ELSEVIER

Carbohydrate Research 310 (1998) 109–115

CARBOHYDRATE
RESEARCH

Preparation of *O*-(Aminopropyl)inulin

Dorine L. Verraest, Emrin Zitha-Bovens, Joop A. Peters *,
Herman van Bekkum

*Laboratory of Organic Chemistry and Catalysis, Delft University of Technology, Julianalaan 136,
2628 BL Delft, The Netherlands*

Received 20 March 1998; accepted 27 June 1998

Abstract

Inulin ethers carrying primary amino groups have many potential applications. *O*-(Aminopropyl)inulin is obtained from *O*-(cyanoethyl)inulin by reduction of the nitrile groups. Heterogeneously catalyzed hydrogenation using *Raney*-cobalt as the catalyst resulted in only partial conversion of the *O*-cyanoethyl into *O*-aminopropyl groups. Complete conversion of the nitriles to primary amines was achieved by a homogeneous reduction with an excess of sodium borohydride and cobaltous chloride or with metals in liquid ammonia–methanol. Optimal results were obtained with the latter method; 83% of the substituents were converted into primary amines and 17% were lost by dealkylation. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Inulin; Cyanoethylation; Primary amines; Hydrogenation; *Raney*-cobalt

1. Introduction

Nitrogen-containing polysaccharides and polysaccharide derivatives are interesting materials with a wide range of applications. They can, for example, act as ligands with N-donor sites in the selective removal of toxic transition metals from deposits or liquid streams and in the recovery of precious metals. Examples of such ligands based on polysaccharides are the naturally occurring nitrogen-containing polysaccharides chitin, a (1→4)-linked 2-acetamido-2-deoxy-β-D-glucan, and its *N*-deacylated product chitosan. The latter material is applicable for the separation of small amounts of transition metals from sodium and magnesium matrices [1] and for the selective recovery of uranium from diluted solutions such as natural waters [2]. The *N*-carboxymethylated derivative of chitosan has been proposed as precipitating agent for the removal of metal ions from waste water [3].

Besides the use as chelating agent, chitosan has many other applications. Under neutral or acidic conditions, the amino groups are protonated and chitosan is, therefore, a cationic biopolymer. It has been shown to adsorb onto the surface of octacalcium phosphate crystals, due to the electrostatic interaction with the negatively charged crystal surface (HPO_4^{2-}). This adsorption results in a decrease of the crystal growth rate [4]. Chitosan also interacts with proteins and fats with an anionic character, which makes it applicable as a coagulation agent, or in the formulation of cosmetics and hair conditioners [5].

---

* Corresponding author. Fax: +00-31-15-278-1415; e-mail: J.A.Peters@stm.tudelft.nl

PII S0008-6215(98)00174-8

Polysaccharides or polysaccharide derivatives containing primary amines may also be used for linking other molecules, which yield materials with interesting properties. Polymeric surfactants may be obtained by linking amine derivatives with fatty acid anhydrides or halides. The products may be used as emulsifiers or in detergency. Coupling of aminoethyldextran with DTPA- or EDTA-bisanhydride (DTPA = diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetate; EDTA = ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetate) affords an adduct that may be used as contrast agent for magnetic resonance imaging when complexed with a gadolinium ion [6,7]. Amine derivatives may also be coupled with aldehydes. An example of such a coupling reaction is the linking of the semi-synthetic antibiotic, formylrifamycin SV, with a hydrazine derivative of dextran [8].

In this paper the synthesis of a primary amino-derivative of the β-(2→1)-linked fructan inulin is described. Inulin (Fig. 1) occurs as a reserve polysaccharide in many plants and has been commercially available since the beginning of this decade in Europe. Until now inulin has been used mainly in the food sector, but the interest in new industrial applications of inulin and inulin derivatives is increasing [9]. Primary amino-derivatives of inulin have many potential applications in the fields described above. A unique property of inulin derivatives, as compared with derivatives of other polysaccharides, is the low viscosity of aqueous solutions [10]. This may be of advantage for special applications. An attractive route toward a primary amino-derivative is the hydrogenation of the nitrile groups of *O*-(cyanoethyl)inulin, a material which is prepared by reaction of inulin with acrylonitrile as described in a previous paper [11]. The analysis of the distribution of substituents in *O*-(cyanoethyl)-inulin has also been described [12]. The most reactive position of the fructofuranoside units is the C-4 position. The distribution along the inulin backbone has been shown to be uniform [12]. These characteristics are expected to be similar in the hydrogenation product of *O*-(cyanoethyl)inulin. The two-step procedure (cyanoethylation, followed by hydrogenation) may also be applied to other polysaccharides and, therefore, it may provide a general way to functionalize polysaccharides with primary amine groups. Methods for the hydrogenation reaction are discussed here.

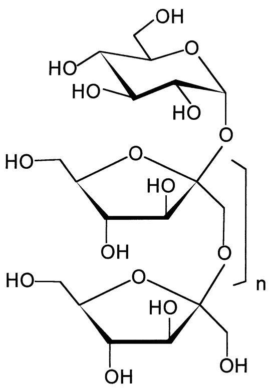

Fig. 1. Structure of inulin.

2. Results and discussion

Hydrogenation of O-*(cyanoethyl)inulin with* Raney-*cobalt as catalyst.*—Various methods are known to convert nitrile groups into primary amines [13,14]. *O*-(Cyanoethyl)cellulose, for example, has been reduced to *O*-(aminopropyl)cellulose with borane-dimethyl sulfide in tetrahydrofuran [15]. From an industrial point of view, hydrogenation using heterogeneous catalysis is very attractive, since the reaction is usually clean and the isolation of the reaction product is easy. *Raney*-nickel catalysts have been applied for the reduction of *O*-cyanoethylated polyvinyl alcohol [16], α-*C*-cyanoethylated polyacrylonitrile [17], and *O*-(cyanoethyl)cellulose [18]. Extreme reaction conditions were needed for the reduction of the latter compound (150 °C, 100 bar H_2) and the characterization of the reaction products was not described. Poly(propylene imine)dendrimers have been prepared in a synthetic sequence, in which *Raney*-cobalt has successfully been applied as the catalyst in the quantitative hydrogenation of cyanoethylated intermediates into the corresponding amines [19].

In the present study, several heterogeneous catalysts, such as Pt–C, Ru–C and *Raney*-nickel have been tested in the hydrogenation of *O*-(cyanoethyl)-inulin, but only traces of primary amines were formed even after prolonged reaction times. Better results were obtained with *Raney*-cobalt, and the reaction conditions were optimized with this catalyst. Optimum results were obtained with 90:10 methanol–water as solvent, at 100 bar H_2 and 50 °C. After 20 h, the reaction was stopped and the catalyst was filtered off. As shown by ^{1}H NMR spectroscopy, about 10% of the *O*-cyanoethyl groups were selectively converted into *O*-aminopropyl groups, whereas another 10% of the groups were lost by dealkylation (see Fig. 2). Prolonged reaction times did not result in an increase of the yield of primary amines, but led to further dealkylation, which may be ascribed to the relatively high pH of the reaction mixture.

The influence of the molecular weight of the starting material on the conversion into primary amines was investigated. To this end, *O*-cyanoethylated methyl α-D-fructofuranoside, *O*-(cyanoethyl)sucrose and *O*-(cyanoethyl)nystose were hydrogenated under similar conditions. The results were compared with those obtained with *O*-(cyanoethyl)inulin. From the results (see Table 1), it is clear that the conversion of cyanoethyl groups into primary amines decreases upon increase of the chain length of the starting material. Also, the conversion appeared to be lower for starting materials with a higher substitution degree (Table 2).

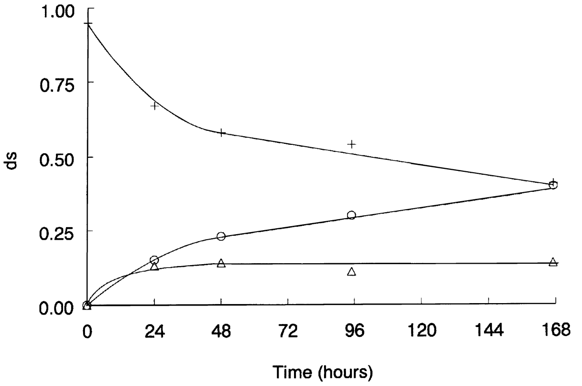

Fig. 2. Hydrogenation of *O*-(cyanoethyl)inulin (ds 1.0; average dp 10) with *Raney*-cobalt (75 mg) as the catalyst. The starting material (0.5 g) was dissolved in 90:10 MeOH–H_2O (30 mL) and hydrogenated with H_2 (100 bar) at 50 °C. The ds in *O*-cyanoethyl groups (+), the ds in *O*-aminopropyl groups (△) and the amount of dealkylation (○) are given as a function of the reaction time.

All reactions were terminated after 20 h. At that time, the hydrogenation of all starting materials had stopped.

A possible explanation for the increasing difficulty of hydrogenation with increasing chain length and substitution degree of the starting material may be poisoning of the catalyst. However, it was shown that the catalyst can be reused without loss of quality after filtering off and rinsing the material with water. Furthermore, no additional conversion was obtained when the filtered reaction mixture (containing partly hydrogenated *O*-(cyanoethyl)inulin) was introduced in a hydrogenation experiment with a fresh catalyst. Alternatively, the deactivation may be explained by adsorption of the reaction products onto the catalyst surface. Primary amines are known to adsorb more strongly than nitriles onto *Raney*-cobalt [20]. The adsorption of polymeric products is expected to be stronger than that of monomers due to the effect of multiple binding sites of the former. The slow desorption of partly hydrogenated products would result in a lower steric availability of the catalyst surface for the remaining nitrile groups and, consequently, in a much slower conversion. Competition experiments confirmed that the presence of reaction products inhibits the hydrogenation of *O*-(cyanoethyl)sucrose. The initial hydrogenation rate of *O*-(cyanoethyl)sucrose in the presence of *O*-(aminopropyl)sucrose or *O*-(aminopropyl)inulin was substantially lower than that of *O*-(cyanoethyl)sucrose alone (Table 3).

Addition of NH_3 to the reaction mixture may enhance the desorption of amines from the catalyst surface. When *O*-(cyanoethyl)sucrose (ds 0.93) was hydrogenated in the presence of 1.1 equiv NH_3 (with respect to nitrile groups), under the same conditions as described above, *O*-(aminopropyl)sucrose with ds 0.69 of *O*-aminopropyl groups

Table 1
Hydrogenation of *O*-cyanoethyl derivatives (*O*-cyanoethylated methyl α-D-fructo-furanoside (CEF), *O*-(cyanoethyl)sucrose (CES), *O*-(cyanoethyl)nystose (CEN) and *O*-(cyano-ethyl)inulin with an average dp 10 (CEI), using *Raney*-cobalt (75 mg) as the catalyst. The starting materials (0.5 g) were dissolved in 30 mL 90:10 MeOH–H_2O and hydrogenated with H_2 (100 bar) at 50 °C during 20 h

Starting material	Product composition		CN[a]	CH_2NH_2[b] (% of original ds)	Dealkylation
	ds CN[a]	ds CH_2NH_2[b]			
CEF ds 0.84	0.19	0.56	22	67	11
CES ds 0.91	0.34	0.45	37	50	13
CEN ds 0.56	0.26	0.21	46	38	16
CEI dp 10 ds 0.98	0.82	0.09	84	9	7

[a] *O*-cyanoethyl substituents.
[b] *O*-aminopropyl substituents.

Table 2
Hydrogenation of *O*-(cyanoethyl)sucroses (CES) with different ds, with *Raney*-cobalt (75 mg) as the catalyst. The starting materials (0.5 g) were dissolved in 30 mL 90:10 MeOH–H_2O and hydrogenated with H_2 (100 bar) at 50 °C during 20 h

ds CES	Product composition		CN[a]	CH_2NH_2[b] (% of original ds)	Dealkylation
	ds CN[a]	ds CH_2NH_2[b]			
0.57	0.15	0.40	26	70	11
0.91	0.34	0.45	37	50	13
1.00	0.42	0.50	42	50	8
1.66	0.84	0.65	51	39	10

[a] *O*-cyanoethyl substituents.
[b] *O*-aminopropyl substituents.

and ds 0.20 of *O*-cyanoethyl groups was obtained after 20 h reaction. Apparently, the conversion toward primary amines was higher in this case (74%) than when no NH_3 was used (see Table 2). When the reaction was carried on for 48 h, complete conversion to *O*-(aminopropyl)sucrose with ds 0.85 was achieved. These results agree with the suggestion that addition of NH_3 to the hydrogenation of cyanoethyl dendrimers results in faster exchange of nitrile and amine groups on the active sites of the catalyst [20]. Another way to enhance the desorption rate of amine groups from the catalyst may be by control of the pH during the reaction, so that the formed amines are protonated and then have a lower affinity for the surface. Hydrogenation of *O*-(cyanoethyl)sucrose (ds 0.85) in a buffered system at pH 6.7 (15 mmol 4-(2-hydroxyethyl)piperazine-1-ethanesulfonate) resulted in complete conversion of nitriles into primary amines after 20 h. However, addition of NH_3 or a buffer to the reaction mixture for the hydrogenation of *O*-(cyanoethyl)inulin did not improve the conversion toward *O*-(aminopropyl)inulin. Most probably, the adsorption of the product on the catalyst surface is too strong due to the cooperative action of several amine groups in one molecule. For cyanoethyl dendrimers, such cooperative action is less pronounced due to the spherical shape of the molecule, which explains why these compounds are completely and selectively hydrogenated with *Raney*-cobalt as the catalyst in the presence of ammonia [20].

Table 3
Initial hydrogenation rate of 0.5 g *O*-(cyanoethyl)sucrose (CES) and of 0.5 g *O*-(cyanoethyl)sucrose in the presence of 0.2 g *O*-(aminopropyl)sucrose (APS) with ds 0.51 of *O*-aminopropyl groups and ds 0.07 of *O*-cyanoethyl groups, or 0.5 g *O*-(aminopropyl)inulin with ds 0.09 of *O*-aminopropyl groups and ds 0.90 of *O*-cyanoethyl groups. The hydrogenations were carried out in 30 mL 90:10 MeOH–H_2O with H_2 (100 bar) at 50 °C over *Raney*-cobalt (75 mg)

	Initial hydrogenation rate (mmol/h)
CES ds 0.57	0.26
CES ds 0.57 + APS ds 0.51	0.18
CES ds 1.00	0.18
CES ds 1.00 + API ds 0.09	0.14

The mixed *O*-cyanoethyl and *O*-aminopropyl ethers obtained by partial hydrogenation of *O*-(cyanoethyl)inulin may be converted in a material containing exclusively aminopropyl substituents by treatment with 1 M NaOH at 70 °C for 1 h. Under these conditions, the *O*-cyanoethyl groups are dealkylated, while the *O*-aminopropyl substituents are stable. This can be explained by the higher acidity of the α-CH_2 group of the *O*-cyanoethyl substituents.

Reduction of O-*(cyanoethyl)inulin with sodium borohydride in combination with cobaltous chloride*.—Sodium borohydride alone is not able to reduce nitriles, but in combination with transition metal salts, primary amines are obtained in a high yield [21]. Metal ion coordination of nitriles results in activation [22,23] for reduction with the borohydride anion. *O*-(Cyanoethyl)inulin was successfully reduced to *O*-(aminopropyl)inulin with 15 mol equiv of sodium borohydride and 4 mol equiv of cobaltous chloride (with respect to nitrile groups). A conversion of 90% of the nitrile groups into primary amines was achieved (Table 4). Dealkylation was negligible under the conditions applied. The conversion was independent of the reaction temperature and increased essentially linearly up to completeness with the amount of cobaltous chloride (see Table 4). A large excess of this metal salt was required because, in a side reaction, Co(II) is reduced by sodium borohydride into metallic Co(0), which does not catalyze the

Table 4
Reduction of *O*-(cyanoethyl)inulin (1.0 g) with ds 0.70 and average dp 10 toward *O*-(aminopropyl)inulin using sodium borohydride in the presence of Co(II) in water (20 mL)

Molar equivalents[a] $CoCl_2.6H_2O$	Molar equivalents[a] $NaBH_4$	Reaction temperature (°C)	Conversion[b] (%)
0.5	10	20	15
2	10	20	50
2	10	45	51
2	20	20	55
4	15	20	90

[a] Molar equivalents with respect to nitrile groups present in the reaction mixture.

[b] Amount of cyanoethyl groups converted into aminopropyl groups.

reduction of nitriles under these mild conditions. The degradation of borohydride into borate and H_2 is catalyzed by Co(II), which explains the high excess of sodium borohydride required. Addition of sodium borohydride to the reaction mixture after complete conversion of Co(II) into Co(0) did not result in any additional reduction of nitriles, which confirms that both metallic Co and sodium borohydride are inactive in the reduction.

Reduction of O-*(cyanoethyl)inulin with metals in liquid ammonia.*—Solutions of alkali metals and certain alkaline earth metals [24] and lanthanides [25] in liquid ammonia are widely employed for the reduction of a variety of organic functional groups. Also, nitriles have been reduced into primary amines using this method [26,27]. In liquid ammonia, these metals dissolve and disproportionate into cations and solvated free electrons, which reduce the nitrile function. Alcohols are generally used as proton donors (Fig. 3). They are converted into strongly basic alkoxide groups.

A first series of experiments was performed in liquid ammonia in the absence of an additional proton donor. Then the hydroxyl groups of *O*-(cyanoethyl)inulin may serve as proton donor. Of the metals tested (Na, Li, Ca, La), lithium gave the best results. Primary amines were formed (25%), but also severe dealkylation of the *O*-cyanoethyl groups (75%) was observed. Better results were obtained with methanol as cosolvent and as proton donor (2:1 ammonia–methanol). The dealkylation was less extensive (about 20%) and primary amines were formed in a good yield (about 80%). *O*-(Aminopropyl)inulin with ds 0.90 was, for example, obtained from *O*-(cyanoethyl)inulin with ds 1.09, applying 8 equiv of Li (with respect to nitrile groups). The severe dealkylation in liquid ammonia in the absence of methanol may be explained by the high basicity of the solvent [28], which enhances the deprotonation of the α-CH_2 group of the substituents. When methanol, a neutral amphiprotic solvent, is added to the reaction mixture, the basicity decreases, which may explain the decreased extent of dealkylation. In addition, strongly basic solvent-derived amide anions may be formed in liquid ammonia in the presence of metals, which is less likely to occur in the presence of methanol. When the reaction was carried out with smaller amounts of Li, incomplete reduction accompanied by more extensive dealkylation took place. The latter may again be ascribed to the high sensitivity for elimination of the cyanoethyl function under basic conditions. Application of 4 equiv of Li in the above example resulted in a product with both *O*-aminopropyl (ds 0.58) and *O*-cyanoethyl groups (ds 0.17) (31% dealkylation).

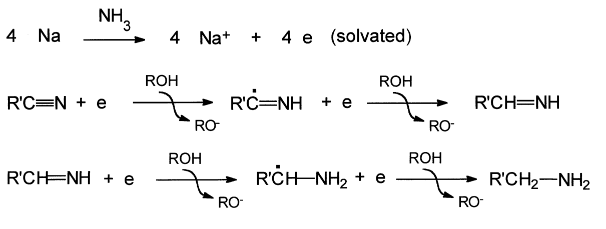

Fig. 3. Reduction of nitriles with Na in liquid ammonia in the presence of an alcohol as proton donor.

Attempts to reduce *O*-(cyanoethyl)inulin with metals in an alcohol (methanol, ethanol) in the absence of ammonia and at higher temperatures (up to boiling point) failed. No conversion was detected. When the reduction was carried out in an alkylamine (propylamine) instead of ammonia, complete dealkylation took place. These experiments show that the use of liquid ammonia as solvent is necessary for the reduction of *O*-(cyanoethyl)inulin with metals.

3. Conclusions

Hydrogenation with *Raney*-cobalt as the catalyst was used to convert *O*-cyanoethyl derivatives into *O*-aminopropyl derivatives. The reaction rate and conversion of low molecular weight starting materials can be improved by the enhancement of the desorption of amines from the catalyst surface by adding NH_3 or by working in a buffered system. The hydrogenation of *O*-(cyanoethyl)inulin, however, is slow and incomplete, even under these conditions. Heterogeneously catalyzed hydrogenation of *O*-(cyanoethyl)inulin is suitable for the preparation of mixed *O*-cyanoethyl and *O*-aminopropyl ethers. A homogeneous process using sodium borohydride in the presence of cobaltous chloride salts gave essentially (90%) complete conversion of *O*-(cyanoethyl)inulin, but the large amount of reactants required make this method less interesting for large scale reactions or industrial processes. By far the best method to prepare *O*-(aminopropyl)inulin is the reduction of the nitriles with metals in liquid ammonia using an alcohol as proton donor. Under these conditions, only about 20% of the *O*-cyanoethyl groups are dealkylated and 80% are selectively and completely converted into *O*-aminopropyl groups. This route provides a simple way to prepare primary amino-derivatives of inulin and may also be applied to other polysaccharides.

4. Experimental

Materials and methods.—Inulin, isolated from chicory roots, 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. Nystose was kindly donated by Südzucker (Darmstadt, Germany) and methyl α-D-fructofuranoside was prepared as described previously [29]. Cyanoethylation of inulin and model compounds and the characterization of the resulting *O*-cyanoethyl compounds was performed following the procedures described in previous work [11].

The *Raney*-cobalt catalyst was a gift from Degussa A.G. (Hanau, Germany). MeOH used for the hydrogenations was of analytical quality (Baker analyzed reagent). All other chemicals were purchased from Acros Chimica (Geel, Belgium).

The hydrogenations were carried out in a 160 mL Parr 4564 pressure reactor. The autoclave was equipped with a motor-driven impeller stirrer, a sampling device and a temperature programming system (M 4841 Parr).

^{13}C NMR and ^{1}H spectra were recorded on a Varian INOVA-300 spectrometer or a Varian VXR-400 S spectrometer using D_2O as solvent and *t*-butyl alcohol as internal standard.

Hydrogenations with Raney-cobalt as the catalyst.—As an example, the hydrogenation of *O*-(cyanoethyl)inulin is described. The hydrogenations of the model compounds and the characterization of the resulting reduction products were performed similarly. *O*-(Cyanoethyl)inulin (1 g, ds 0.9) was dissolved in 60 mL 90:10 MeOH–H_2O. *Raney*-cobalt catalyst (150 mg) was added and the hydrogenation was carried out at 100 bar and 50 °C. After 20 h, the catalyst was filtered off, the mixture was neutralized with 2 M HCl and concentrated under reduced pressure. Low–molecular–weight material was removed using membrane filtration (UTC 60, Toray Industries Inc., Tokyo, Japan) at 20 bar N_2. Freeze-drying yielded 0.9 g reaction product, which was a mixed *O*-(cyanoethyl) and *O*-(aminopropyl) ether of inulin. ^{13}C NMR: δ 19.7–20.3 ($\mathit{C}H_2CN$), 29.5–32.0 ($\mathit{C}H_2CH_2NH_2$), 38.0–40.0 ($CH_2\mathit{C}H_2NH_2$), 61.0–85.0 (C-1, C-3–C-6, and O$\mathit{C}H_2$), 104.5–105.2 (C-2), 121.3–121.5 ($\mathit{C}N$). The degree of substitution (ds) was determined by integration of the ^{1}H NMR signals (δ 1.7–2.0 ($C\mathit{H_2}CH_2NH_2$), 2.7–2.8 ($C\mathit{H_2}CN$), 2.9–3.1 ($CH_2C\mathit{H_2}NH_2$), 3.3–4.5 (H-1a,b, H-3–H-5, H-6a,b, and O$C\mathit{H_2}$), 5.3–5.5 (Glc H-1)).

A mixed *O*-cyanoethyl and *O*-aminopropyl ether (ds 0.82 and 0.09, respectively) was dissolved in 1 M aq NaOH (0.5 g/10 mL). Heating at 70 °C for 1 h yielded an inulin derivative containing exclusively aminopropyl substituents (ds 0.09).

Reduction of O-*(cyanoethyl)inulin with sodium borohydride and cobaltous chloride.*—*O*-(cyanoethyl)inulin (1 g) and cobaltous chloride hexahydrate (4 mol equiv with respect to nitrile groups) were dissolved in water (20 mL) and $NaBH_4$ (15 mol equiv) was added in portions with stirring at 20 °C. Evolution of H_2 gas was observed and a black precipitate [of Co(0)] appeared during the reaction. When the addition was complete, stirring was continued for 1 h. The black precipitate was filtered off and washed with water. Inorganic salts, such as borate, were removed using membrane filtration (UTC 60, Toray Industries) at a pressure of 20 bar. Finally, the HCl salt of *O*-(aminopropyl)-inulin was obtained by freeze-drying in a yield of 0.8 g. The structure was established using ^{13}C NMR spectroscopy and the degree of substitution was determined by integration of the signals in the ^{1}H NMR spectrum (assignments see above).

Reductions of O-*(cyanoethyl)inulin with metals in liquid ammonia.*—As an example, a reaction using 8 equiv Li with respect to cyanoethyl functions in NH_3–MeOH is described. The other reductions were performed similarly. *O*-(Cyanoethyl)inulin (1.00 g) was dissolved in 1:2 dry

MeOH–liq NH_3 (75 mL). The metal (Na or Li, 8 equiv with respect to nitrile groups) was added in small portions with stirring of the mixture at −45 °C over a period of 30 min. After stirring at −45 °C for another hour, the cooling was removed, allowing NH_3 to evaporate. After standing overnight the remaining solution contained the product in MeOH saturated with NH_3, and some methoxide. About 50 mL water was cautiously added and CO_2 was bubbled through until the pH was neutral. In this way, NH_3 was converted into $(NH_4)_2CO_3$, which was removed by sublimation. Finally, remaining salts and low-molecular-weight material was removed by membrane filtration (20 bar N_2, UTC 60 membrane) and 1.52 g product (bicarbonate salt of *O*-(aminopropyl)inulin) was obtained by freeze-drying. The structure was established using ^{13}C NMR spectroscopy and the degree of substitution was determined to be 0.90 via ^1H NMR spectroscopy (assignments see above).

Acknowledgements

This work was financially supported by Sensus, Coöperatie Cosun U.A. (Roosendaal, The Netherlands). We are grateful to Südzucker (Darmstadt, Germany) for donating nystose and to Degussa A.G. (Hanau, Germany) for a generous gift of *Raney*-cobalt. Mr. E. Wurtz is thanked for performing the autoclave experiments.

References

[1] R.A.A. Muzzarelli, G. Raith, and O. Tubertini, *J. Chromatogr.*, 47 (1970) 414–420.

[2] S. Hirano, Y. Kondo, and Y. Nakazawa, *Carbohydr. Res.*, 100 (1982) 431–434.

[3] R.A.A. Muzzarelli, F. Tanfani, M. Emanuelli, and S. Mariotti, *Carbohydr. Res.*, 107 (1982) 199–214.

[4] S. Viala, M. Freche, and J.L. Lacout, *Carbohydr. Polym.*, 29 (1996) 197–201.

[5] B.F. Tuinstra, *Chemisch Magazine*, 11 (1996) 439–441.

[6] P. Rongved and J. Klaveness, *Carbohydr. Res.*, 214 (1991) 315–323.

[7] P. Rongved, T.H. Fritzell, P. Strande, and J. Klaveness, *Carbohydr. Res.*, 287 (1996) 77–89.

[8] L. Molteni, *Methods Enzymol.*, 112 (1985) 285–297.

[9] L. de Leenheer, Production and use of inulin: industrial reality with a promising future, in H. van Bekkum, H. Röper and A.G.J. Voragen (Eds.), *Carbohydrates as Organic Raw Materials III*, VCH, Weinheim, 1996, pp 67–79.

[10] D.L. Verraest, J.A. Peters, H. van Bekkum, and G.M. van Rosmalen, *J. Am. Oil Chem. Soc.*, 73 (1996) 55–62.

[11] D.L. Verraest, L.P. da Silva, J.A. Peters, and H. van Bekkum, *Starch/Stärke*, 48 (1996) 191–195.

[12] D.L. Verraest, J.A. Peters, H.W.C. Raaijmakers, H.C. Kuzee, and H. van Bekkum, *Carbohydr. Res.*, 302 (1997) 203–212.

[13] C. De Bellefon and P. Fouilloux, *Catal. Rev.-Sci. Eng.*, 36 (1994) 459–506.

[14] A. Rosenthal and D.A. Barker, *J. Org. Chem.*, 38 (1973) 193–197, 198–201.

[15] W.H. Daly and A. Munir, *J. Polym. Sci. Chem. Ed.*, 22 (1984) 975–984.

[16] L. Alexandru, M. Opris, and A. Ciocanel, *J. Polym. Sci.*, 59 (1962) 129–137.

[17] W.H. Schuller and L.C. Beegle, US Patent 3 122 526 (1964).

[18] L.M. Soffer, US Patent 3 236 834 (1962); *Chem. Abstr.*, 64 (1962) P12955b.

[19] E.M.M. de Brabander-van den Berg and E.W. Meijer, *Angew. Chem. Int. Ed.*, 105 (1993) 1308–1310.

[20] J.C.M. van Hest, D.A.P. Delnoye, M.W.P.L. Baars, C. Elissen-Román, M.H.P. van Genderen, and E.W. Meijer, *Chem. Eur. J.*, 2 (1996) 1616–1626.

[21] T. Satoh, S. Suzuki, Y. Suzuki, Y. Miyaji, and Z. Imai, *Tetrehedron Lett.*, 52 (1969) 4555–4558.

[22] F.C. Schaefer, Nitrile reactivity, in Z. Rappoport (Ed.), *The Chemistry of the Cyano Group*, Interscience, New York, 1970, pp 239–305.

[23] N.E. Dixon and A.M. Sargeson, Roles for the metal ion in reactions of coordinated substrates and in some metalloenzymes, in T.G. Spiro (Ed.), *Zinc Enzymes*, John Wiley and Sons, New York, 1983, pp 254–266.

[24] A.J. Birch and G. Subba Rao, *Adv. Org. Chem.*, 8 (1972) 1–15.

[25] J.D. White and G.L. Larson, *J. Org. Chem.*, 43 (1978) 4555–4556.

[26] R. Schröter, Reduktionen von Nitrilenzu Aminen, in E. Muller (Ed.), *Methoden der Org. Chemie, Band XI/1*, G. Thieme Verlag, Stuttgart, 1957, pp 547–549.

[27] A.R. Doumaux Jr., *J. Org. Chem.*, 37 (1972) 508–510.

[28] O. Popovych and R.P.T. Tomkins, *Nonaqueous Solution Chemistry*, John Wiley and Sons, New York, 1981, pp 54–57.

[29] L. Johnson, D.L. Verraest, J. van Haveren, K. Hakala, J.A. Peters, and H. van Bekkum, *Tetrahedron: Asymmetry*, 5 (1994) 2475–2484.