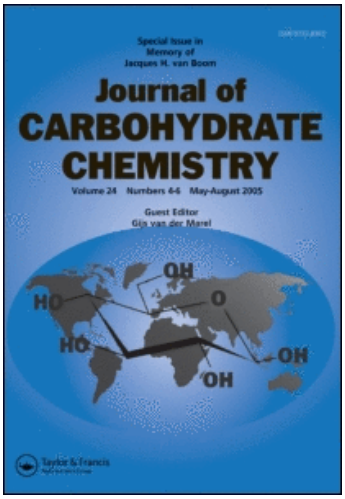


Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Influence of Temperature and pH on the Platinum Catalysed Oxidation of Sucrose

Les A. Edye[ab]; George V. Meehan[a]; Geoffrey N. Richards[a]
[a] Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, Australia [b] Sugar Processing Research Institute, Inc., New Orleans, LA, USA

To cite this Article Edye, Les A. , Meehan, George V. and Richards, Geoffrey N.(1994) 'Influence of Temperature and pH on the Platinum Catalysed Oxidation of Sucrose', Journal of Carbohydrate Chemistry, 13: 2, 273 — 283
To link to this Article: DOI: 10.1080/07328309408009192
URL: http://dx.doi.org/10.1080/07328309408009192

J. CARBOHYDRATE CHEMISTRY, 13(2), 273-283 (1994)

INFLUENCE OF TEMPERATURE AND pH ON THE PLATINUM CATALYSED OXIDATION OF SUCROSE

Les A. Edye,[1*] George V. Meehan, Geoffrey N. Richards[2]

Department of Chemistry and Biochemistry, James Cook University of North Queensland, Townsville, 4811, Australia.

Received October 15, 1992 - Final Form October 20, 1993

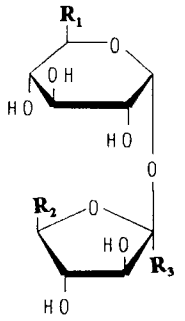
ABSTRACT

The influence of temperature and pH on the platinum catalysed oxidation of sucrose has been studied. Decreasing reaction temperature from 100 °C to 80 °C markedly reduced oxidation rate but had little or no effect on selectivity. At pH 7.0, the C6 and C6′ hydroxyl groups were oxidised, but there was no oxidation at the C1′ hydroxyl group. At pH 9.0 the C1′ hydroxyl group was oxidised and the resulting product mixture contained a higher proportion of dicarboxylic acid disaccharides and decomposition products. ^{1}H NMR was used to analyse complex product mixtures.

INTRODUCTION

We have reported[3] previously that platinum catalysed oxidation of sucrose using Pt on carbon as catalyst and the De Wilt *et al.*[4,5] pH-stat technique at pH 7.0 and 100 °C effected rapid formation of a complex mixture of acid products. Two of the three possible disaccharide monocarboxylic acid (*viz.* 6-carboxysucrose [**1**] and 6′-carboxysucrose [**2**]) and one of the three possible disaccharide dicarboxylic acid derivatives of sucrose shown in Scheme 1 (*viz.* 6,6′-dicarboxysucrose [**4**]) were isolated from the product mixture and identified. There was no evidence of oxidation at the C-1′ hydroxyl group, and neither the product mixture nor its acid hydrolysate contained the 2-

ketogluconic acid which would result from hydrolysis of such an oxidation product. We noted that the resistance of the C-1′ hydroxyl group to oxidation is consistent with the earlier conclusions on the order of reactivity to catalytic oxidation of hydroxyl groups in partially protected ketoses[6] (*i.e.*, prim 6-OH [furanoses] > 5-OH_{ax} = 4-OH_{ax} ≥ 3-OH_{ax} ≥ prim 1-OH > sec OH [furanoses]).



	R_1	R_2	R_3
1	COOH	CH_2OH	CH_2OH
2	CH_2OH	COOH	CH_2OH
3	CH_2OH	CH_2OH	COOH
4	COOH	COOH	CH_2OH
5	COOH	CH_2OH	COOH
6	CH_2OH	COOH	COOH

SCHEME 1

The present study reports the effect of reaction temperature and pH on sucrose oxidation rate and the resulting product mixture.

RESULTS AND DISCUSSION

The Effect of Temperature on Rate and Selectivity. Mehltretter *et al.*[7] investigated the effect of temperature (up to 70 °C) on the platinum catalysed oxidation of 1,2-isopropylidene-α-D-glucofuranose using a batch method, wherein one or more equivalents of base were added at the beginning of the reaction and pH decreased as acid products formed. At higher temperatures reaction rate increased, but the uronic acid product yield decreased due to further oxidation and decomposition. In the case of the catalytic oxidation of D-fructose using the batch method,[8] increasing the reaction temperature above 30 °C significantly reduced the yield of 2-ketogluconic acid. In contrast, De Wilt *et al.*[5] used a pH-stat method, wherein constant pH was maintained by continuous addition of alkali, to investigate the Pt catalysed oxidation of D-glucose and reported that temperature had little effect on the reaction selectivity (*i.e.*, the yield of D-gluconic acid only slightly decreased with increasing temperature).

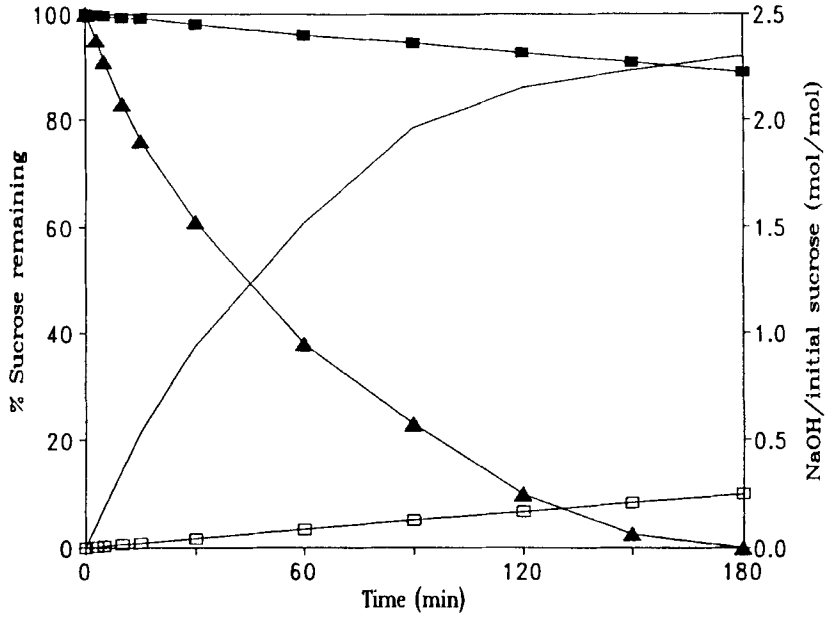
Table 1. Alkali Consumption During Sucrose Oxidation at 80 °C and 100 °C

Reaction temperature (°C)	Reaction time (min)	% Sucrose remaining	NaOH/Sucrose oxidized (mol/mol)
100	5	91	2.0
80	240	86	1.9
100	10	83	2.1

In the present investigation the rate and selectivity of the Pt catalysed oxidation of sucrose at 80 °C and 100 °C were compared. The temperature effect was investigated for sucrose oxidations at pH 10.0; at pH 7.0 the reaction rate at 80 °C was far too slow by comparison to the rate at 100 °C (*i.e.*, no measurable oxidation of sucrose after 4 hours at 80 °C and pH 7.0).

The reaction profiles for sucrose oxidations at 80 °C and 100 °C are compared in Figure 1. Although the reaction rate at 100 °C was much faster than at 80 °C, the amounts of alkali consumed per mole of sucrose oxidised were similar (see Table 1). Therefore, while reduction in reaction temperature from 100 °C to 80 °C had a profound effect on reaction rate, it appeared to have little effect on selectivity.

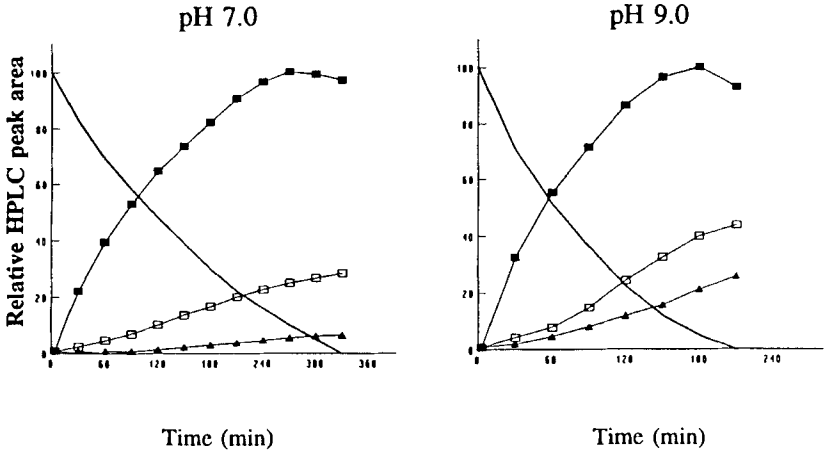
The Effect of pH on Rate and Selectivity. Sucrose was oxidised at pH 7.0 and 9.0 and analysed by ion exchange HPLC. HPLC of the reaction solution resolves sucrose and three product groups, *i.e.*, monocarboxylic acid disaccharides, dicarboxylic acid disaccharides and a third group tentatively identified as monosaccharide acids. The peak areas of the three products (represented as peak areas relative to the maximum monocarboxylic acid disaccharide product peak area of all reaction samples) are plotted against time in Figure 2. It is reasonable to assume that the dicarboxylic acid disaccharide product has a detector response similar to that of the monocarboxylic acid disaccharide product. Therefore, the relative peak areas are equivalent to the relative amounts of the acids. It is not reasonable to assume the same equivalence for the monosaccharide acids and the disaccharide acids. Therefore, the relative HPLC peak



% sucrose remaining versus time, ■ 80 °C, ▲ 100 °C

NaOH/initial sucrose (mole/mole), □ 80 °C, △ 100 °C

Fig. 1. The Effect of Temperature on the Platinum Catalyzed Oxidation of Sucrose.



■ monocarboxylic acid disaccharides, □ dicarboxylic acid disaccharides,

▲ monosaccharide acids, curves without points are 100 to 0 % sucrose remaining

Fig. 2. The Platinum Catalysed Oxidation of Sucrose at pH 7.0 and pH 9.0.

areas of the monosaccharide acids represent relative proportions of this product that are undetermined with respect to the disaccharide acid products.

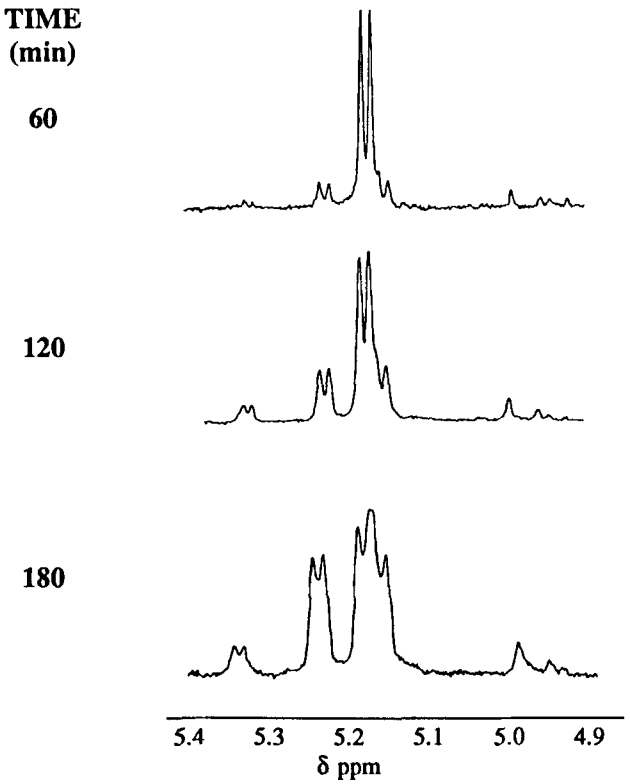
Figure 2 clearly shows that an increase in reaction pH effects an increase in the extent of oxidation. At pH 9.0 the proportions of dicarboxylic acids and monosaccharide acids (decomposition products) in the oxidation product both increase.

We have previously reported the isolation of **4** and a mixture of **1** and **2** from the platinum catalysed oxidation of sucrose at 100 °C and neutral pH.[3] **1** and **2** could not be resolved by chromatographic techniques but upon treatment of the mixture with invertase **1** was completely hydrolysed and subsequently **2** was isolated. We have reported the ^{1}H and ^{13}C NMR of **2** and **4**, and the ^{13}C NMR of **1** could be assigned from the mixture of **1** and **2** by difference.[3] Not surprisingly the ^{1}H NMR spectrum of the **1** + **2** mixture was extremely complex, especially in the region between δ 3.1 and 4.3 ppm. However, two resolved doublets at δ 5.163 ppm (d, J = 4.2 Hz) and δ 5.238 ppm (d, J = 3.6 Hz) were observed, and could be assigned to the C1-H nuclei of **2** and **1** respectively (by comparison with the spectrum of pure **2**).

After examination of the ^{1}H NMR spectra of sucrose and the pH 7.0 oxidation products, including possible decomposition products (*viz.* glucuronic acid, 5-ketogluconic acid, 2-ketogluconic acid, glucose and fructose), it became apparent that integration of the ^{1}H NMR spectra between δ 4.9 and 5.4 ppm of sucrose oxidation samples could be used to determine the relative proportions of the disaccharide acid products.

The ^{1}H NMR spectra between δ 4.9 and 5.4 ppm of reaction samples from sucrose oxidation at pH 7.0 (Figure 3) contained a series of doublet resonances that could be assigned to the C1-H nuclei of sucrose and known products of oxidation (*viz.* **1**, **2** and **4**). The assignments are footnoted in Figure 3. The relative proportions of sucrose and the three acid disaccharides, calculated as percentages of the total integral of the C1-H resonances in the ^{1}H NMR spectra, are reported in Table 2. The integration of the C1-H resonances of sucrose and **2** is subject to some error since the two resonances are nearly coincidental. Therefore, the C6 hydroxyl group is possibly only slightly more susceptible than the C6′ hydroxyl group to oxidation at pH 7.0 and 100 °C.

These results are in good agreement with the ion exchange HPLC results. The ratio of monocarboxylic acid disaccharides to dicarboxylic acid disaccharides in the product of sucrose oxidation at pH 7.0, determined by HPLC, was 6.5:1 (at *ca.* 30% sucrose



δ 5.34 ppm (d, *J*=3.6 Hz) C1-H 4; 5.24 ppm (d, *J*=3.6 Hz) C1-H 1; 5.18 ppm (d, *J*=3.9 Hz) C1-H sucrose; 5.16 ppm (d, *J*=4.2 Hz) C1-H 2; 4.98 ppm unidentified.

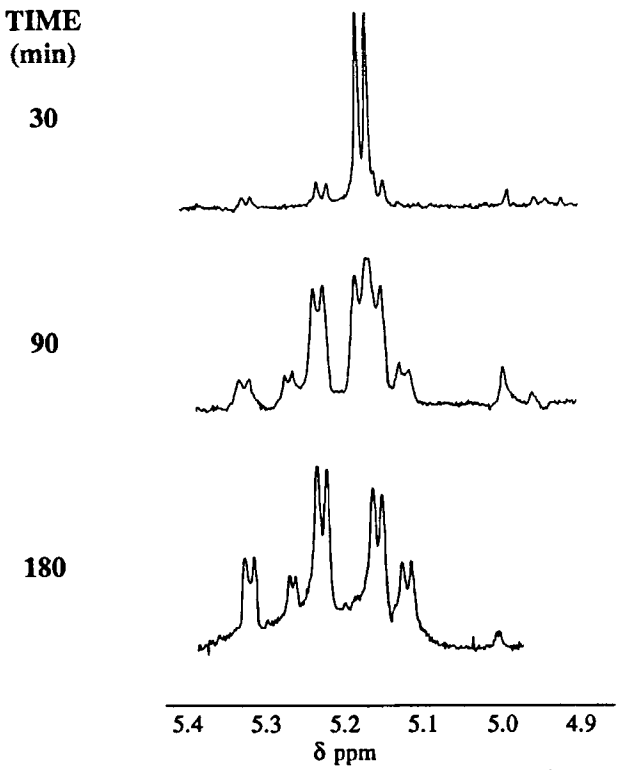
Fig. 3. Platinum catalysed oxidation of sucrose at pH 7.0 followed by ^{1}H NMR.

Table 2. Sucrose Oxidation at pH 7.0 Followed by ^{1}H NMR.

Time (min)	% Sucrose remaining [a]	Relative proportions of sucrose and products [b]			
		Sucrose	1 C6 Acid	2 C6′ Acid	4 C6,C6′ Acid
60	74	70.7	12.8	12.6	3.9
120	50	55.2	20.5	18.4	5.9
180	32	35.9	30.3	25.3	8.5

a. From HPLC peak areas.

b. Percent of the total integral of C1-H resonances in the ^{1}H NMR spectra of reaction samples.



δ 5.34 ppm (d, *J*=3.6 Hz) C1-H **4**; 5.28 ppm (d, *J*=2.4 Hz) C1-H **5**; 5.24 ppm (d, *J*=3.6 Hz) C1-H **1**; 5.18 ppm (d, *J*=3.9 Hz) C1-H sucrose; 5.16 ppm (d, *J*=4.2 Hz) C1-H **2**; 5.12 ppm (d, *J*=3.9 Hz) C1-H **3**; 4.9 ppm unidentified.

Fig. 4. Platinum catalysed oxidation of sucrose at pH 9.0 followed by ^{1}H NMR.

remaining). The ratio determined from ^{1}H NMR spectrum of the reaction sample at 180 min (at 32% sucrose remaining) was 6.3:1.

The ^{1}H NMR spectra of reaction samples from sucrose oxidation at pH 9.0 (Fig. 4.) also contained a series of doublet resonances between δ 5.1 and 5.4 ppm. However, the reaction product was more complex and not all of the resonances could be assigned to the C1-H nuclei of sucrose and previously isolated products of oxidation (*viz.* **1**, **2** and **4**). Since the two additional resonances at δ 5.12 ppm (d, J = 3.9 Hz), and δ 5.28 ppm (d, J = 2.4 Hz) were doublets in the sucrose-like C1-H shift region it was tempting to speculate that they resulted from the products of oxidation of the C1′ hydroxyl group. Examination of molecular models indicated that a carboxyl group at C1′ would have a shielding effect on the C1-H nuclei, therefore the resonance at δ 5.12 ppm was tentatively

Table 3. Sucrose Oxidation at pH 9.0 Followed by ^{1}H NMR.

Time (min)	% Sucrose remaining	Relative proportions of sucrose and products [a]					
		Sucrose	**1** C6 Acid	**2** C6′ Acid	**4** C6,C6′ Acid	**3** C1′ Acid [b]	**5** C6,C1′ Acid [b]
30	70	71.8	11.7	11.4	5.1	-----	-----
90	34	27.8	23.3	21.8	12.8	8.8	5.5
180	5	-----	32.8	27.6	19.9	13.1	6.6

a. Percent of the total integral of C1-H resonances in the ^{1}H NMR spectra of reaction samples.
b. Tentative assignments of doublets based on models and acid hydrolysis products.

assigned to the C1-H of 1′-carboxysucrose (**3**). The remaining resonance at δ 5.28 ppm was tentatively assigned to the C1-H of 6,1′-dicarboxysucrose (**5**); since a carboxyl group at C6′ also has a slight shielding effect on the C1-H nuclei a C1′,C6′ dicarboxylic acid C1-H shift would be expected to be upfield of sucrose.

The relative proportions of sucrose and the five acid disaccharides, calculated as percentages of the total integral of the C1-H resonances in the ^{1}H NMR spectra, are reported in Table 3. The relative proportions of the resonances tentatively assigned to **3** and **5** are in agreement with previous observations that oxidation at C1′ is less favoured than oxidation at C6 or C6′. Since very little sucrose remained at 180 min, the integration error associated with the near coincidental C1-H resonances of sucrose and **2** is not significant, and it appears that the C6 hydroxyl group is in fact slightly more susceptible than the C6′ hydroxyl group to oxidation.

Again these results appear to be in good agreement with the ion exchange HPLC results. The ratio of monocarboxylic acid disaccharides to dicarboxylic acid disaccharides in the product of sucrose oxidation at pH 9.0, determined by HPLC, was 2.7:1 (at *ca.* 5% sucrose remaining). If the tentative assignments of the above-mentioned resonances to the products of oxidation at C1′ are accepted, then the ratio from ^{1}H NMR at 180 min (5% sucrose remaining) would be 2.7:1.

HPLC analysis of an acid hydrolysate of the sucrose oxidation reaction solution at pH 9.0 (180 min) resolved 5-ketomannonic acid, 2-keto-D-gluconic acid, and D-glucuronic acid with a peak area ratio of 1:2.4:12.1. 5-Ketomannonic acid is assumed to behave similarly to 5-ketogluconic acid and to decompose partially under the conditions

of acid hydrolysis, and therefore is present in the hydrolysate in less than stoichiometric amount. Although the proportion of 2-keto-D-gluconic acid (acid monosaccharide resulting from hydrolysis of the product of oxidation at the C1′ hydroxyl group of sucrose) was less than would be predicted from the ^{1}H NMR spectra (*i.e.*, 5-ketomannonic acid:2-keto-D-gluconic acid:D-glucuronic acid, 6.6:2.7:12.1), the presence of C1′ acid derivatives of sucrose was nevertheless confirmed.

Comparison of the ^{1}H NMR spectra from sucrose oxidations at pH 7.0 and 9.0 clearly establishes the profound effect of reaction pH on the sucrose oxidation product composition. An increase in reaction pH from 7.0 to 9.0 increased the extent of oxidation (*i.e.*, more oxidations per sucrose molecule), resulted in a greater proportion of dicarboxylic acid disaccharides in the product, and effected oxidation at the C1′ hydroxyl group (this oxidation reaction is not observed at pH 7.0). The proportion of decomposition products also increased with increasing pH.

The relative susceptibility of the three primary hydroxyl groups of sucrose to platinum catalysed oxidation is C6 > C6′ >>> C1′. Whereas oxidation at pH 7.0 produced only two of the possible monocarboxylic acid derivatives of sucrose (*viz.* **1** and **2**), and only one of the three possible dicarboxylic acid derivatives of sucrose (*viz.* **4**), oxidation at pH 9.0 appears to have produced all three monocarboxylic acids, and two of the possible three dicarboxylic acids (*viz.* **4** and **5**). There was no evidence of formation of **6** or the possible tricarboxylic acid derivative. There have been claims in a symposium abstract[9] and in a patent,[10] to the isolation of high yields of a sucrose tricarboxylic acid from this type of oxidation, but few details were provided and no more detailed publication has appeared. The procedure utilized pH 6.5 with more concentrated sucrose solutions and much larger amounts of catalyst than are described herein.

Attempts to isolate disaccharide acids from the pH 9.0 oxidation product were unsuccessful. The high proportion of decomposition products (monosaccharide and lower molecular weight acids) frustrated all attempts to resolve the monocarboxylic acid disaccharides from the dicarboxylic acid disaccharides by chromatographic methods.

EXPERIMENTAL

General Methods. All general methods, the apparatus for the catalytic oxidation reactions, the method of reaction pH control, and a discussion of the accuracy of pH values measured at 100°C have been reported previously.[3]

Sucrose Oxidation. Sucrose (5 g, in 500 mL water) was oxidized with platinum (0.5 g, 10% Pt on C) as catalyst at 100 °C (except where indicated); after the sucrose solution was equilibrated at the reaction temperature and pH the oxidation was started by simultaneous addition of oxygen (600 cm^3min^{-1}) and catalyst. The continuous sodium hydroxide titrations (pH-stat method[3-5]) were recorded and are reported here as moles of NaOH consumed per mole of initial sucrose. Samples (1 mL) were removed at regular intervals, filtered (Millipore, 0.45 μm) and sucrose concentration determined by reverse phase HPLC.[3] Quantative results were determined by comparing peak areas with those of standards in separate consecutive injections (all values corrected for volume changes).

Acid products were analysed by ion exchange HPLC (Aminex A-28 (Bio-Rad Labs) in the formate form), as previously described.[3,11] HPLC (eluant; 0.6 M ammonium formate at pH 5.0, 0.5 mL min^{-1}, 60 °C) of the reaction solutions resolved sucrose (4.14 min) and three product peaks, *viz.* monocarboxylic acid disaccharides at 7.35 min, unknown product at 11.43 min (broad peak), and dicarboxylic acid disaccharides at 20.99 min. Peak identification was based on retention times of standards; **4** (scheme 1) and a mixture of **2** and **3** (scheme 1) have previously been isolated and identified.[3] The broad product peak at 11.43 min could not be unequivocally identified from retention times of standards. However, since it eluted near to glucuronic acid (10.76 min), 5-ketogluconic acid (12.01 min), and 2-ketogluconic acid (12.76 min) it was tentatively identified as an unresolved mixture of monosaccharide acids.

^{1}H NMR Spectroscopy. For ^{1}H NMR (300 MHz) spectra, sucrose oxidation reaction samples (*ca.* 10 mL) were mixed with Amberlite IR120(H) ion exchange resin, filtered (Millipore, 0.45 μm), dried (40 °C, 2 mm Hg), and then twice pre-exchanged with D_2O. The spectra were recorded in D_2O, using 1,4-dioxane-d_8 as an internal standard (for ^{1}H NMR 3.55 ppm).

Acid Hydrolysis of Sucrose Oxidation Product. A slurry of Amberlite IR120(H) ion exchange resin (0.5 mL, prewashed in boiling water) was added to a filtered 180 min pH 9.0 oxidation reaction solution (*ca.* 2.0 mL) and heated to 100 °C. After 60 min the solution was cooled and filtered. Ion exchange HPLC analysis ([Aminex A-28 column] eluant; 0.3 M ammonium formate at pH 3.5, 0.5 mL min^{-1}, 60 °C) resolved D-glucuronolactone at 7.97 min, 5-ketomannonic acid at 25.65 min, D-glucuronic acid at 28.12 min and 2-keto-D-gluconic acid at 36.9 min.

REFERENCES AND NOTES

1*. Present address for correspondence: Sugar Processing Research Institute, Inc., 1100 Robert E. Lee Blvd., New Orleans, LA 70124 USA.

2. Wood Chemistry Laboratory, University of Montana, Missoula, MT 59812 USA.

3. L. A. Edye, G. V. Meehan, and G. N. Richards, *J. Carbohydr. Chem.*, **10**(1), 11 (1991).

4. H. G. J. De Wilt, and B. F. M. Kuster, *Carbohydr. Res.*, **19**, 5 (1971).

5. H. G. J. De Wilt, and H. S. van der Baan, *Ind. Eng. Chem. Prod. Res. Dev.*, **11**, 374 (1972).

6. K. Heyns, W.-D. Soldat, and P. Köll, *Chem. Ber.*, **108**, 2619 (1975).

7. C. L. Mehltretter, and B. H. Alexander, R. L. Mellies, and C. E. Rist, *J. Am. Chem. Soc.*, **73**, 2424 (1951).

8. K. Heyns, *Ann. Chem. Pharm.*, **558**, 177 (1947).

9. I. Leupold, M. Wiesner, and W. Fritsche-Lang, *Eurocarb*, **5**, D-1 (1989), Prague.

10. W. Fritsche-Lang, I. Leupold, and M. Schlingmann, *European Patent*, EP 0 218 150 A3 (1986).

11. J. D. Blake, M. L. Clarke, and G. N. Richards, *J. Chromatogr.*, **312**, 211 (1984).