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The platinum-catalyzed oxidation of inulin

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Abstract

The oxidation of inulin with Pt/C as catalyst was studied. Methyl α-D-fructofuranoside was used as a model compound for the monomeric unit of inulin. Oxidation occurred selectively at the C-6 position in a high yield (79%). The rate of oxidation and the degree of oxidation obtained for inulin oligosaccharides decreased upon increase of the chain length of the substrate. Inulin could only be oxidized partially: the oxidation degree obtained was 20% of the primary hydroxy groups for inulin with an average dp 30. Possible explanations for these relatively low conversions are discussed. Adsorption and desorption phenomena appear to play an important role during the oxidation process. © 1998 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Conversion of inulin, a linear β-(2 → 1)-linked fructan with a D-glucose unit at the reducing end, into industrially relevant products, such as polycarboxylates, has become of increasing interest. These polycarboxylates have many potential applications, for example, as calcium sequestering agents, metal ion carriers and dispersing agents. Selective oxidation of inulin is a possible way to convert it into polycarboxylates.

The noble metal catalyzed oxidation with oxygen as the oxidant is a clean oxidation method: water is used as solvent, molecular oxygen as oxidant and the catalysts are heterogeneous. The oxidation proceeds under mild conditions (temperature < 90 °C, pH neutral or slightly alkaline, atmospheric pressure). Therefore, it is an attractive method which has been widely studied for carbohydrates [1,2].

The selectivity of the platinum-catalyzed oxidation of polyols has been shown to decrease in the order: hemi-acetal > primary alcohol > secondary alcohol [3]. Aldoses are converted into the corresponding aldonic acids. For example, D-glucose is converted into D-gluconic acid with 72% selectivity over a Pt/C catalyst [4]. With a bismuth-promoted Pd/C catalyst, a conversion of > 97% toward D-gluconic acid has been achieved [2]. Primary hydroxy functions are selectively oxidized over platinum during the oxidation of carbohydrates with protected hemi-acetal functions [5]. Recently, it has been reported that fructose gives, by contrast, both oxidation of the C-1 primary and the C-5 secondary hydroxy function

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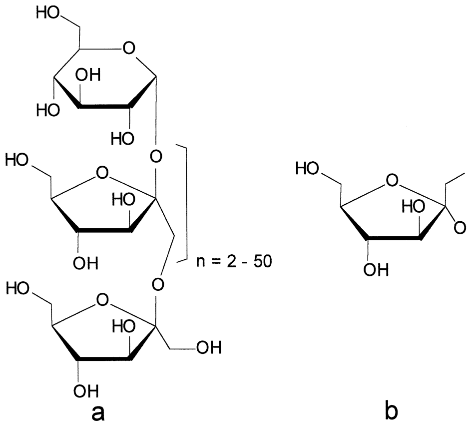


Scheme 1. Inulin (a) and methyl α-D-fructofuranoside (b).

to give a mixture of 2-ketogluconic acid (44%) and 5-ketofructose (30%) [6].

The platinum-catalyzed oxidation of sucrose, the smallest inulin member, has been investigated by several groups. Fritsche-Lang et al. [7] claimed that all three primary hydroxy functions are oxidized, leading to the formation of tricarboxysucrose. A yield of 35% of tricarboxylic acid was obtained upon oxidation (80 °C, pH 9) of sucrose in water over Pt/C. Edye et al. [8,9] observed selective oxidation of sucrose at the C-6 and C-6′ position (yield 68%) when Pt/C was used at neutral pH and 100 °C. There was no evidence of oxidation of the 1′-hydroxymethyl group. An attempt to oxidize inulin over Pt/C resulted in a product with an oxidation degree of 7% after 8.5 h reaction. Also in this case, the selectivity for the C-6 position was high [8]. Recently, a new sucrose oxidation process leading to sucrose monocarboxylic acids was developed by Südzucker [10]. In this process an oxygen-saturated aqueous sucrose solution is continuously fed to a fixed bed of a 5% Pt/C catalyst. The pH is adjusted by adding $NaHCO_3$. The product stream is separated by electrodialysis into oxidized products and a recycle stream. The catalyst is reported to be perfectly stable under these conditions of relatively low oxygen concentration and sucrose conversion. Sucrose monocarboxylic acids are formed with a selectivity of 96%. The three primary CH_2OH groups are converted in a ratio 47:44:5 [C-6 (fructose):C-6′ (glucose):C-1 (fructose)]. This ratio is understandable in terms of Pt-surface accessibility for the three CH_2OH groups.

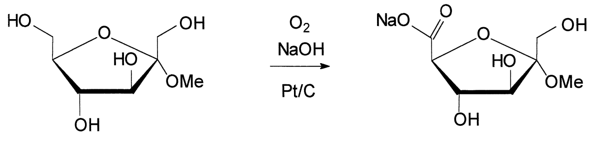
This paper deals with the Pt-catalyzed oxidation of inulin. The analysis of the products of inulin, which is a complex mixture of oxidized oligosaccharides with different chain lengths (dp 2–50), is not trivial. Therefore, methyl α-D-fructofuranoside [11], a molecule which represents the basic unit of the inulin chain (Scheme 1), was used as a model compound.

2. Results and discussion

Pt-catalyzed oxidation of methyl α-D-fructofuranoside.—Previously, we have shown that methyl α-D-fructofuranoside can be oxidized with oxygen as the oxidant and Pt on activated carbon (5%) as the catalyst at 60 °C and pH 9. The main oxidation product is methyl 6-carboxy-α-D-fructofuranoside (Scheme 2, selectivity: 83%) [11].

Apparently, the oxidation is selective for the primary hydroxy function at C-6 in the furanoside. When D-fructose was oxidized under the same conditions, the selectivity was low and degradation to small organic acids such as carbonate, oxalate, glyceric acid and glycolate prevailed [6]. Under milder conditions (pH 7.3, 30 °C), the oxidation was selective for C-1 and C-5. D-Fructose consists mainly of the β-pyranose form, in which the C-1 primary hydroxy function and the axial C-5 hydroxy function are sterically most favored for oxidation. The 2-*O*-methyl group in methyl α-D-fructofuranoside fixes the fructose ring in the α-furanose form, of which the C-6 hydroxy function is the most exposed. Moreover, the 2-*O*-methyl group may play a protecting role for the oxidation of the other hydroxy functions in the furanose ring. Further enhancement in selectivity might be achieved by enlarging the 2-*O*-alkyl group, as was observed with the alkyl glucosides [12,13].

Acid hydrolysis of methyl 6-carboxy-α-D-fructofuranoside yielded D-fructuronic acid (D-*lyxo*-5-hexulosonic acid) [11]. In literature [14–16], a preparation of D-*lyxo*-5-hexulosonic acid by isomerization of glucuronic acid (pH 7, 110 °C) has been described. A complex mixture of acids was obtained from which D-*lyxo*-5-hexulosonic acid was isolated via an ion-exchange chromatography procedure. The Pt-catalyzed oxidation of methyl α-D-fructofuranoside followed by acid hydrolysis provides a new simple route for the synthesis of D-fructuronic acid.



Scheme 2. Pt-catalyzed oxidation of methyl α-D-fructofuranoside.

Pt-catalyzed oxidation of inulin.—Inulin (ex chicory, average dp 10) was oxidized under the same conditions as methyl α-D-fructofuranoside. The oxidation products were oxidized inulin and some by-products (bicarbonate, oxalate, glycolate, small amounts of unidentified compounds). Isolation of the oxidized inulin was achieved by precipitation in methanol followed by redissolution and membrane filtration for removal of the low-molecular-weight by-products. The oxidation degree was determined by quantitative ^{13}C NMR spectroscopy and hydrolysis followed by HPLC analysis. HPLC–MS showed that the oxidized monosaccharide units were fructuronic acid and glucuronic acid. Apparently, the oxidation took preferably place at the C-6-position. The oxidation rates of inulin with an average dp 10 and sucrose were compared (Fig. 1), applying the same saccharide concentration (on a monosaccharide basis). The reactions were followed by monitoring the hydroxide consumption and the conversion of glucose and fructose units by HPLC analysis (after hydrolysis to monosaccharides) of samples taken during the reaction.

The chain length of the starting material appeared to have an important influence on the rate of oxidation and the maximum oxidation degree which can be obtained (Table 1). For determining the maximum oxidation degree, the oxidations were carried out for 24 h. After this reaction time, the hydroxide consumption had stopped or become very slow, showing that essentially no further oxidation took place. The initial turnover frequencies for the oxidation of methyl α-D-fructofuranoside, sucrose and inulin with an average dp 10 were determined to be 234, 114 and 42 h^{-1}, respectively (see Table 1). Problems with the oxidation of polysaccharides using heterogeneous catalysis have been encountered by several researchers. Aspinall and Cairncross [17] noticed that the oxidation of arabinoxylan with a Pt catalyst was slow and even after long oxidation periods, the conversion of primary hydroxy groups was incomplete. A recent comparison of the oxidation of methyl α-D-glucopyranoside, octyl α-D-glucopyranoside and β-cyclodextrin over a Pt/C catalyst showed that the initial oxidation rate increases upon decrease of the size of the substrate (ratio of the initial oxidation rates for the three substrates: 100:10:1, respectively) [18]. Also the oxidation of β-cyclodextrin using a bismuth–ruthenium oxide catalyst appeared to be slow in contrast to the oxidation of small substrates, such as methyl α-D-glucopyranoside [19].

Table 1
Oxidation degree of inulin oxidized with O_2 as oxidant and Pt/C as the catalyst (pH 9, 60 °C, 24 h)

Substrate	Oxidation degree (%)	Turnover frequency (h^{-1})
Inulin average dp 30	20	28
Inulin average dp 10	28	42
Nystose (GF_3)	40	116
Sucrose (GF)	75	114
Methyl α-D-fructofuranoside	100[a]	234

[a] After 2 h, maximum yield 83%, see text.

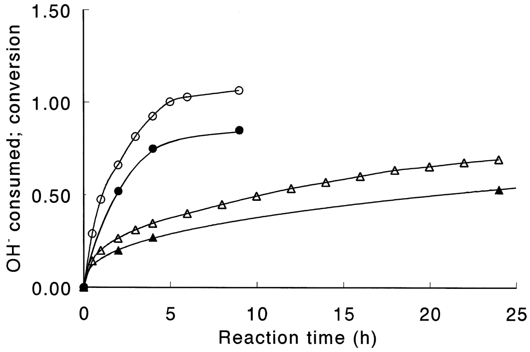


Fig. 1. Hydroxide consumption (open markers) and monosaccharide units converted (filled markers), expressed in mol/mol sugar units, during the Pt-catalyzed oxidation (pH 9, 60 °C, 1 g/80 mL, 0.5 g 5% Pt/C) of inulin (average dp 10, △) and sucrose (○).

Several explanations are possible for the decrease in conversion upon increase of the chain length of the starting material during the Pt-catalyzed oxidation of inulin. Firstly, diffusion of large inulin molecules into the smallest pores of the activated carbon may be limited, so that the Pt-crystallites in these pores are not reached. However, when the oxidation of inulin (dp 10) was repeated with platinum black as the catalyst, the reaction was again slow and incomplete. The maximum oxidation degree obtained was 20% after 24 h. The selectivity of the inulin oxidation with the unsupported catalyst was found to be lower (50% at 25% conversion as compared to 65% at 25% conversion with the Pt/C catalyst). Moreover, Vleeming [18] showed that transport limitation is not responsible for the differences in initial oxidation rate observed for substrates with different sizes (methyl α-D-glucopyranoside, octyl α-D-glucopyranoside and β-cyclodextrin). The turnover frequencies appeared to be independent on the pore size of the catalyst support for the various substrates [18].

Secondly, oxidized oligosaccharides, which carry a negative charge at the pH of the reaction (pH 9), may be expelled by the catalyst surface, so that further oxidation is retarded. This is supported by the fact that *O*-(carboxymethyl)inulin [20] with a low degree of substitution (ds 0.30) is oxidized very slowly. Although 95% of the C-6 positions are free (5% carry a carboxymethyl group), only 8% additional glucose and fructose units were oxidized after 2 h reaction (as compared to 20% for inulin having the same chain length).

A third explanation might be that the catalyst is deactivated rapidly during the oxidation of long chain substrates. Irreversible deactivation may occur by metal particle growth and leaching of the metal during the reaction [18]. However, we found that a catalyst, which was regenerated by filtering off, rinsing with water and reactivating with H_2 for 30 min, is as active during oxidation as a fresh catalyst, showing that irreversible deactivation does not take place under the conditions applied.

Reversible deactivation may be caused by overoxidation (oxygen poisoning) [18]. The redox potential of platinum is, however, high in comparison with other metals used for oxidation (e.g., palladium) and is, therefore, less prone to overoxidation [1]. Inulin with an average dp 10 was oxidized for 1.5 h, then the oxygen was removed from the metal surface by bubbling through nitrogen for about 1 h. Subsequently, the oxidation was restarted by supplying oxygen. The oxidation rate directly after the nitrogen treatment of the catalyst was somewhat higher than before, but it decreased quickly again (Fig. 2). Apparently, overoxidation takes place to a low extent but it cannot be the only reason for the slow oxidation of high-molecular-weight material.

Finally, the catalyst may also be deactivated by covering of the active sites by adsorption of starting material, oxidation products or by-products formed during the oxidation [21]. Polysaccharides (and their intermediate oxidation products) are expected to adsorb stronger than monosaccharides due to the effect of multiple binding sites of the former. Therefore, site-covering and, consequently, deactivation of the catalyst may occur. In competition experiments, the oxidation rate of sucrose was compared with that of sucrose in the presence of inulin and in the presence of *O*-(carboxymethyl)inulin (ds 0.30) by monitoring the hydroxide consumption. Both polymeric substrates appeared to inhibit the oxidation of sucrose (see Fig. 3). The extent of inhibition was somewhat higher with inulin than with *O*-(carboxymethyl)inulin.

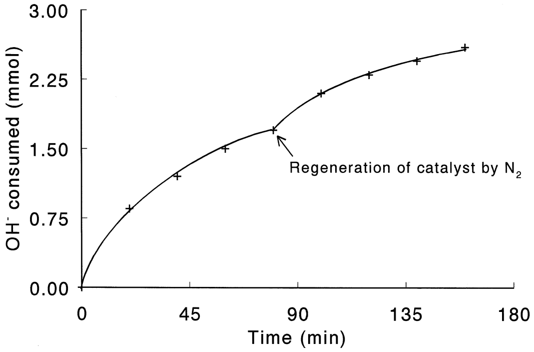


Fig. 2. Oxidation rate of inulin (average dp 10) before and after treatment with N_2 (1 g/80 mL, 0.5 g 5% Pt/C, 60 °C, pH 9).

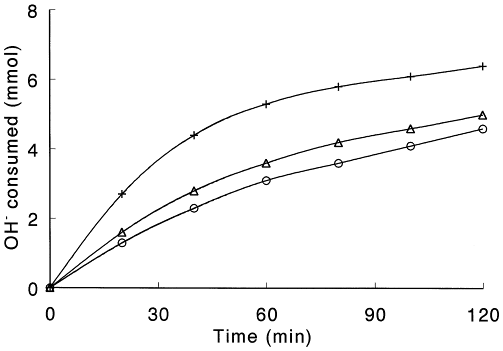


Fig. 3. Hydroxide consumption during the Pt-catalyzed oxidation of 1 g sucrose (+), of 1 g sucrose in the presence of 1 g inulin (○) and of 1 g sucrose in the presence of 1 g *O*-(carboxymethyl)inulin with ds 0.30 (△). The oxidations were carried out in 80 mL water, at pH 9, 60 °C, with 0.5 g 5% Pt/C.

To eliminate the effect of the catalyst support, similar competition experiments were carried out with platinum black as catalyst. Now, the oxidation of sucrose was not inhibited by the presence of inulin. Apparently, strong adsorption of the polysaccharide and its intermediate oxidation products occurs mainly on the support of the Pt/C catalyst. In analogy with Pt/C catalysts, the affinity of the platinum black surface for the substrate once it carries some carboxylate groups, is low: with platinum black as the catalyst, the oxidation of the polycarboxylate *O*-(carboxymethyl)inulin with ds 0.30 was sluggish: the reaction rate and conversion were about the same as with a Pt/C catalyst.

In conclusion, the low conversions obtained for the oxidation of substrates with high molecular weight with platinum on carbon as catalyst can be largely explained by a combination of site-covering of the catalyst by starting materials and intermediate oxidation products due to adsorption on the catalyst sup-

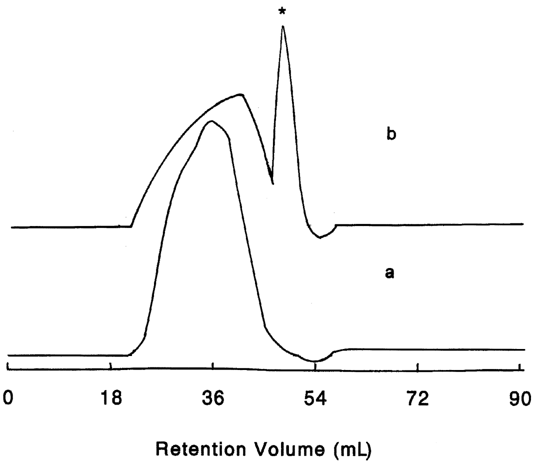


Fig. 4. Elution profiles on Bio-Gel P-6 (RI detection) of inulin (average dp 30) (a) and 20% oxidized inulin (b). The peak marked with a '*' contained low-molecular-weight oxidation products (carbonate, oxalate, glycolate).

port and the low affinity for the platinum surface of carboxylates already formed.

A consequence of the strong adsorption of polymeric starting materials and intermediate oxidation products on the catalyst surface is that the selectivity of the oxidation is lower than for monomeric substrates. Slow desorption of the product enhances the probability of oxidative degradation towards small molecules such as carbonate, oxalate and glycolate. While oxidation of methyl α-D-fructofuranoside at the C-6 position occurred with a selectivity of 83% at 100% conversion, the selectivity during the oxidation of inulin for the C-6 position was about 65% at 25% conversion of the fructose units. Degradation of the inulin chains during oxidation was confirmed by studying the molecular weight distribution of inulin and its oxidation product using gel-permeation chromatography (GPC) on a polyacrylamide gel (Bio-Gel P-6). Inulin with an average dp 30 was oxidized (up to an oxidation degree of 20%) and the reaction mixture obtained was injected onto the column, fractions were collected, hydrolyzed and analyzed by HPLC. The elution profile of the oxidation product of inulin (Fig. 4) shows a broad peak containing oxidized inulin and a peak containing low-molecular weight material (glycolate, oxalate, bicarbonate). The peak maximum of oxidized inulin is shifted towards higher elution volume (lower-molecular-weight) as compared to the peak maximum of inulin, which shows that chain degradation occurs during oxidation. The fractions of low-molecular-weight material and of high molecular weight were combined towards two fractions. The oxidation degree of the material eluting in the first fraction was lower (17%) than in the second fraction (28%). This confirms that the chain length of the substrate is a determining factor for the oxidation degree that can be obtained.

In conclusion, it can be stated that inulin can only partially be oxidized on the C-6 position with Pt/C as catalyst. For the preparation of completely oxidized 6-carboxy inulin, a homogeneous catalyst is more promising. Recently, a new method for the selective oxidation of primary hydroxy groups of polysaccharides, using a nitroxyl radical as the catalyst and hypochlorite as the primary oxidant has been developed [22,23]. However, a low carboxylate content in polysaccharides results already in relatively large changes in properties (solubility, behavior as an electrolyte), which makes the materials of Pt-catalyzed oxidation suitable for special applications. For the preparation of partially oxidized inulin, the Pt-catalyzed oxidation seems an attractive alternative with some advantages as compared to homogeneous catalyzed systems.

3. Experimental

Materials.—Methyl α-D-fructofuranoside was synthesized, purified and oxidized as described before [11]. Two types of inulin were used. The first type, with an average dp of 30, was obtained from E. Merck (Darmstadt, Germany). The second type, isolated from chicory root, was a gift from Sensus (Coöperatie Cosun U.A., Roosendaal, The Netherlands) and is commercially available under the name 'Frutafit'. The average dp is 10.

The Pt/C catalyst was purchased from Janssen Chimica and contained 5% (w/w) platinum on activated carbon. The active metal surface of the catalyst was 1.7 m^2/g (dispersion 13%) as determined by the measurement of the H_2 chemisorption using a Quantachrome Autosorb-1C after reduction of the catalyst with H_2 at 250 °C and evacuation.

^{13}C NMR spectroscopy.—^{13}C NMR spectra were recorded on a Nicolet NT-200 WB and a Varian VXR-400 S spectrometer using D_2O as solvent and *tert*-butanol as internal standard (CH_3 at 31.2 ppm). Quantitative ^{13}C NMR spectra were used to determine the oxidation degree of inulin. The spectra were recorded with a 45° flip angle, an acquisition delay of 30 s, 32 K datapoints and ^1H decoupling during the acquisition only.

HPLC analysis.—The oxidation products were hydrolyzed to monosaccharides by heating (70 °C) in aqueous solution (10 mg/mL) at pH 1.5 (diluted HCl) for 1 h. After neutralization, the solution was analyzed by HPLC (column: Phenomenex [Bester, Amstelveen, The Netherlands], Rezex Organic Acid, 300 × 7.8 mm i.d.; eluent: 0.01 M CF_3COOH; 60 °C; flow rate: 0.6 mL/min; RI and UV_{215} detection). Monochloroacetic acid was used as internal standard. The identity of the compounds was confirmed by LC–MS analysis using the same HPLC system coupled to a VG 70-SE mass spectrometer. Retention times: 8.2 min: oxalate; 9.1 min: fructuronic acid and glucuronic acid [177 ($M^+ - H_2O + 1$), 159 ($M^+ - 2H_2O + 1$), 115 ($M^+ - 2H_2O - CO_2 + 1$), 97 ($M^+ - 3H_2O - CO_2 + 1$)]; 10.1 min: glucose; 10.8 min: fructose [163 ($M^+ - H_2O + 1$), 145 ($M^+ - 2H_2O + 1$), 127 ($M^+ - 3H_2O + 1$)]; 13.1 min: glycolic acid [95 ($M^+ + H_2O + 1$)]; 16.3 min: monochloroacetic acid.

Oxidation with Pt on activated carbon as catalyst.—The oxidation set-up consisted of a glass batch reactor (200 mL) equipped with a gas tight stirrer (1500 rpm) and a thermostat (60 °C). During the reaction, the pH was kept constant automatically using a pH meter (Metrohm 654), coupled to a pH controller (Metrohm 614 Impulsomat) and a motor burette (Metrohm 655 dosimat) containing 1 M NaOH. The O_2 pressure in the reactor was kept constant with an automatic O_2 supply system [24]. This system consisted of a motor burette containing a displacing liquid for dosing O_2 from a thermostated (30 °C) oxygen burette. The burette was operated by a differential pressure sensor. The O_2 and hydroxide consumption were monitored during the reaction.

The catalyst (5% Pt on activated carbon, Janssen Chimica, 500 mg; or Platinum black, Janssen Chimica, 98% Pt, 150 mg) was introduced into the reactor together with 50 mL of water. The reactor was flushed with N_2 for 5 min to remove O_2 from the catalyst, with H_2 for 30 min to activate the catalyst, and then again with N_2 for 5 min. The substrate (1.00 g), dissolved in 30 mL water, was added to the reactor and the reaction was started by increasing the O_2 partial pressure to 0.20 bar and adjusting the pH to 9.00. Samples were withdrawn from the reaction mixture at regular time intervals. After removal of the catalyst, 500 μL of a monochloroacetic acid solution (10 mg/mL) was added as internal standard to 500 μL of the sample. The samples were analyzed by HPLC.

Isolation of oxidized inulin.—The neutralized reaction mixture was concentrated under reduced pressure to a volume of about 10 mL. The resulting mixture was poured into 100 mL well-stirred absolute MeOH. The product precipitated as a white solid, which was filtered off, washed with absolute MeOH and dried under reduced pressure. Finally, salts and traces of low-molecular-weight material were removed by membrane filtration (UTC 60, Toray Industries, Tokyo, Japan) at a pressure of 20 bar. The solution was freeze-dried (yield: 74%).

Gel-permeation chromatography (GPC).—The molecular weight distribution of inulin and oxidized inulin was determined by GPC on a Bio-Gel P-6 (Bio-Rad) column, using the following conditions: column diameter: 0.8 cm; column length: 65 cm; eluent: 0.02 M NH_4HCO_3; flow rate: 6 mL/h; sample: 100 mg/0.5 mL; detection: RI. Fractions of 3 mL were collected with an automatic fraction collector. The fractions containing organic material were combined, hydrolyzed and analyzed by HPLC as described above. The column was calibrated by fractionation of D-fructose, nystose (GF_3) and inulin with an average dp 30 (GF_n).

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