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TEMPO-mediated oxidation of maltodextrins and D-glucose: effect of pH on the selectivity and sequestering ability of the resulting polycarboxylates

Jean-François Thaburet, Nabyl Merbouh, Mathias Ibert, Francis Marsais,* Guy Queguiner

UMR 6014 (CNRS), Institut de Recherche en Chimie Organique Fine (IRCOF), INSA of Rouen, BP 08, F-76131 Mont-Saint-Aignan, France

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Abstract

Maltodextrins were oxidized to polyglucuronic acids with the ternary oxidation system: NaOCl–NaBr–2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). The chemoselective oxidation at the primary alcohol groups was shown to be strongly pH dependent. Oxidation of polysaccharides was best achieved at pH 9.5 in order to minimize depolymerization, whereas oxidation of oligosaccharides required stronger alkaline conditions (pH 11–11.5). The resulting sodium polyglucuronates present interesting sequestering properties, the best of which being obtained from maltodextrins with the highest degrees of polymerization. The same oxidation process allowed the convenient conversion of D-glucose to D-glucaric acid in high yield ($>90\%$), under strongly basic conditions (pH >11.5).

Keywords: Primary alcohol group oxidation; TEMPO; Maltodextrins; Polyuronic acids; Water softeners

1. Introduction

Oxidation of carbohydrates such as starch and maltodextrins is an important approach to modify the physical and chemical properties of these compounds.[1] Thus, oxidized derivatives of starch can be used as gelling agents, binders, and complexing agents (phosphate substitutes).

Many processes for the oxidation of carbohydrate polymers are known, however most of them result in some depolymerization. The carbohydrate can be oxidized both at the C-6 primary hydroxyl groups and at the C-2 and C-3 secondary positions, which induces carbon–carbon cleavage of glucose units to carboxy residues. In few cases, oxidation can be limited to the primary hydroxyl groups, resulting in polyglucuronates. Such polyuronic acids are often advantageous for applications such as complexing agents or stabilizers. Some regio-controlled oxidations at the C-6 hydroxyls have been reported, but they are not completely satisfactory. So, dioxygen in the presence of platinum on carbon[2–4] oxidizes mono and disaccharides in moderate yields, but only low yields were observed with polysaccharides. The use of nitrogen dioxide in the presence of sodium nitrite allows the conversion of polysaccharides to polyglucuronic acids, but depolymerization competitively occurs and secondary alcohol

* Corresponding author. Tel.: +33-2-35522475.
E-mail address: francis.marsais@insa-rouen.fr (F. Marsais).

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functionalities are partly converted to ketones.[5] Similarly, autocatalytic oxidation of glucans has been reported using sodium nitrate with catalytic amount of sodium nitrite in phosphoric acid.[6] Maltodextrins and starch have been also oxidized by the sodium tungstate–hydrogen peroxide system leading to polycarboxylic acids by cleavage of the C-2–C-3 bonds.[7]

In the course of the 1980s, the new water-soluble oxidation catalyst, 2,2,6,6-tetramethyl-1-piperidinyloxy free radical (TEMPO) became commercially available, and has been successfully used with cooxidants for the oxidation of primary alcohols,[8] and more recently of carbohydrates. The TEMPO–NaBr–NaClO system was first applied[9] to the oxidation of partly protected monosaccharides. The same conditions allow to oxidize some high-molecular-weight polysaccharides (starch, pullulan, …) to polyuronic acids.[10–12] Starch was selectively oxidized to polyglucuronates with a selectivity and yield of at least 95%, and a C-6 conversion rate of 98%. Interesting results were recently published concerning the TEMPO-mediated oxidations of polysaccharides including starch, maltodextrins, amylose, amylopectin and hyaluronan.[13] However, to our knowledge, no TEMPO-mediated oxidations of small oligosaccharides or unprotected monosaccharides have still been described. Moreover, little has been done to study the reaction parameters such as pH, in the case of TEMPO-mediated oxidation of poly- and oligosaccharides.

Therefore, in order to prepare sodium polyglucuronates, and to characterize the properties of these potential sequestering agents substitutes, we decided to investigate the TEMPO-mediated oxidation of various maltodextrins and glucose syrups, as well as D-glucose itself. The sequestering properties of the resulting products were also evaluated and compared to reference products such as sodium tripolyphosphate.

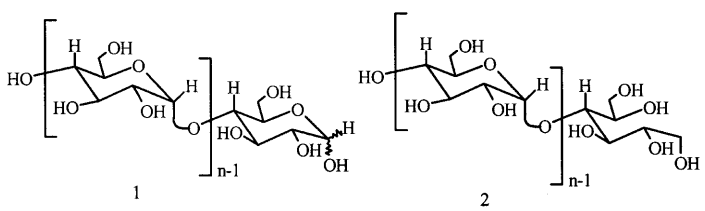
Our attention was mainly focused on the oxidation of sugars with general structure **1** ($n = 1$ to $n > 200$) such as D-glucose, glucose syrups, maltodextrins and modified starch, as well as hydrogenated oligosaccharides **2** such as maltitol and maltotriitol (Scheme 1).

The average number of glucosidic units of these poly-(1→4)-α-D-glucopyranosides is characterized by the degree of polymerization (DP). The average number of lactol functions (terminal hemiacetal group) is defined as the dextrose equivalent (DE) and is a function of the degree of polymerization: DE = 100/DP. The commercial maltodextrins (Entries 4–6; DP > 5) and glucose syrups (Entries 1–3; 5 > DP > 1.25) are known as Glucidex™ (Table 1).

2. Experimental

Materials.—Water-soluble starch hydrolysis products were supplied by Roquette Frères (F-62080 Lestrem, France). Anhydrous α-D-glucose and TEMPO were acquired from Aldrich. All other chemicals were analytical-grade commercial products and were used without purification.

Equipment.—Reactions were carried out in a 200 mL reactor, cooled in a salt–ice mixture, and equipped with a thermometer and a pH electrode. The reaction kinetics appeared to be very fast for some pH values, and the temperature can rise to 20 or 30 °C, if all the oxidant is added at once. So, the reaction temperature was kept about 5 °C, and addition of oxidant was monitored by a Logilap™ system. Using the same automatic system, the pH was maintained by titration with 1.5 M NaOH solution.



Scheme 1. Maltodextrins (**1**) and malto-itols (**2**).

Table 1
Oligo- and polysaccharides used for the oxidation experiments

Entry	Oligosaccharide (trade name)	DP	Common name	Entry	Polysaccharides (trade name)	DP	Common name
1	Glucidex 47	2.2	glucose syrup	5	Glucidex 6	17	maltodextrin
2	Glucidex 39	2.6	glucose syrup	6	Glucidex 2	50	maltodextrin
3	Glucidex 32	3.1	glucose syrup	7	Pregeflo P250	>200	starch
4	Glucidex 17	5.9	maltodextrin				

Procedure.—Oxidation experiments were performed as follows: the carbohydrate (5 g containing x mmol of primary alcohol and hemiacetal functions), TEMPO (0.01 equiv), and NaBr (0.15 equiv) were dissolved in water (60 mL). A 1.8 M NaClO solution (2.2 mmol NaClO/mmol primary alcohol and 1.1 mmol NaClO/mmol of hemiacetal, which is a 10% excess compared to the stoichiometric amounts) was adjusted to the desired pH by adding 4 M aq HCl. Both solutions were cooled to 0 °C.

The oxidant solution was added at about 5 °C, and the appropriate pH was kept constant by addition of NaOH. When the oxidation was finished (stable pH value), the reaction was quenched with EtOH, and the pH adjusted to 8.5 by adding 1 M aq HCl. Then, the solution was concentrated to 50 mL, and the oxidized carbohydrate was precipitated by adding 150 mL of EtOH. The precipitate was dissolved in 50 mL water, and the precipitation operation was repeated. The resulting solid was washed with a 4:1 EtOH–water mixture, and dried at 50 °C under reduced pressure.

Analysis.—NMR spectra were recorded on a Bruker AC 300F spectrometer, operating a ^{13}C NMR frequency of 75 MHz. All oxidized products as their carboxylate form were dissolved in D_2O, and the carbon spectra recorded in gate decoupling mode; chemical shifts (δ) are reported in ppm downfield from Me_4Si.

Carboxylate content of the oxidized samples was measured by passing an aqueous product solution (2 g) through a column of Dowex (H^+) resin to obtain the free-acid form. The solutions were then titrated with 0.5 M NaOH. Oxalate amounts were determined by precipitation as calcium salt form at pH 2.

Electrospray ionization mass spectrometry (ESIMS) was performed at a flow of 5 μL/s with samples dissolved in a 1:3 MeOH–water solution (2.0 mg/L) containing 5 M NaOAc. The GC-coupled mass spectrometry (DB1 column) used a Finnigan SSQ7000 spectrometer, with samples (acid form) derivatized with a mixture of bis(trimethylsilyl)trifluoroacetamide and trimethylsilylimidazole.

In GPC, products in the Na^+ form were fractionated with 3 columns (a precolumn OH Pack SBG and two columns OH Pack SB806HQ and OH Pack SB 804HQ) in series. The products were detected by refractive index and molar mass was determined on-line with a DAWN-DSP-F (Wyatt Technology Co.) MALLS detector (after pullulan calibration). Samples (50 g/L) were dissolved in 0.1 M $LiNO_3$ solutions.

The calcium-complexing ability of the oxidized carbohydrates was evaluated by titration of a 100 mL solution containing 40 mg of Ca(II) with known amounts of the substrate (if necessary, the pH was adjusted to 10.5). The activity of uncomplexed Ca(II) was measured using a XS530 Tacussel membrane electrode reversible to calcium. The calcium-sequestering capacity is defined as the number of mg of Ca(II) bound by one gram of complexant, until the concentration of the free Ca(II) reaches 10^{-5} M (this value is generally considered as the upper limit for Ca(II) during a washing process[14]).

3. Results and discussion

Conversion of primary hydroxyl groups to carboxylates by oxidation was estimated from

the ^{13}C NMR spectra (C-6 signal) (Table 2, converted CH_2OH). This overall conversion rate is independent of the pH, and more than 98% of the primary hydroxyl functions were oxidized (the signals corresponding to the primary alcohol functions at 61–62 ppm have disappeared).

The oxidation selectivity was estimated by comparison of the carboxylates amount of the oxidized product (estimated by acid–base titration) with the expected value calculated for a total and selective oxidation of the primary hydroxyl and hemiacetal functions. The oxidation yield (Table 2, molar yield) was calculated as the weight ratio of recovered polycarboxylates (mass of oxidized product − mass of oxalate) to the theoretical mass of sodium polyglucuronate.

Both conversion ratio and selectivity show that oxidation is highly selective for the primary hydroxyl functions, which is in good agreement with the corresponding good molar yield. This latter value is directly related to the very low amounts of recovered sodium oxalate (^{13}C NMR signal at 173.4 ppm, Fig. 1) resulting from oxidative degradation.

The high selectivity of the oxidation was gained from the macroscopic analysis of the recovered products (disappearance of the signal corresponding to the primary alcohol groups in ^{13}C NMR), but it lacked structural information. So, a more accurate approach could be achieved by a precise study of the ^{13}C NMR spectra of the oxidized products (Fig. 1). Sodium polyglucuronates should show one signal in the carboxylic acid region (170–180 ppm) and one signal around 98 ppm corresponding to the acetal C-1 carbon atom, since all the internal (1→4)-linked D-glucose units are similar. On examination, the observed ^{13}C NMR spectra appeared to be more complex, especially for the product oxidized at pH 11.4. This could be due to the presence of smaller chains, in which both the carboxylate and acetal carbon atoms have different chemical shifts from those of the higher terms. Deviation of the terminal glucose unit can be excluded since it would be independent of the oxidation pH.

Table 2
Effect of pH on the TEMPO-mediated oxidation of polysaccharides at 5 °C

Entry	Carbohydrate (trade name)	pH	Converted CH_2OH (%)	Carboxylates (mmol/g)		Molar yield (%)	Sodium oxalate (wt%)
				Titration	Theory		
1	Glucidex 2	9.5	>98	5.3	5.12	>95	<1.0
2	Glucidex 2	11.4	>98	5.2		>95	<1.0
3	Pregeflo P250	9.5	>98	5.1	5.06	>95	<1.0
4	Pregeflo P250	11.4	>98	5.1		>95	<1.0

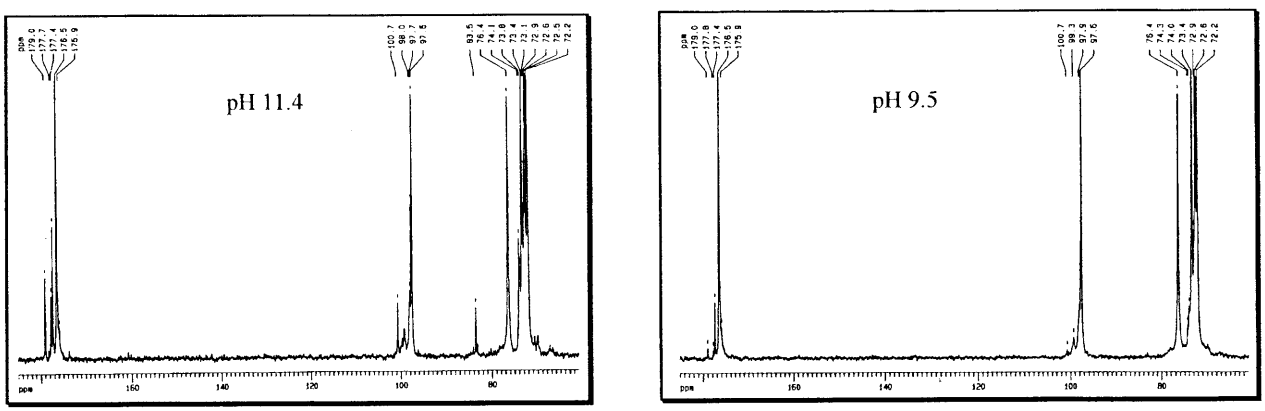


Fig. 1. ^{13}C NMR spectra of oxidized Glucidex 2 according to pH.

Table 3
GPC analysis of oxidized polysaccharides

Entry	Polysaccharide (trade name)	pH	Converted CH_2OH (%)	Carboxylates (mmol/g)	M_w ($\times 10^{-3}$) (g/mol)	M_n ($\times 10^{-3}$) (g/mol)
1	Glucidex 2		starting product		$600 \pm 6\%$	$68 \pm 50\%$
2	Glucidex 2	9.5	>98	5.3	$270 \pm 5\%$	$38 \pm 34\%$
3	Glucidex 2	11.4	>98	5.2	$3 \pm 40\%$	$2.3 \pm 40\%$
4	Pregeflo 250P		starting product		$2500 \pm 20\%$	
5	Pregeflo 250P	9.5	>98	5.1	$250 \pm 6\%$	$67 \pm 11\%$
6	Pregeflo 250P	11.4	>98	5.1	$6.4 \pm 23\%$	$2.6 \pm 48\%$

Table 4
Effect of pH on TEMPO-mediated oxidation of oligosaccharides at 5 °C

Entry	Oligosaccharide (trade name)	pH	Converted CH_2OH (%)	Carboxylates (mmol/g)		Molar yield (%)	Sodium oxalate (wt%)
				Titration	Theory		
1	Maltitol	10.2	91	6.8	6.64	87	7.5
2	Maltitol	11.4	>98	6.6		96	1.5
3	Maltotriitol	8.6	85	6.2	6.15	84	11.0
4	Maltotriitol	9.5	89	6.2		87	8.0
5	Maltotriitol	10.5	97	6.1		92	3.0
6	Maltotriitol	11.4	>98	6.1		94	1.5
7	Glucidex 39	9.5	88	6.5	6.33	88	6.0
8	Glucidex 39	10.2	92	6.4		92	2.0
9	Glucidex 39	11.4	>98	6.3		95	<1.0
10	Glucidex 47	11.4	>98	6.5	6.51	94	<1.0
11	Glucidex 32	11.4	>98	6.2	6.11	95	<1.0
12	Glucidex 17	11.4	>98	5.9	5.64	95	<1.0

GPC analysis was achieved on the starting polysaccharides and on the resulting oxidation products in order to confirm the hypothesis of a competitive depolymerization. Comparison of both number and mass average molecular weights (M_n and M_w) of starting sugars and oxidized products (Table 3, Entries 2, 3 and 5, 6, respectively, compared to Entries 1 and 4), clearly proves that hydrolysis of these polysaccharides occurs during the oxidation process. So, oxidation of maltodextrins by the TEMPO–NaClO–NaBr system must be achieved at a pH lower than 10 (Entries 2 and 5) in order to minimize hydrolysis of the polymeric structure. A similar behaviour has been observed in the oxidation of pullulan.[15]

Contrary to polysaccharides, oligosaccharides and reduced oligosaccharides of low DP, such as maltitol (DP 2), maltotriitol (DP 3) or Glucidex 39 (average DP 2.6), present a high ratio of terminal oxidizable functions (hemiacetal for Glucidex or primary alcohols for polyols) compared to the C-6 primary alcohol. For these oligosaccharides, it has been demonstrated that the oxidation selectivity is highly dependent on the pH (Entries 3–6 and 7–9 for example). The best selectivity is obtained for pH higher than 11 (Table 4, Entries 2, 6, and 9–12): the rate of converted CH_2OH increases with pH, and the formation of by-products such as oxalates decreases.

In order to understand the oxidative degradation of oligosaccharides, the oxidation products of a low DP sugar (Glucidex 47) were analyzed by GLC–MS, after trimethylsilylation of the analytical sample.

The resulting GLC–MS spectrogram (Fig. 2) presents two groups of signals, corresponding to the oxidation products of the two main families of the starting sugar, i.e., DP 2 and DP 3. Compounds **a**–**d**, corresponding to the DP 2 family, were identified by their MS

signals (Fig. 2). They have been oxidized at C-6, and only differ from their terminal unit, this one being more or less decarboxylated (compounds **a** and **b**), or unchanged (compounds **c** and **d**). Compounds **e**–**h** are similar products, corresponding to the DP 3 series with m/z values moved forward 392 units.

Electrospray analysis (ESIMS) of the same sample — sodium salt — shows a similar distribution for the DP 3, DP 2 and DP 1 terms, and confirms that oligosaccharides were converted to polyglucuronic acids with dicarboxylic hydroxylated terminal units being more or less decarboxylated. No degradation was detected on the internal glucosidic units.

These analytical results clearly show that when degradation takes place, it mainly affects the terminal units by stepwise decarboxylation or by diol cleavage, but very few of the diols of other units. From a theoretical point of view, oxidation of a polymeric sugar could be simply schematized by three basic oxidative pathways as described in Scheme 2. Oxidation of primary alcohol and hemiacetal units by the TEMPO–NaOCl–NaBr system would only compete with the oxidative path 2, but not with path 3 (the rate of reaction 3 seems to be very low, since no corresponding dicarboxylic derivatives were observed). The secondary reaction 2 could be due to the direct reaction of the hypobromite and/or hypochlorite ions on the diol functions.

In summary, oxidation of low DP carbohydrates, or reduced carbohydrates is selective at the primary alcohol and hemiacetal functions for pH's higher than 11, thus indicating a kinetic constant k_1 higher than k_2 and k_3 (Scheme 2). On the other hand at pH lower than 10.5, the oxidation selectivity decreases due to greater influence of side reaction 2, and the higher 'concentration' of terminal oxidizable units of the oligosaccharides.

The catalytic effect of the bromide anions was clearly established with an optimum ratio of 0.15 equiv against primary alcohol and hemiacetal functions. This effect is especially important for pH values higher than 10.5. It has been demonstrated that oxidation of maltodextrins and starch by sodium hypochlorite only leads to the C-2–C-3 bonds cleavage without oxidation of the primary alcohol groups.[16] The catalytic effect of the bromide anions has been reported for the oxidation of inulin by alkaline sodium hypochlorite.[17] More recently, it has been claimed that sonocatalysis allows TEMPO-mediated oxidation

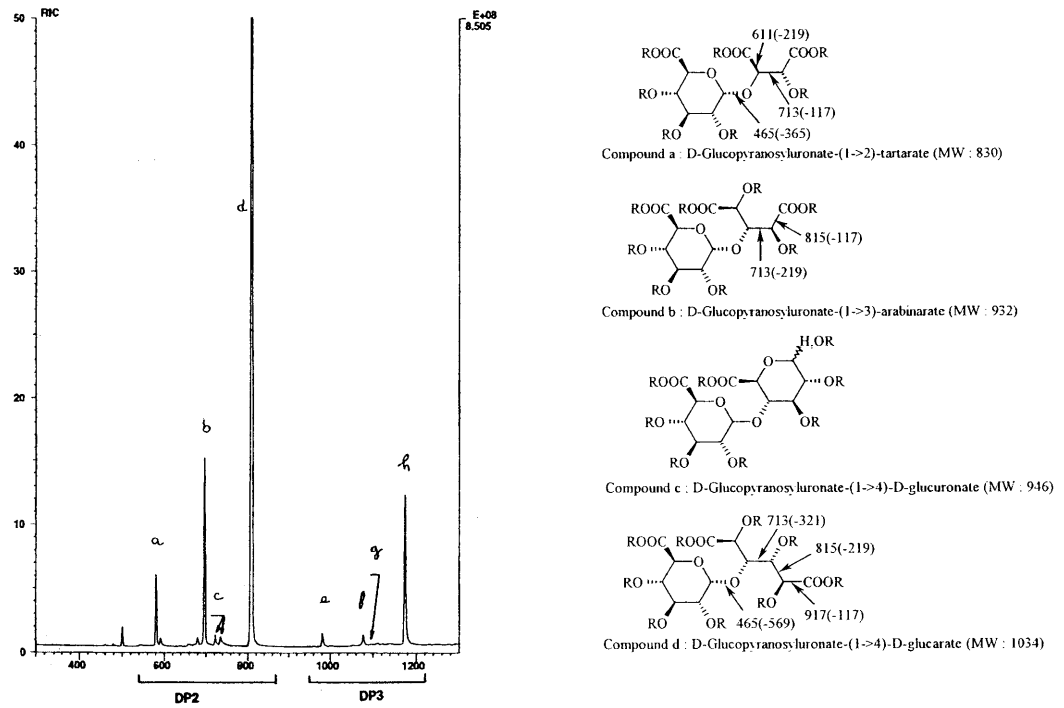
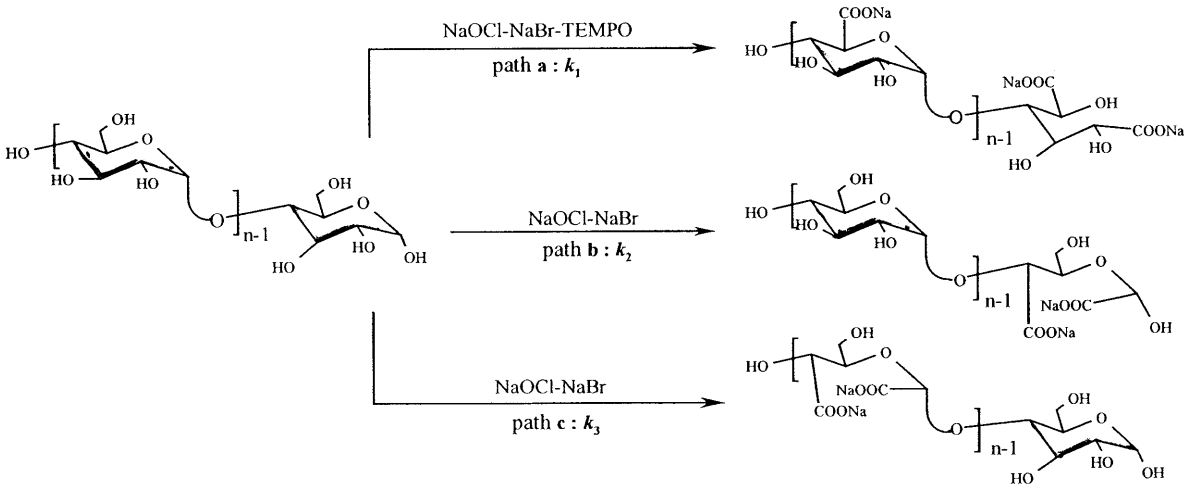


Fig. 2. GLC–MS characterization of oxidized Glucidex 47 (R = $SiMe_3$).



Scheme 2. Hypohalite ion behaviour in the TEMPO-mediated oxidation of maltodextrins. Path a: selective oxidation at primary hydroxyl and hemiacetal units by TEMPO. Path b: cleavage of the C-2–C-3 bonds of the terminal hemiacetal units. Path c: cleavage of the C-2–C-3 bonds of the glucose units.

Table 5
Effect of pH on the TEMPO-mediated oxidation of monosaccharides at 5 °C

Entry	Sugar	pH	Sodium glucarate (% isolated yield)	By-products (% molar yield)[a]
1	D-glucose	9.5	<10	ST: 35; SG: 45; SO: 20
2	D-glucose	10.5	25	ST: 28; SG: 40. SO: 15
3	D-glucose	11.2	64	ST: 10; SG: 20; SO: 7
4	D-glucose	11.7	90	ST: 5; SG: 1; SO: 2
5	D-glucitol	10.5	27	ST: 18; SG: 24; SO: 14
6	D-glucitol	11.7	89	ST: 5; SG: 1; SO: 3

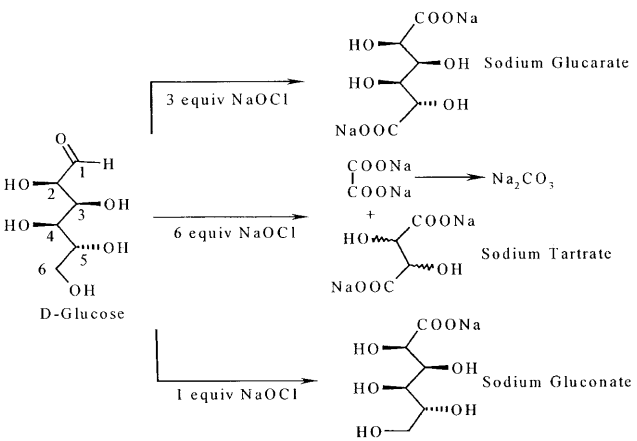
[a] ST, sodium tartrate; SG, sodium gluconate; SO, sodium oxalate.

of glucosides using basic sodium hypochlorite without bromide.[18]

Our experience of the control of carbohydrates oxidation was then successfully extended to glucose and its reduction product, glucitol. Since oxidation of oligosaccharides proved to be strongly pH dependent due to the competitive degrading oxidation of the terminal glucose unit, oxidation of monosaccharides to glucaric acid should be more difficult to control.

As expected, oxidation of glucose and glucitol (Table 5) with the TEMPO–NaOCl–NaBr system proved to be selective only for the highest pH values, 11.5–12 (Entries 4 and 6). At pH 9.5, less than 10% glucaric acid was obtained (Entry 1). Mainly degradation products such as sodium tartrate, oxalate and carbonate were formed by oxidative diol cleavage (Scheme 3).

Pure glucaric acid was therefore isolated in good yield (90%) as the mono potassium salt (precipitation at pH 3.4), after oxidation of D-glucose at pH 11.7 by the TEMPO–



Scheme 3. Oxidation reactions of D-glucose.

Table 6
Sequestering capacity of TEMPO-mediated oxidized carbohydrates

Entry	Oxidized sugar	Oxidation pH	Oxidation degree (%)	'SC' (mg of Ca/g)
1	glucose	11.7	>98	6
2	maltitol	11.4	>98	8
3	Glucidex 47	11.4	>98	8
4	Glucidex 32	11.4	>98	10
5	Glucidex 17	11.4	>98	14
6	Glucidex 2	11.4	>98	20
7	Glucidex 2	9.5	>98	32
8	Pregeflo P250	9.5	>98	32

NaOCl–NaBr system. Oxidation of protected sugar such as α-methyl glucoside to sodium methyl α-D-glucuronate, with a selectivity of 95% at pH 10.0, has been reported,[9] but no selective oxidations to glucaric acid are currently available.

When the oxidation was achieved at a pH lower than 11, other carboxylates observed in ^{13}C NMR were formed such as sodium tartrate, oxalate or carbonate (Entries 1, 2 and 5). For information, signals of the different carbons in ^{13}C NMR in D_2O are as follows: δ (sodium glucarate) 179.2, 179.0, 74.0(2), 73.9, 71.9, δ (sodium gluconate) 179.5, 74.3, 72.8, 71.4, 71.2, 62.9, δ (sodium tartrate) 178.9 and 177.9, 75.1 and 74.1, δ (sodium oxalate) 73.4, δ (sodium carbonate) 168.5 (depending on pH).

Careful identification of the ^{13}C signals of tartaric acid in the crude oxidation product was done by addition of meso or racemic sodium tartrate. This allows us to identify the sodium tartrate as a mixture of the two diastereoisomers, with only 20% of the meso compound. The ratio of the two diastereoisomers was calculated from the ^{1}H NMR spectrum of the crude oxidation product (δ 3.98 and 4.05). This would be in favour of two degradative oxidations of D-glucose by cleavage of both the C-4–C-5 and the C-2–C-3 bonds, the former being major (characterization of the major stereoisomer, presumably the L form, and mechanistic explanation of its formation are currently in progress).

Formation of these by-products by degrading oxidation of diols requires greater amounts of oxidant; this could explain the simultaneous presence of sodium gluconate, resulting from partial oxidation of glucose or glucitol due to the inadequate amount of oxidant (Scheme 3).

The previously prepared sodium polyglucuronates obtained by oxidation of various maltodextrins were compared with sodium tripolyphosphate (TPPNa) as water softeners. The sequestering ability was measured by an addition method with determination of their sequestering capacities (SC) (Table 6).

Compared to sodium tripolyphosphate (SC 120 mg of Ca/g), we observed lower sequestering properties for the sodium salts of polyglucuronic acids obtained by oxidation of maltodextrins. The sequestering power is clearly related to the molar mass of the starting carbohydrates (Table 6), most likely due to the double-helical structure of polysaccharides which could favour the Ca^{2+} cations complexation. So, oxidation of Glucidex 2 at pH 11.4 led to a sodium salt with a SC of 20 mg Ca/g (Entry 6), whereas oxidation at pH 9.5 gave a less depolymerized product with a higher SC value of 32 (Entry 7).

In conclusion, TEMPO-mediated oxidation of carbohydrates is a reliable method to chemoselectively oxidize primary alcohol groups of starch hydrolysis products (maltodextrins). The applied pH is quite important and depends on the degree of polymerization of the starting carbohydrates. Oxidation of polysaccharides has been best achieved at pH 9.5 to limit depolymerization, whereas more alkaline conditions were required for lower DP oligosaccharides (i.e., pH 11.0–11.5), as well as for D-glucose or D-glucitol (i.e., pH > 11.5).

Glucaric acid has been synthesized with high selectivity and good yield (90%), which is better than the known methods for oxidation of unprotected glucose (highest yield of 65%).[3,19]

The sequestering capacities of the oxidation products increase with DP, and can reach a value of 32 mg Ca/g of substrate. This value could be increased by creating more carboxylate functions, for example by partial oxidative cleavage of internal vicinal C-2–C-3 diols of maltodextrins without degrading the structure. Such investigations have been realized and will be reported in a following paper.

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