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Oxidation of methyl and *n*-octyl α -D-glucopyranoside over graphite-supported platinum catalysts: effect of the alkyl substituent on activity and selectivity

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Abstract

The oxidation of methyl and *n*-octyl α -D-glucopyranoside to methyl and *n*-octyl α -D-glucopyranosiduronate with molecular oxygen over a graphite-supported platinum catalyst was investigated. An increase of the length of the *n*-alkyl substituent from methyl to *n*-octyl resulted in a ten-fold decrease of the catalyst activity and an increase of the selectivity at pH 8.0 and 323 K. The selectivity decreased with increasing pH. The lower activity for a longer *n*-alkyl substituent is attributed to steric effects upon adsorption on the platinum surface and not to internal diffusion limitations. A tentative reaction scheme is presented, which describes the formation of side products through oxidation of secondary hydroxyl groups, ring cleavage and hydrolysis. Major side products are mono- and di-carboxylates with 2, 4, and 6 carbon atoms and mono-carboxylates, resulting from the oxidation of the alkyl substituent. C–C-Bond cleavage mainly occurs between C-2 and C-3 or C-4 and C-5, the former being less important for a longer alkyl substituent. The higher selectivity for a longer alkyl substituent is attributed to its protecting ability against hydrolysis and the exposition of neighboring hydroxyl groups to the platinum surface. © 1997 Elsevier Science Ltd.

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1. Introduction

The platinum catalyzed selective oxidation of alkyl α -D-glucopyranosides is an environmentally friendly and industrially attractive process [1,2]. The oxidation products of these renewable-based chemicals can, for example, be applied as anionic surface active agents [3,4].

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Although the high number of hydroxyl groups in alkyl α -D-glucopyranosides may give rise to selectivity problems, the aqueous phase platinum catalyzed oxidation can be performed very selectively [1]. In neutral or slightly alkaline media, the oxidation of methyl or *n*-octyl α -D-glucopyranoside (1, 4) proceeds via methyl or *n*-octyl α -D-gluco-hexodialdo-1,5-pyranose (2, 5) to methyl or *n*-octyl α -D-glucopyranosiduronate (3, 6):



The selectivity aspect of carbohydrate oxidation has been reviewed by Heyns and Paulsen [5]. It was concluded that, when the hemi-acetal group is protected by an alkyl substituent the primary alcohol group is preferentially oxidized with respect to secondary alcohol groups. Schuurman et al. [6] reported that the selectivity for C-6 oxidation of methyl α -Dglucopyranoside is approximately 70% at full conversion. For longer *n*-alkyl chains (C-8–C-12) a higher selectivity is reported [1,7]. Side products are formed due to hydrolysis or ring cleavage upon oxidation of secondary alcohol functions, which leads to C-1-C-5 mono- and di-carboxylic acids [8,9]. The effect of the alkyl substituent on the selectivity for C-6 oxidation is generally attributed to its stabilizing effect preventing hydrolysis and oxidation of secondary hydroxyl groups [1]. The stabilizing effect may be caused by a change of the pK_a values of alcohol groups, the ease at which hydrogen abstraction occurs and the way in which the adsorption of the carbohydrate molecule on

the platinum surface occurs [7]. Furthermore, due to steric effects the exposition of secondary hydroxyl groups to the catalytic active surface is reduced for larger n-alkyl substituents [1,7]. Also, side products may be formed via reactions that are not catalyzed by platinum, such as alkaline degradation [10].

For heterogeneous catalyzed oxidation reactions, the overall rate or the catalyst activity will strongly depend on the physical and chemical properties of the alkyl α -D-glucopyranoside. The external and internal diffusion coefficient will be smaller for longer n-alkyl chains due to their larger molecular size, especially in case micelles are formed due to the hydrophobic character of long alkyl chains [3]. Pore diffusion may be influenced by the hydrophobic alkyl chain, which has a low affinity for the aqueous phase and may physisorb on the catalyst support. Furthermore, steric factors will determine the orientation of the hydroxyl group upon adsorption of the alkyl α -D-glucopyranoside on a platinum particle as well as the maximum fractional coverage of the platinum surface.

In this paper, the effect of the alkyl substituent on the activity and selectivity for the oxidation of methyl and *n*-octyl α -D-glucopyranoside is investigated with emphasis on the side products that are formed. A tentative reaction scheme is developed, which accounts for the formation of side products during the oxidation of alkyl α -D-glucopyranosides.

2. Results and discussion

Activity.—As shown in Table 1, the initial rate of consumption of methyl α -D-glucopyranoside (1) at pH 10.0 is smaller than at pH 8.0. It is also shown that the initial rate of consumption of hydroxide at pH 10.0 is equal to the rate at pH 8.0. These results are different from those of Schuurman et al. [6], who reported a linear increase of the rate at a pH higher than 8.5 for the oxidation of methyl α -D-glucopyranoside over a carbon-supported platinum cata-

Table 1

Initial rate of carbohydrate consumption, $R_{w,RCH,OH}^0$, and hydroxide consumption, $R_{w,OH}^0$ for the oxidation of methyl and *n*-octyl α -D-glucopyranoside (1, 4). Conditions: T = 323 K, $p_{O_2} = 40$ kPa, $C_{cat} = 2$ kg m⁻³, $C^0 = 100$ mol m⁻³

Reactant	pH [-]	$R^{0}_{w,RCH_{2}OH} \left[mmol kg^{-1}_{cat} s^{-1} \right]$	$R_{w,OH}^{0}$ [mmol kg _{cat} ⁻¹ s ⁻¹]
Methyl α -D-glucopyranoside (1)	8.0	5.0	4.7
Methyl α -D-glucopyranoside (1)	10.0	3.9	4.5
<i>n</i> -Octyl α -D-glucopyranoside (4)	8.0	0.56	0.57

lyst. The pH effect was described by a separate reaction path for the methyl α -D-glucopyranoside anion, of which the concentration increases with increasing pH. However, the effect of the pH may be attributed to other parameters as well, such as the physical and chemical properties of the catalyst support or the pH dependence of the concentration of intermediate aldehyde and side products, which will be discussed in the next section.

The initial oxidation rate decreases significantly with increasing molecular size. The initial rate of consumption of *n*-octyl α -D-glucopyranoside (4) is almost 10 times smaller than the initial rate of consumption of methyl α -D-glucopyranoside (1), as indicated in Table 1.

A recent kinetic study [11] in which platinum catalysts with different supports were used, showed that intraparticle diffusion limitation does not play an important role for *n*-octyl α -D-glucopyranoside (4). Therefore, the much lower rate observed for a larger *n*-alkyl substituent cannot be explained by the occurrence of transport limitation, resulting from the larger molecular size or the formation of micelle-like structures [3].

The decrease of the rate for a longer *n*-alkyl substituent is therefore most likely caused by steric effects upon adsorption on the platinum surface. The size of the *n*-alkyl substituent and its interaction with the catalyst will determine the orientation of the molecule, when it is adsorbed on a platinum particle. If the orientation of the hydroxyl group to be oxidized becomes less favorable, the rate of the surface reaction decreases. As a result the overall rate decreases, since recent kinetic studies [6,12] show that the reaction between the adsorbed carbohydrate and chemisorbed oxygen is the rate determining step. Another explanation to account for the lower rate for a longer *n*-alkyl substituent is that the maximum fractional coverage of the platinum surface decreases with an increase of the molecular size.

Selectivity for C-6 oxidation.—There are remarkable differences between the oxidation of methyl α -D-glucopyranoside (1) at pH 8.0 (Fig. 1a) and at pH 10.0 (Fig. 1b). Firstly, the concentration of the reactive intermediate, methyl α -D-gluco-hexodialdo-1,5-pyranose (2), is relatively higher at pH 8.0. At pH 10.0 the intermediate (2) vanishes rapidly, whereas at pH 8.0 the intermediate concentration still equals 1.0 mol m⁻³ at the end of the reaction. The higher concentration of 2 observed for pH 8.0 may explain that the initial rate of consumption of methyl α -Dglucopyranoside (1) is higher, although an equal ini-



Fig. 1. Concentration (left axis) and selectivity (right axis) versus reaction time for the oxidation of (a) methyl α -D-glucopyranoside (1) at pH 8.0, (b) methyl α -D-glucopyranoside (1) at pH 10.0, (c) *n*-octyl α -D-glucopyranoside (4) at pH 8.0. Other conditions: T = 323 K, $p_{O_2} = 40$ kPa, $C_{cat} = 2$ kg m⁻³.

tial hydroxide consumption is observed (Table 1), since hydroxide is not involved in the formation of 2. The relatively low concentration of 2 observed at pH 8.0 and 10.0 is in agreement with Schuurman et al. [6], who showed that the ratio of the rate of oxidation of methyl α -D-gluco-hexodialdo-1,5-pyranose (2) to that of methyl α -D-glucopyranoside (1) is larger than 100. Dirkx [8] reported that this ratio increases with increasing pH, comparing the rate of oxidation of D-glucose and D-gluconic acid. This pH dependence for the oxidation of aldehyde functions may well explain the lower concentration of 2 at pH 10.0.

Secondly, the selectivity at which methyl α -D-glucopyranosiduronate (3) is formed, decreases with increasing pH. At pH 8.0 the selectivity is higher than 87% (Fig. 1a), whereas at pH 10.0 the selectivity drops to less than 80% (Fig. 1b).



Fig. 2. Side product formation during oxidation of methyl α -D-glucopyranoside (1) at pH 8.0, reported in Fig. 1a. (a) Mono- and (b) di-carboxylates. Numbering: see Scheme 1.

The results of the oxidation of *n*-octyl α -D-glucopyranoside (4) are depicted in Fig. 1c. The intermediate aldehyde (5) was not detected and may only be present in very small amounts since up to a conversion of 0.4 the carbon balance reaches 100%. The selectivity for *n*-octyl α -D-glucopyranosiduronate (6) amounts to more than 93% up to a conversion of 0.4. *n*-Octyl α -D-glucopyranoside (4) is thus oxidized with a higher selectivity than methyl α -D-glucopyranoside (1). Note that this higher selectivity is obtained, although side reactions are relatively more important during the oxidation of 4, since the rate of the main reaction is significantly lower (Table 1) and the total oxidation time is longer (Fig. 1). The observed increase of the selectivity for a longer alkyl substituent is in agreement with van Bekkum [1], who reported a selectivity of more than 90% for the oxidation of octyl α -D-glucopyranoside, compared to 70% for methyl α -D-glucopyranoside.

Side products.—Figs. 2–4 show the evolution of the concentration of mono- and di-carboxylates that could be identified as side products for the oxidations reported in Fig. 1. No distinction could be made between D-erythronate (11) and glycerate (14) on the basis of retention times, but it is expected that the concentration of glycerate is low, since tartronate (15), which is produced upon oxidation of glycerate, was not observed at pH 8.0. For the same reason, the D-gluconate (7) concentration could not be determined separately from that of 1 and 4. Due to the



Fig. 3. Side product formation during oxidation of methyl α -D-glucopyranoside (1) at pH 10.0, reported in Fig. 1b. (a) Mono- and (b) di-carboxylates. Numbering: see Scheme 1.

uncertainties in the identification of side products, conclusions are preliminary and should be considered with care.

Major side products are D-erythronate (11), glycolate (16) and formate (9) as mono-carboxylates and D-glucarate (8), tartrate (12, 17), and oxalate (13) as di-carboxylates. For the oxidation of *n*-octyl α -Dglucopyranoside octanoate, (10) is also observed.



Fig. 4. Side product formation during oxidation of *n*-octyl α -D-glucopyranoside (4) at pH 8.0, reported in Fig. 1c. (a) Mono- and (b) di-carboxylates. Numbering: see Scheme 1.

The amount of side products produced during the oxidation of methyl α -D-glucopyranoside is larger at higher pH. Except for D-erythronate (11) and tartrate (12, 17), the concentration of each side product is higher at pH 10.0 than at pH 8.0. For *n*-octyl α -D-glucopyranoside (4), the total amount of side products is lower than for methyl α -D-glucopyranoside (1), resulting in a higher selectivity (Fig. 1).

The oxidation of secondary hydroxyl functions may start from methyl or *n*-octyl α -D-glucopyranoside (1, 4) or methyl or *n*-octyl α -D-glucopyranosiduronate (3, 6). Beside the C-6 carboxylate product other mono-carboxylates - in small amounts - are formed at the start of the oxidation, indicating that side oxidation reactions can occur starting from alkyl α -D-glucopyranoside. No clear conclusion can be drawn on whether di-carboxylates originate from side oxidations starting from alkyl α -D-glucopyranosiduronate or that they are only formed through consecutive oxidation of primary side products. It was reported by van Dam et al. [9] for the oxidation of D-glucose 1-phosphate that side reactions primarily start from the D-glucose 1-phosphate rather than its C-6 oxidation product, because the COO⁻ substituent at C-5 has a higher protecting ability towards C-4 oxidation than the CH₂OH substituent. Side oxidation reactions starting from the aldehyde intermediate (2, 5) are less likely, because the aldehyde function is oxidized much more readily than an alcohol function [6]. Dirkx [8], for example, reported that the oxidation of D-glucuronic acid yields D-glucaric acid with a selectivity of almost 100%.

The primary side products undergo further oxidation. This is clear from Fig. 4a, in which the concentration of mono-carboxylates, which still contain hydroxyl functions, reaches a maximum, due to consecutive oxidation to di-carboxylates and further C-Cbond cleavage. The decrease of the concentration of mono-carboxylates may be attributed to the low catalyst activity for *n*-octyl α -D-glucopyranoside oxidation as indicated in Table 1, which necessitated a longer reaction time of 1×10^5 s. In this way the contribution of slow consecutive reactions is relatively larger for *n*-octyl α -D-glucopyranoside than for methyl α -D-glucopyranoside. Still, at pH 8 the selectivity for *n*-octyl α -D-glucopyranoside oxidation is higher than for methyl α -D-glucopyranoside (Fig. 1).

Oxalate (13) is the main dicarboxylate that is produced. During the oxidation of *n*-octyl α -D-glucopyranoside, further oxidation to carbon dioxide is likely since calculations show that only 80% of the total hydroxide consumption was accounted for by the carboxylates analyzed. This is in agreement with the observed decrease of the carbon balance and the selectivity after a conversion of 40%. For the oxidation of methyl α -D-glucopyranoside, the amount of unidentified side products must be rather small since the carbon balance does not deviate significantly from 100%, the calculation of the selectivity with Eqs. (1) and (2) gives equal results, and the hydroxide consumption is nearly completely accounted for by the total amount of carboxylates analyzed.

A simplified reaction scheme for side product formation, starting from methyl or *n*-octyl α -D-glucopyranoside (1, 4) or methyl or *n*-octyl α -D-glucopyranosiduronate (3, 6) is shown in Scheme 1. Four routes are considered: (I) direct hydrolysis, which results in C-1/C-8 and C-6 products; (II) C-2/C-3 oxidation followed by hydrolysis, resulting in C-1/C-8, C-2, and C-4 products; (III) C-3/C-4 oxidation and hydrolysis giving C-1/C-8 and C-3 products; and (IV) C-4/C-5 oxidation and hydrolysis, which results in C-1/C-8, C-2, and C-4 products. It is assumed that the primary di-carboxylate anions in routes II and III undergo rapid hydrolysis. Since no C-5 products were observed, C-1/C-2 or C-5/C-6 oxidation were not considered as possible routes. Aldehyde intermediates are not incorporated, because of their high reactivity towards O_2/Pt . This is in agreement with the HPLC analysis results, since no products containing an aldehyde group were detected. Also, consecutive oxidation products and further C-C-bond cleavage are not taken into account.

In spite of its simplicity, the scheme accounts for all side products that were identified and shown in Figs. 2-4. The side products formed are predominantly products with 1, 2, 4, or 6 carbon atoms and for *n*-octyl α -D-glucopyranoside oxidation also the C-8 product. The C-1 product, formate (9), or the C-8 product, octanoate (10), are formed through hydrolysis and oxidation of the leaving -OR group. These products are formed in all four routes, which is in agreement with the relatively high concentrations reported in Figs. 2-4. The relatively high concentrations of D-glucarate also indicate that direct hydrolysis occurs, according to route I. Hydrolysis leading to the removal of the alkyl substituent must be regarded as a heterogeneously rather than a homogeneously catalyzed reaction, because it was observed that the rate at which hydrolysis occurs is much lower in the absence of the catalyst or in the absence of oxygen. Formate anions also result from C-C-bond cleavage due to consecutive oxidation of primary side prod-



Scheme 1. Simplified reaction scheme for the formation of side products during the oxidation of alkyl α -D-glucopyranosides.

ucts, since formate is also observed during the oxidation of *n*-octyl α -D-glucopyranoside (Fig. 4), in which case it can only originate from consecutive oxidations. C-2 And C-4 products are the result of ring cleavage between C-2 and C-3 or C-4 and C-5, followed by hydrolysis. This corresponds to routes II and IV in Scheme 1. C-4/C-5 oxidation is considered, because of the higher concentration of glycolate (16) relative to oxalate (13), which can only be explained by this route. At C-5, the hydroxyl group may not be directly accessible for oxidation because of the hemi-acetal structure, but oxidation can take place upon hydrolysis.

It is less clear which secondary alcohol function is preferably oxidized. Heyns and Paulsen [5] showed that, for the platinum catalyzed oxidation of carbohydrates, the increasing order of reactivity of the functional group towards oxygen is: equatorial hydroxyl < axial hydroxyl < primary hydroxyl < hemiacetal. In the stable conformation of alkyl α -D-glucopyranoside the C-2, C-3, and C-4 secondary hydroxyl groups are all equatorially directed. Consequently, no preference can be concluded. However, for the oxidation of glucose 1-phosphate, van Dam et al. [9] concluded from the dependence of the stabilization towards ring oxidation on the substituent at C-5 that the oxidation would start at C-4. This would indicate that, in Scheme 1, the preferred route of side product formation is route IV rather than route II, which takes place beside direct hydrolysis according to route I. A more detailed analysis of tartrate [*meso-* (12) or optically active (17)] could be of further help.

Two important effects of the pH are observed. First, the higher concentration of tartronate (15) at pH 10.0 in comparison with pH 8.0 may indicate that route III becomes more favorable at higher pH. Second, consecutive oxidation may be faster at pH 10.0. The lower concentration of D-erythronate (11) at higher pH may be attributed to consecutive oxidation to oxalate (13) or tartronate (15), which would explain the higher concentrations of these di-carboxy-lates at pH 10.0. Two effects of the alkyl chain on the side product formation are observed. First, direct hydrolysis occurs much faster for methyl α -D-glucopyranoside than for *n*-octyl α -D-glucopyranoside oxidation, since the concentration of D-glucarate (8) is much higher for the oxidation of the former reactant. The lower hydrolysis rate for the *n*-octyl chain may be attributed to the stabilizing effect of the more bulky group.

Second, for *n*-octyl α -D-glucopyranoside C-4/C-5 oxidation according to route IV occurs faster than C-2/C-3 oxidation according to route II, whereas for methyl α -D-glucopyranoside the opposite is observed. This is concluded from the fact that, for *n*-octyl α -D-glucopyranoside oxidation, the ratio of the glycolate (16) to D-erythronate (11) concentration is larger than unity and for methyl α -D-glucopyranoside it is less than unity. It is postulated that the alkyl substituent hampers the exposition of the most nearby hydroxyl groups, which is in agreement with earlier work [1,7,13]. Especially in case micelles are formed due to the hydrophobic character of the long alkyl chain, the hydroxyl groups at C-4 and C-5 are likely to be more exposed to the platinum surface upon adsorption than C-2 and C-3. This results in an increase of the C-4/C-5 to C-2/C-3 oxidation ratio for a longer alkyl substituent.

3. Conclusions

The platinum-catalyzed C-6 oxidation of alkyl α -D-glucopyranoside occurs at a higher selectivity, but at a lower rate for longer alkyl substituents. The latter is attributed to the steric effect of the bulky substituent upon adsorption on the platinum surface. The higher selectivity for a longer alkyl substituent is attributed to its protection against hydrolysis and oxidation of secondary hydroxyl groups, located near the alkyl substituent.

The side products that are mainly formed are mono- or di-carboxylates with 2, 4, and 6 carbon atoms and mono-carboxylates, resulting from the oxidation of the alkyl chain. Side oxidation reactions can start from alkyl α -D-glucopyranoside as well as the C-6 oxidation product. Consecutive oxidation of primary side products was also observed. The concentration of alkyl α -D-gluco-hexodialdo-1,5-pyranose decreases and the amount of side products increases with increasing pH. C–C-Bond cleavage mainly takes place between C-2 and C-3 or C-4 and C-5, the former becoming less important for longer alkyl substituents. This is attributed to steric effects upon adsorption, which reduces the exposition of the hydroxyl groups in the vicinity of the alkyl substituent.

4. Experimental

Catalyst.—A 3.3 wt% platinum on graphite catalyst with a BET surface area of $1.02 \times 10^5 \text{ m}^2 \text{ kg}_{cat}^{-1}$ and a maximum powder diameter of 30 μ m was prepared according to the procedure of Richard and Gallezot [14]. Details of this procedure are described elsewhere [15].

Experimental set-up.—Semi-batch oxidation reactions were performed in a 0.7 L three-phase slurry reactor. The reactor was equipped with a stirrer, a pH electrode (Radiometer PHC2402), and an oxygen electrode (Ingold 341003005). The temperature in the reactor was measured with a Pt-100 probe and controlled by a thermostatic water bath (Beun de Ronde, CS6, R22) through circulation of water through the double wall of the reactor. The pH in the reactor was controlled by feeding a NaOH soln by means of a titration unit (Radiometer TTT80).

Reaction procedure.-Before each experiment, 0.7-1.25 g fresh and dry catalyst was reduced in 0.2 L water at 323 K for half an hour in a hydrogen flow. Next, a carbohydrate containing soln was added, which was kept at 323 K, and 0.35 L of a 100 mol m⁻³ soln was obtained. The reactor was purged with nitrogen for 1000 s and the reaction was started by feeding oxygen. A constant total gas feed flow rate of $1.4 \times 10^{-4} \text{ mol s}^{-1}$ (200 N mL min⁻¹) and a temperature of 323 K were maintained. The stirring rate amounted to 20 s⁻¹ and to 10 s⁻¹ for *n*-octyl α -D-glucopyranoside in order to reduce the formation of foam. Deactivation by over-oxidation of the catalyst [12] was overcome by replacement of the oxygen containing gas feed by nitrogen for 1000 s, which resulted in an increase of the catalyst activity upon resumption of the oxygen feed [12]. It was verified experimentally and by calculations that the experiments were not significantly influenced by mass and heat transport limitation.

Reagents.—All reagents were of analytical grade. Methyl α -D-glucopyranoside (1) was obtained from Fluka. *n*-Octyl α -D-glucopyranoside (4) was prepared from D-glucose (Janssen) and 1-octanol (Aldrich) according to the procedure of Straathof et al. [16]. As a catalyst a cation-exchange resin in the H⁺-form (K2411 supplied by Bayer) was used. Recrystallization in water gave white needles. Purity was checked by HPLC, the clearing point, 389.7 K, lit. 390 K [16], and the specific rotation, $[\alpha]_D^{20} + 121 \pm 2^\circ$, lit. +118° [17].

HPLC analysis.-Samples of the reaction mixtures were obtained by collection of 1.5-mL reaction mixture with a syringe, followed by a filtration over a Millipore membrane filter with a pore diameter of 0.45 μ m. Quantitative analysis of methyl α -D-glucopyranoside (1) was performed on two columns in series: (1) a 70×4.6 -mm ID Lichroma SS tube packed with an anion-exchange resin (Benson BA-X8) having quaternary ammonium groups brought into the acetate-form. On this column, carboxylic acids exchange with acetate ions and are adsorbed on this column; (2) a 280×4.6 -mm ID Lichroma SS tube packed with a cation-exchange resin (Benson BC-X8) in the H⁺-form. Analysis was done at 343 K at a flow rate of 0.4 mLmin⁻¹ with water as eluent using refractive index detection. Reaction mixtures of n-octyl α -D-glucopyranoside were analyzed using a 280 \times 4.6 mm reversed-phase C₁₈ ID Lichroma SS column (Chrompack). The eluent consisted of 2:3 50 mol m^{-3} formate buffer (pH 3.45)-MeOH. The column temperature was 333 K and the flow rate amounted to 0.5 mL min⁻¹. Refractive index detection was used. In order to avoid crystallization of *n*-octyl α -D-glucopyranoside, the samples were kept in the autosampler above the Krafft-point [18] at 328 K. Carboxylic acid products were separated on a 280×4.6 mm ID Lichroma SS tube packed with a anion-exchange resin (Benson BA-X8), brought in the SO_4^{2-} -form by washing with a 200 mol m⁻³ ammonium sulfate soln prior to packing. Analysis was done at 343 K at a flow rate of 1.1 mLmin⁻¹ 200 mol m⁻³ (NH₄)₂SO₄ soln brought at a pH of 8. Both UV-VIS at 212 nm and refractive index (RI) detection were used. Identification and quantification of all products was based on external standards.

Selectivity.—The selectivity for C-6 oxidation resulting in methyl or *n*-octyl α -D-glucopyranosiduronate (3, 6), S, is calculated as:

$$S = \frac{C_{3,6}}{C_{1,4}^0 - (C_{1,4} + C_{2,5})} \tag{1}$$

where $C_{3,6}$ is the methyl or *n*-octyl α -D-glucopyranosiduronate concn, $C_{1,4}^0$ is the initial methyl or *n*-octyl α -D-glucopyranoside concn, $C_{1,4}$ is the methyl or *n*-octyl α -D-glucopyranoside concn and $C_{2,5}$ is the methyl or *n*-octyl α -D-gluco-hexodialdo-1,5-pyranose concn. Note that, in Eq. (1), the intermediate aldehyde (2, 5) is still considered as a reactant. Hence, S will only deviate from 100% if other than C-6 oxidation occurs. At low conversion, the accuracy of Eq. (1) is limited, since a relatively small denominator results from the substraction of two relatively large numbers. Therefore, at low conversion the calculation of the selectivity is based on the side products observed and calculated according to:

$$S = \frac{n_{C(3,6)}C_{3,6}}{\sum n_{C,i}C_i}, \quad i \neq 1,2,4,5$$
(2)

where $n_{C,i}$ is the number of carbon atoms and C_i is the concentration of product i ($i \neq 1, 2, 4, \text{ or } 5$). In Eq. (2) the intermediate aldehyde (2, 5) is also not taken into account, i.e. it is still considered as a reactant. Note that at high conversion, Eq. (1) is more accurate than Eq. (2) in case side products are produced, which are not detected or identified.

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