaOCl, NaBr) regenerated **2**. The electrochemical method leads to slightly lower yields but has the advantage that sodium bromide which is used in the chemical reaction in high concentration (49 mol%) is avoided.

Conclusion

Anodic oxidation with 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, **1**) as mediator converts primary hydroxyl groups in polyols selectively to the corresponding carboxylates. Secondary OH-groups are in most cases inert against oxidation. This selectivity allows the chemoselective oxidation of carbohydrates **4–15** into the corresponding carboxylic acids **16–32**, which are isolated in moderate to excellent yield. The electrochemical oxidation with TEMPO as mediator can favorably compete with respect to yield, chemoselectivity and workup with alternative oxidations, e.g. with oxygen at a platinum catalyst or sodium hypochlorite combined with TEMPO.

All chemicals are commercially available and used without further purification; dodecyl α,β-D-glucopyranoside from Henkel AG, Düsseldorf, Germany, was purified by flash chromatography on silica gel (EtOHc/MeOH, 10:1). IR spectra were obtained with a Bruker IFS 28 FT-IR-spectrometer. NMR spectra were recorded on a Bruker spectrometer WM 300 (300 MHz and 75.4 MHz, for ^1H and ^{13}C, respectively; D_2O, $CDCl_3$ as solvent). The measurement of GC/MS spectra was conducted on a Finnigan-MAT 312 (70 eV) with a capillary column HP 5 (25 m, 0.2 mm i.d., 0.33 μm film). For DCI ammonia served as reactant gas. ESI mass spectra were recorded on a micromass quadrupole mass spectrometer Quattro LC-Z. Gas chromatography was carried out on a Hewlett-Packard HP 5890 Series II with the capillary columns HP 1 (25 m, 0.32 mm i.d., 0.3 μm film) and HP 5 (25 m, 0.20 mm i.d., 0.52 μm film). Elemental analyses were conducted by the analytical laboratory of Organisch-Chemisches Institut der Universität Münster. For cyclic voltammetry the Metrohm/Eco Autolab System PG STAT 20 and Metrohm VA-Stand 663 V were used with a glassy carbon disc anode (3 mm diameter) and a glassy carbon rod cathode. The reference electrode was Ag/AgCl/3 M KCl in H_2O (+0.21 V vs. NHE). Preparative scale electrolyses were carried out in undivided beaker-type glass cells (capacity 60, 100 or 200 mL) with a platinum foil anode (18 cm^2) on a teflon frame and a graphite cathode (24 cm^2, electrographite, Sigri). As reference electrode served a saturated calomel electrode (Hg/Hg_2Cl_2/saturated KCl in H_2O, +0.20 V vs. SCE). The applied current source was a Wenking HP 88.

General Procedure for the Electrolyses

The given amounts of the carbohydrate and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) were dissolved in carbonate buffered water (100 mL of 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 20 °C at a potential of 0.53 V versus SCE. After the electrolysis a strongly acidic cation-exchange resin (93 mL, 49 mequiv of Amberlite IR 120) was added and after stirring for 0.5 h the resin was filtered off and the solvent removed at 50 °C in vacuo.

For the isolation and characterization of the reaction products the carboxylic acids were usually converted into their methyl esters as follows. A part of the crude product was dissolved in MeOH (10 mL) and treated with 2,2-dimethoxypropane (1.0 mL, 8.2 mmol) and one drop of concd aq HCl (p.A.). After stirring for 1 d, the solvent was removed under reduced pressure and the crude product purified by flash chromatography on silica gel.

Methyl (Methyl α-D-glucopyranosid)uronate (Methyl Ester of 16)

Electrolysis with TEMPO: Methyl α D-glucopyranoside (**4**, 970 mg, 5.00 mmol) and TEMPO (156 mg, 1.00 mmol) were electrolyzed according to the general procedure. After a consumption of 2660 C (5.5 F/mol) the electrolysis was stopped and the solution was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and the solvent removed in vacuo. Flash chromatographic purification (petroleum ether/Et_2O, 5:1) afforded TEMPO (122 mg, 0.78 mmol, 78%). The aqueous layer was worked up as described in the general procedure. This afforded 1.12 g of crude product, a part of which (229 mg) was esterified. By flash chromatographic purification (silica gel, EtOAc/MeOH, 3:1) **16** (219 mg, 0.99 mmol, 96%) was isolated as a colourless oil.

Electrolysis with 4-Acetamido-TEMPO: According to the general procedure, methyl α-D-glucopyranoside (**4**; 970 mg, 5.00 mmol) was electrolyzed with 4-acetamido-TEMPO (213 mg, 1.00 mmol) until a consumption of 2740 C (5.7 F/mol). The solution was extracted three times with Et_2O (100 mL). After drying the combined organic layers ($MgSO_4$) and subsequent removal of the solvent in vacuo 4-acetamido-TEMPO (42 mg, 0.20 mmol, 20%) was recovered. The aqueous layer was worked up according to the general procedure to give the crude product (1.22 g), a part of which (201 mg) was esterified. Subsequent isolation of the methyl ester of **16** (173 mg, 0.78 mmol, 95%) was achieved by flash chromatography (silica gel, EtOAc/MeOH, 3:1). The spectroscopic data were in accordance with the literature values.[50]

Methyl (Methyl β-D-glucopyranosid)uronate (Methyl Ester of 17)

Methyl β-D-glucopyranoside hemihydrate (1.015 g, 5.00 mmol) and TEMPO (156 mg, 1.00 mmol) were dissolved in carbonate buffered water (100 mL) and electrolyzed according to the general procedure until 2895 C (6.0 F/mol) were consumed. Workup afforded 1.19 g of crude product, from which 193 mg was esterified to the methyl ester of **17** (173 mg, 0.78 mmol, 96%), which was isolated by flash chromatography (silica gel, EtOAc/MeOH, 3:1) as a colourless oil.The spectroscopic data corresponded to those in the literature.[13]

Methyl (Methyl α-D-galactopyranosid)uronate (Methyl Ester of 18)

Methyl α-D-galactopyranoside (**6**; 974 mg, 5.02 mmol) and TEMPO (156 mg, 1.00 mmol) were electrolyzed according to the general procedure. After consumption of 2900 C (6.0 F/mol) the electrolysis was stopped and worked up. 1.07 g of crude product was obtained from which 485 mg was esterified. By flash chromatographic purification (silica gel, EtOAc/MeOH, 3:1) the methyl ester of **18** (300 mg, 1.35 mmol, 59%) was isolated as a white solid, mp 148–149 °C. The spectroscopic data corresponded to those in the literature.[51]

Methyl (Methyl α-D-mannopyranosid)uronate (Methyl Ester of 19)

According to the general procedure methyl α-D-mannopyranoside (**7**; 972 mg, 5.01 mmol) was electrolyzed with TEMPO (156 mg, 1.00 mmol) until 3540 C (7.3 F/mol) of charge were consumed. A part (499 mg) of the crude product (1.07 g) was esterified. This pro-

cedure had to be conducted twice to achieve total conversion. Subsequent isolation of the ester by flash chromatography (EtOAc/MeOH, 3:1) afforded the methyl ester of **19** (234 mg, 1.05 mmol, 45%) as a pale yellow oil besides the starting material **7** (53 mg, 0.27 mmol, 12%). The spectroscopic data of the methyl ester of **19** were in accordance with those in the literature.[50]

Methyl (Octyl β-D-glucopyranosid)uronate (Methyl Ester of 20)
Octyl β-D-glucopyranoside (**8**; 488 mg, 1.67 mmol) and TEMPO (52 mg, 0.33 mmol) were electrolyzed according to the general procedure with the following deviation: only 33 mL of electrolyte were used instead of 100 mL and the area of the electrodes was halved. After a consumption of 714 C (4.4 F/mol), the electrolysis was stopped and worked up. In this case the solution was not treated with an acidic cation-exchange resin but acidified with 2 M aq HCl until pH 1 and continuously extracted with Et_2O (600 mL) for 2 d. The organic layer was dried ($MgSO_4$) and the solvent evaporated in vacuo. 472 mg of crude product was obtained from which 119 mg was esterified. By flash chromatography (EtOAc/MeOH, 40:1) the methyl ester of **20** (85 mg, 0.27 mmol, 63%) was isolated as white solid, mp 50–52 °C. Additionally the starting material **8** (6 mg, 0.02 mmol, 5%) was recovered. The spectroscopic data of the methyl ester of **20** corresponded to those in the literature.[13]

Methyl (Dodecyl D-glucopyranosid)uronate (Methyl Ester of 21)
According to the general procedure dodecyl D-glucopyranoside (**9**; 344 mg, 0.99 mmol, α/β = 80:20 determined by GC) were electrolyzed with TEMPO (32 mg, 0.20 mmol). The same deviations in the general procedure as in the oxidation of **8** were applied. At first a pale yellow suspension was formed which cleared up in the course of the electrolysis. After a consumption of 672 C (6.7 F/mol) the electrolysis was stopped. For workup the solution was not treated with an acidic cation-exchange resin but acidified with 2 M aq HCl until pH 1 and continuously extracted with Et_2O (600 mL) for 3 d. After drying of the organic layer ($MgSO_4$) and evaporation of the solvent in vacuo 186 mg of the 379 mg of crude product were esterified. Product **21** (166 mg, 0.44 mmol, 91%) was isolated as a colourless oil by flash chromatography (EtOAc).

IR (KBr): ν = 3470 (s, OH), 1738 cm^{-1} (s, C=O).

^{1}H NMR (DMSO-d_6): δ = 0.85 (t, ^3J = 6.6 Hz, 3 H, CH_2CH_3), 1.15–1.38 [m, 18 H, $(CH_2)_9CH_3$], 1.43–1.59 (m, 2 H, OCH_2CH_2), 3.12–3.47, 3.49–3.74 (2 m, 6 H, OCH_2CH_2, 2-H, 3-H, 4-H, OH), 3.64 (s, 3 H, OCH_3), 3.71 (d, ^3J = 9.8 Hz, 0.20 H, 5-$H_β$), 3.88 (d, ^3J = 9.5 Hz, 0.80 H, 5-$H_α$), 4.22 (d, ^3J = 7.6 Hz, 0.20 H, 1-$H_β$), 4.67 (d, ^3J = 3.8 Hz, 0.80 H, 1-$H_α$), 4.68, 4.84, 5.01, 5.19 (4 d, br, 2 H, 2 OH).

^{13}C NMR (DMSO-d_6): δ = 14.0 (q, CH_2CH_3), 22.2, 25.7, 28.8, 29.0, 29.1, 29.1, 29.2, 29.2, 29.4, 31.4 [10 t, $(CH_2)_{10}CH_3$], 51.9 (q, $COOCH_3$), 67.8, 69.1 (2 t, OCH_2CH_2, α and β), 71.6, 71.6, 71.8, 71.9, 72.8, 73.2, 75.6, 76.0 (8 d, C-2, C-3, C-4, C-5, α and β), 99.5, 103.4 (2 d, C-1, α and β), 170.0, 170.1 (2 s, CO_2CH_3, α and β).

MS (70 eV): *m/z* (%) = 577 ($M^+ - CH_3$, 3), 487 [$M^+ - CH_3 - Si(CH_3)_3OH$, 1], 401 (5), 313 [$(CH_3)_3SiOCHCHCHCHOC_{12}H_{25}^+$, 15], 247 (14), 234 (32), 217 [$(CH_3)_3SiOCHCHCHOSi(CH_3)_3^+$, 100], 204 [$(CH_3)_3SiOCHCHOSi(CH_3)_3^+$, 84], 147 [$(CH_3)_3SiOSi(CH_3)_2^+$, 17], 73 [$Si(CH_3)_3^+$, 57].

HRMS (NH_3, DCI): *m/z* calcd. for $C_{19}H_{36}O_7 + NH_4$, 394.2805; found, 394.2833.

Potassium α-D-glucopyranosiduronate 1-(Dipotassium Phosphate) (Tripotassium Salt of 22)
α-D-Glucopyranoside-1-(disodium phosphate)monohydrate (1.52 g, 5.00 mmol) and TEMPO (156 mg, 1.00 mmol) were electrolyzed in carbonate buffered water (100 mL) and, after a charge of 2245 C (4.7 F/mol) was consumed, worked up according to the general procedure with cation-exchange resin (110 mL). The obtained aqueous solution was not evaporated in vacuo and methylated, but 0.5 M aq KOH was added until a pH of 7 was reached. The solution was concentrated in vacuo to 6 mL and the product precipitated by dropwise addition of MeOH (28 mL). The precipitate was filtered off and recrystallized in H_2O/MeOH (113 mL, 8:3). The tetrahydrate of the tripotassium salt of **22** (1.20 g, 2.61 mmol, 52%) was obtained as a white solid, mp 191–193 °C (dec). The ^{1}H NMR spectroscopic data corresponded to those in the literature for the sodium potassium salt of **22**.[37]

Anal. $C_6H_{16}K_3O_{14}P$ (460.5): calcd C 15.65, H 3.50; found C 15.57, H 3.44.

Methyl (2-Methoxycarbonyl-phenyl β-D-glucopyranosid)uronate (Dimethyl Ester of 23)
D-(–)-Salicin (**11**; 716 mg, 2.50 mmol) and TEMPO (78 mg, 0.50 mmol) were electrolyzed according to the general procedure. After a consumption of 2700 C (11.2 F/mol) the electrolysis was worked up. 808 mg of crude product was obtained from which 209 mg was esterified. The dimethyl ester of **23** (67 mg, 0.20 mmol, 30%) and a portion of only partially methylated diacids were isolated by flash chromatography (EtOAc/MeOH, 6:1). The latter was subjected repeatedly to the methylation procedure and the product was purified by flash chromatography (EtOAc/MeOH, 10:1) which afforded an additional amount of the dimethyl ester of **23** (32 mg, 0.09 mmol, 15%) as a colourless oil.

IR (film): ν = 3411 (s, OH), 1731 (m, C=O), 1713 (s, C=O), 1602 (m, C=C), 1491 cm^{-1}(m, C=C).

^{1}H NMR (D_2O): δ = 3.56–3.89 (m, 9 H, 2-H, 3-H, 4-H, 2 OCH_3), 4.14 (d, $^3J_{4,5}$ = 9.3 Hz, 1 H, 5-H), 5.10 (d, $^3J_{1,2}$ = 7.4 Hz, 1 H, 1-H), 7.11 (dd, $^3J_{4',5'}$ = 8.0 Hz, $^3J_{5',6'}$ = 7.8 Hz, 1 H, 5'-H), 7.20 (d, $^3J_{3',4'}$ = 8.6 Hz, 1 H, 3'-H), 7.48 (ddd, $^3J_{3',4'}$ = 8.6 Hz, $^3J_{4',5'}$ = 8.0 Hz, $^4J_{4',6'}$ = 1.8 Hz, 1 H, 4'-H), 7.66 (dd, $^4J_{4',6'}$ = 1.8 Hz, $^3J_{5',6'}$ = 7.8 Hz, 1 H, 6'-H).

^{13}C NMR (D_2O): δ = 52.3, 52.6 (2 q, 2 OCH_3), 70.5, 72.1, 74.2, 74.5 (4 d, C-2, C-3, C-4, C-5), 100.6 (d, C-1), 116.8, 123.0, 130.6, 133.9 (4 d, 4 $CH_{arom.}$), 120.9 (s, $OC_{arom.}$), 154.8 (s, H_3CO_2C–$C_{arom.}$), 168.0 (s, H_3CO_2C–$C_{arom.}$), 169.9 (s, $OCHCO_2CH_3$).

MS (70 eV): *m/z* (%) = 543 ($M^+ - CH_3$, 2), 437 [$M^+ - OCH_3 - Si(CH_3)_3OH$, 1], 407 (4), 379 (2), 317 (60), 275 (10), 217 [$(CH_3)_3SiOCHCHCHOSi(CH_3)_3^+$, 16], 209 (29), 147 [$(CH_3)_3SiOSi(CH_3)_2^+$, 16], 73 [$Si(CH_3)_3^+$, 100].

HRMS (NH_3, DCI): *m/z* calcd. for $C_{15}H_{18}O_9 + NH_4$, 360.1295; found 360.1277.

(Methyl α-D-glucopyranosyluronate) (Methyl α-D-glucopyranosiduronate) (Dimethyl Ester of 24)
According to the general procedure α,α-trehalose (**12**; 856 mg, 2.50 mmol) was electrolyzed with TEMPO (78 mg, 0.50 mmol) until a consumption of 2120 C (8.8 F/mol) was reached. After the electrolysis the mixture was worked up with cation-exchange resin (129 mL). A part (302 mg) of the obtained of crude product 1.03 g) was esterified. Subsequent isolation of the hemihydrate of the dimethyl ester of **24** (181 mg, 0.44 mmol, 61%) was conducted by flash chromatography (EtOAc/MeOH, 3:1). The spectroscopic data were in accordance with those in the literature.[39]

α-D-Glucopyranosyl β-D-arabino-2-hexulofuranosidonic Acid (25), α-D-glucopyranosyl β-D-fructofuranosiduronic Acid (26) and β-D-fructofuranosyl α-D-glucopyranosiduronic Acid (27)

Sucrose (**13**; 5.13 g, 15.0 mmol) and TEMPO (469 mg, 3.0 mmol) were dissolved in a mixture of carbonate buffered water (100 mL) and water (100 mL), and electrolyzed according to the general procedure. After a consumption of charge of 6970 C (4.8 F/mol) the

electrolysis was stopped. The yields of sucrose monocarboxylic acids were determined by GC after silylation with *N,O*-bis(trimethylsilyl)acetamide (BSA) and Me_3SiCl (TMSCl). Methyl α-D-galactopyranoside was used as internal standard. Reference compounds for the calibration of **25–27** were prepared according to the literature.[34,41,42] Sucrose (**13**; 17%), C-6-sucrose monocarboxylic acid (**26**, 10%) and C-6'-sucrose monocarboxylic acid (**27**; 12%) were isolated. The yield of **25** was too small to be detectable. The ratio of **25**, **26** and **27** was measured by calibrated HPLC as 17:40:43.[52] Products **25–27** were characterized by mass spectrometry. The spectra of the silylated compounds were in accordance with those in the literature.[53]

(Sodium α-D-glucopyranosyluronate) (Disodium β-D-arabino-2-hexulofuranarat) (Trisodium Salt of 28)

According to the general procedure sucrose (**13**; 5.13 g, 15.0 mmol) was electrolyzed with TEMPO (469 mg, 3.0 mmol). Deviating from the general procedure a mixture of aq Na_2CO_3 buffered solution (100 mL) and water (100 mL) was used as electrolyte. TEMPO was added in five portions of 77 mg (0.49 mmol) in equal time intervals during the electrolysis. After a consumption of 28450 C (19.7 F/mol) the electrolyte was treated with strongly acidic cation-exchange resin (184 mL). The resin was filtered off and the free carboxylic acid was converted into the sodium salt with 2 M aq NaOH which was added until a pH of 8.6 was reached. Evaporation of the solvent afforded 8.75 g of crude product from which 1.28 g was suspended in H_2O (4.5 mL), and the residue was filtered off. The polar reaction products were precipitated by dropwise addition of MeOH (20 mL), filtered, washed with MeOH/H_2O (3 mL, 3:1) and dried in vacuo. The procedure of dissolving in H_2O (3 mL) and reprecipitation with MeOH/H_2O (3:1, 13 mL) was repeated four times. The nonahydrate of the trisodium salt of **28** (523 mg, 0.85 mmol, 39%) was isolated as a white solid. The spectroscopic data of the trisodium salt of **28** corresponded to those in the literature.[44]

Tris(5-dehydroxymethyl-5-carboxy)cyclomaltoheptaose (29), Tetrakis(5-dehydroxymethyl-5-carboxy)cyclomaltoheptaose (30) and Pentakis(5-dehydroxymethyl-5-carboxy)cyclomaltoheptaose (31)

β-Cyclodextrin (**14**; 1.27 g, 0.99 mmol) containing water (11.5%) and TEMPO (219 mg, 1.40 mmol) were suspended in an aqueous carbonate buffered solution (100 mL) and electrolyzed according to the general procedure until 3725 C (39.0 F/mol) were consumed. After the electrolysis, the clear solution was extracted with Et_2O (2 × 25 mL) and subsequently worked up in accordance to the general procedure. A mixture of **29**, **30** and **31** was obtained as crude product (1.33 g, 113%) containing water (27%) and minor side products (<10%, determined by NMR and ESI-MS) as pale yellow crystals, mp 180–182 °C (dec). The ratio of **29**:**30**:**31** was 1:2:1 (determined by ESI-MS).

IR (KBr): ν = 3416 (s, OH), 1737 (s, C=O), 1033 cm^{-1} (s, CO).

^{1}H NMR (D_2O): δ = 3.49–3.96 (m, 4.29 H, 2-H, 3-H, 4-H, 0.43 C*H*CH_2OH, 0.43 CH_2OH), 4.14–4.27 (m, 0.57 H, C*H*CO_2H), 4.99–5.44 (m, 1 H, 1-H).

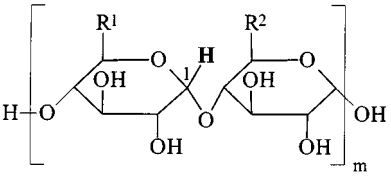
^{13}C NMR (D_2O): δ = 59.0, 59.1, 59.6 (3t, 3 CH_2OH), 70.2, 70.2, 70.5, 70.5, 70.5, 70.7, 70.7, 70.7, 70.8, 71.0, 71.0, 71.0, 71.0, 71.1, 71.1, 71.1, 71.2, 71.6, 71.7, 71.9, 71.9, 72.2, 72.2, 72.2, 72.2, 72.3, 72.6, 72.6 (28d, 7 C-2, 7 C-3, 7 C-4, 7 C-5), 99.0, 99.0, 99.1 (3 d, 3 HOCH_2CHOC*H*), 101.2, 101.2, 101.2, 101.3 (4 d, 3 HO_2CCHOC*H*), 171.4, 171.6, 172.0, 172.5 (4 s, 4 CO_2H).

MS (ESI-MS, nanospray, negative ions, solvent H_2O): *m/z* (%) = 1204.4 [(M(**31**) – H)$^-$, 7], 1189.3 [(M(**30**) – H)$^-$, 29], 1175.4 [(M(**29**) – H)$^-$, 12], 803.0 [(2 M(**31**) – 3H)$^{3-}$, 14], 797.5 [(2 M(**30**) – 3H)$^{3-}$, 22], 792.8 [(2 M(**29**) – 3H)$^{3-}$, 30], 601.8 [(M(**31**) – 2H)$^{2-}$, 57], 594.5 [(M(**30**) – 2H)$^{2-}$, 100], 587.6 [(M(**29**) – 2H)$^{2-}$, 46], 544.9 (25), 536.4 (19).

Sodium (1→4)-α-D-glucuronan (Sodium Salt of 32)

Soluble potato starch (**15**; 812 mg, 5.00 mmol of glucose units) was to a major part dissolved, a minor part formed a suspension in boiling water (100 mL) and was electrolyzed at 20 °C according to the general procedure with TEMPO (156 mg, 1.00 mmol), Na_2CO_3 (4.28 g, 40.4 mmol) and $NaHCO_3$ (2.48 g, 29.5 mmol). After 3326 C (6.9 F/mol per glucose unit) were consumed, 25 mL of the solution were diluted with H_2O (6 mL), filtered and neutralized with 1 M aq HCl. Subsequently, the product was precipitated by dropwise addition of EtOH (490 mL) and filtered. The white solid was dissolved in H_2O (10 mL) and the solution extracted with Et_2O (2 × 10 mL). After removal of water in vacuo the sodium salt of **32** was obtained as crude product (80 mg, 70%) containing less than 10% of side products (determined by NMR) as a white solid, mp 245–247 °C (dec).

The carboxylate content of **32** was measured by NMR spectroscopy, by integrating the peak of 1-H. The chemical shift of 1-H in the case of 'hydroxymethylcarboxylate' **32a** was found to be 5.04 ppm and for the 'dicarboxylate' **32** 5.44ppm (see also the ^{1}H NMR values given below). A signal for the 'diol' **32b** was not observed. From the integrated value of 0.13 H-atoms for the signal of 1-H in 'hydroxymethylcarboxylate', a hydroxymethyl content of 13%/2 = 7% was calculated. This gives a carboxylate content of 93% for **32**.



32 : $R^1 = R^2 = CO_2Na$

32a : $R^1 = CH_2OH$, $R^2 = CO_2Na$
or $R^1 = CO_2Na$, $R^2 = CH_2OH$

32b : $R^1 = R^2 = CH_2OH$

IR (KBr): ν = 3427 (s, OH), 1618 cm^{-1} (s, C=O).

^{1}H NMR (D_2O): δ = 3.16–4.27 (m, 4.13 H, 2-H, 3-H, 4-H, 5-H, 6-H), 5.04 (d, 0.13 H, ^3J = 3.8 Hz), 5.44 (d, 0.87 H, ^3J = 3.8 Hz). ^{13}C NMR (D_2O): δ = 57.1 (t, CH_2OH), 71.3 (d, C-2), 71.8 (d, C-5), 72.5 (d, C-3), 75.4 (d, C-4), 96.5 (d, C-1), 175.5 (s, C-6).

The spectroscopic data were in accordance with values from the literature[15,16,18] except for a few minor peaks assigned to unreacted primary alcohol groups.

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