Chemistry of Natural Compounds and Bioorganic Chemistry

Synthesis of highly branched oligomannosides

1. Synthesis of 1,2-*O*-[(1-cyano)ethylidene]-3,6-di-*O*-(α-D-mannopyranosyl)-β-D-mannopyranose nonaacetate as a trisaccharide glycosyl donor

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Helferich glycosylation of 1,2-*O*-[(1-cyano)ethylidene]-β-D-mannopyranose with acetobromomannose results in selective 3,6-bis-glycosylation of the acceptor. The peracetylated trisaccharide cyanoethylidene derivative is an efficient glycosyl donor, which is exemplified by preparation of a branched tetrasaccharide.

Key words: carbohydrate 1,2-*O*-(1-cyano)ethylidene derivatives, trityl-cyanoethylidene condensation, branched mannotetraoside, synthesis.

Synthesis of highly branched (dendritic) structures is one of the new areas of chemistry that is currently being extensively developed.[1] Due to the interest in studies and modifications of dendrimers, some of them are becoming commercially available.[2]

This class of compounds involves the so-called glycodendrimers in which monosaccharide (or, less commonly, disaccharide) residues are attached through mono- or polyfunctional spacers to a branched skeleton of a macromolecule built of noncarbohydrate elements and are arranged at its periphery.[3,4]

In principle, other types of glycodendrimers are possible, *viz.*, with carbohydrates constituting both the periphery and the "internal" part of a molecule. In other words, they should belong to highly branched oligo- or polysaccharides. Such polysaccharides as starch and glycogen, plant arabinogalactans,[5] yeast mannans,[6] and snail galactans[7,8] can serve as spectacular examples of natural carbohydrate dendrite-like structures. Highly branched, dendrite-like oligosaccharides are the components of glycoproteins with D-mannose as the branching point of N-chains and D-galactose or *N*-acetyl-D-galactosamine as the branching point of O-chains (see, for example, Ref. 9).

Recently, a stepwise synthesis of a benzoylated branched heptasaccharide 3,6-[(3,6-G_2)G]$_2$GO$(CH_2)_6$NHR, where G is a β-D-glucopyranosyl residue, has been accomplished

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1631—1636, August, 1998.

1066-5285/98/4708-1589 $20.00

using ethyl 1-thioglycoside derived from a branched trisaccharide as a glycosyl donor.[10] This synthesis may be regarded as an initial step *en route* to purely carbohydrate dendrimers.

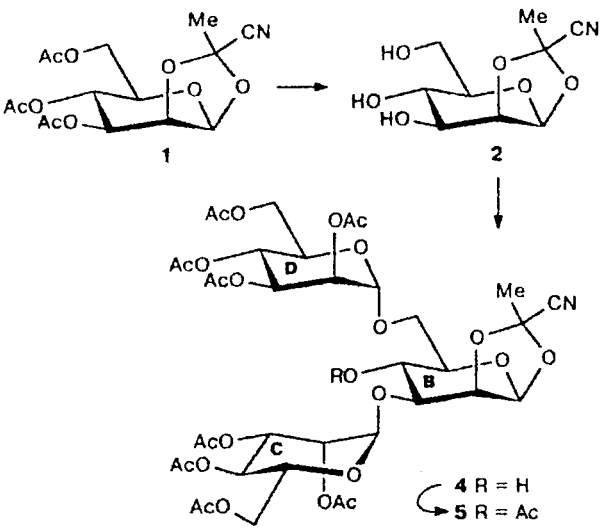
Trityl-cyanoethylidene condensation, which is based on the reaction of sugar 1,2-*O*-(1-cyano)ethylidene derivatives (CED) as efficient glycosyl donors with tritylated sugars as glycosyl acceptors, has been successfully used in the synthesis of oligosaccharides[11] and regular polysaccharides.[12] Therefore, it is quite reasonable to expect that this method of glycosylation would also be applicable to the preparation of highly branched (dendrite-like) oligosaccharides.

Our synthetic work is aimed at obtaining branched oligomannosides that can be regarded as analogs or models of mannose-rich N-glycans of glycoproteins. Here, we describe the preparation of a trisaccharide cyanoethylidene derivative and its use as a glycosyl donor for glycosylation of a model trityl ether.

Results and Discussion

Synthesis of the trisaccharide CED envisaged the conversion of D-mannose 1,2-*O*-(1-cyano)ethylidene triacetate **1** into the triol **2** and its subsequent selective glycosylation.

Scheme 1



The known CED **1**, which is easily accessible[13] through the reaction of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (acetobromomannose, **3**) with KCN, served as the starting material. The transformation of **1** into the triol **2**, which has been previously utilized in the preparation of monomers for the synthesis of (1→6)-[14] and (1→4)-α-D-mannopyranans,[15] D-mannuronic acid CED,[16] and cyclic oligosaccharides, cyclodextrin analogues,[17] was carried out by MeONa- or Et_3N-catalyzed methanolysis. Here, we resort to deacetylation with MeONa in a MeOH—Py mixture,[16] and the product **2** was then subjected to glycosylation.

Glycosylation of hydroxyl-containing cyanoethylidene derivatives, which can be considered as an example of orthogonal glycosylation,[18] has substantially extended the potentialities of trityl-cyanoethylidene condensation. This has usually been performed with acylglycosyl bromides under conditions of the Helferich reaction, *i.e.*, in MeCN in the presence of $Hg(CN)_2$.[19] Successful glycosylation has also been carried out in the presence of such an active promoter as AgOTf in combination with 2,4,6-collidine.[17] To ensure selective glycosylation of the triol **2**, we employed a milder promoter, $Hg(CN)_2$ together with $HgBr_2$. That the selective introduction of *O*-substituents into the molecule of **2** is possible is evident from the preparation of its 3,6-di-*O*-benzoate.[15,17] Thus the action of 4 equiv. of BzCl in Py afforded the dibenzoate in more than 70% yield.[17] Analogous regioselectivity might be expected for the glycosylation of the triol.

In fact, the reaction of triol **2** with 3.5 equiv. of acetobromomannose (**3**) resulted in a trisaccharide CED **4** isolated in 62% yield (Scheme 1).

The structure of this compound, 3,6-disubstitution in particular, followed unambiguously from NMR data.

The signals of all the protons (Table 1) were assigned from the 1D and 2D spectra (NOE, COSY, and COSYRCT) taken altogether. The correlations between H-1—H-4 and H-5—H-6,6′ of the units **C** and **D** were established using COSY and COSYRCT spectra. Chemical shifts for H-3 of each of these residues coincided with those for H-4, which precluded linking of the above-mentioned groups of signals. This could be done using the 1D-NOE technique in a difference mode: pre-irradiation of a signal for H-5 at δ 4.06 resulted in a response of H-3 at δ 5.28, thus establishing H-5D/H-3D correlation. The same procedure, but with pre-irradiation of anomeric protons H-1C and H-1D, allows one to demonstrate the presence of **C**(1→3)**B** and **D**(1→6)**B** linkages, *i.e.*, the 3,6-disubstitution in the unit **B**. This is also supported by the fact that the free hydroxy group is located at C-4**B**, which followed from the correlation HO/H-4**B** (COSY).

The anomeric region of the ^{13}C NMR spectrum (δ ≈ 100) contains 4 signals one of which (δ 101.7) belongs to the "central" carbon atom of the cyanoethylidene group. Chemical shifts of the other characteristic signals (δ 26.7 (Me) and 116.8 (CN) (*cf.* Ref. 17)) prove the retention of this group under conditions of deacetylation of the CED **1** and glycosylation of the triol **2**.

Assignment of the signals in the ^{13}C NMR spectrum (Table 2) was accomplished by heteronuclear multiple quantum coherence (HMQC) spectroscopy taking into account the position of the protons in the ^1H NMR spectrum. The signals of the **C** and **D** units are in good

Table 1. Parameters of ^{1}H NMR spectra of the compounds synthesized ($CDCl_3$)

Compound	Unit[a]	δ							
		H-1	H-2	H-3	H-4	H-5	H-6	H-6'	Other signals
4	**B**	5.42	4.64	3.80	3.96	3.46	3.73	3.97	1.97—2.15 (Ac, MeCCN)
	C	5.09	5.40	5.36	5.36	4.27	4.14	4.36	
	D	4.84	5.26	5.28	5.28	4.06	4.12	4.27	
5	**B**	5.46	4.63	3.96	5.16	3.61	3.52	3.72	1.95—2.17 (Ac, MeCCN)
	C	4.95	5.08	5.27	5.28	4.17	4.08	4.32	
	D	4.74	5.19	5.26	5.26	4.00	4.00	4.27	
7	**A**	4.65	5.20	5.32	5.30	3.85	3.56	3.72	1.95—2.10 (Ac);
	B	4.86	5.24	4.15	5.22	3.78	3.48	3.72	3.38 (OMe)
	C	4.97	5.02	5.16	5.26	4.05	4.05	4.25	
	D	4.79	5.22	5.30	5.25	4.05	4.05	4.23	
8[b]	**A**	4.76	3.94	3.93	3.74	3.75	3.79	3.95	3.41 (OMe)
	B	4.88	4.14	3.91	3.89	3.78	3.77	3.97	
	C	5.13	4.06	3.87	3.67	3.78	3.76	3.86	
	D	4.91	4.06	3.84	3.66	3.70	3.78	3.89	

[a] Designations of the units are shown in the schemes. [b] Recorded in D_2O at 40 °C.

Table 2. Parameters of ^{13}C NMR spectra of the compounds synthesized ($CDCl_3$)

Compound	Unit[a]	δ						
		C-1	C-2	C-3	C-4	C-5	C-6	Other signals
4	**B**	97.0	79.9	81.1	64.8	74.1	66.1	20.7—20.8 ($\underline{C}H_3CO$);
	C	100.5	69.2	69.2	65.5	69.4	62.6	26.7, 101.7, 116.8
	D	97.6	69.3	69.0	66.3	68.4	62.2	(Me—C—CN)
5	**B**	96.9	79.2	77.9	66.4	72.6	67.2	20.6 ($\underline{C}H_3CO$);
	C	100.1	69.6	68.4	65.7	69.4	62.2	26.3, 101.5, 116.5
	D	97.6	69.2	69.0	65.7	68.4	62.1	(Me—C—CN)
7	**A**	98.4	69.4	68.9	65.9	69.2	65.8	20.6, 20.7 ($\underline{C}H_3CO$);
	B	97.2	70.6	74.8	65.8	69.3	66.6	55.1 (OMe)
	C	99.0	69.8	68.3	65.9	68.6	62.0	
	D	97.4	69.2	68.0	65.6	69.3	62.3	
8[b]	**A**	100.7 (171)[c]	69.6	70.7	66.3	70.5[d]	65.1[e]	54.4 (OMe)
	B	99.2 (172)[c]	69.2	78.1	65.5	70.3[d]	65.4[e]	
	C	101.8 (173)[c]	69.8	70.1	66.5	72.9	60.7	
	D	99.0 (171)[c]	69.7	70.3	66.5	72.4	60.7	

[a] Designations of the units are shown in the schemes. [b] Recorded in D_2O at 24 °C. [c] $^1J_{C\text{-}1,H\text{-}1}$/Hz. [d,e] Assignments may be interchanged.

agreement with the published data for methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside,[20] which is evidence of the α-configuration of the newly formed glycosidic linkages.

The difference between the chemical shifts for C-1C and C-1D (as well as for H-1C and H-1D, see Table 1) parallels that observed earlier in the spectra of unprotected manno-oligosaccharides:[21] the H(C)-1 atoms of the units involved in 1→3-bonds resonate at lower fields than those linked by 1→6-bonds.

Additional proof of the **C**(1→3)[**D**(1→6)]**B** type of structure of compound **4** can be obtained from an analysis of chemical shifts of the carbon atoms of unit **B**. The signals for C-3 and C-6 are markedly shifted downfield as compared to their position in the spectrum of the triol **2**,[17] while those for C-2, C-4, and C-5 are shifted upfield due to the α- and β-effects of glycosylation, respectively. Thus, glycosylation of triol **2** gave 1,2-*O*-[1-(*exo*-cyano)ethylidene]-3,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-β-D-mannopyranose (**4**).

The transition from the monohydroxy compound **4** to the target compound **5** was accomplished by acetylation in the presence of a catalytic amount of 4-dimethylaminopyridine (DMAP).

The structure of the resulting crystalline derivative **5** was also unequivocally established by NMR spectroscopy. The signals for the protons of the unit **B** were

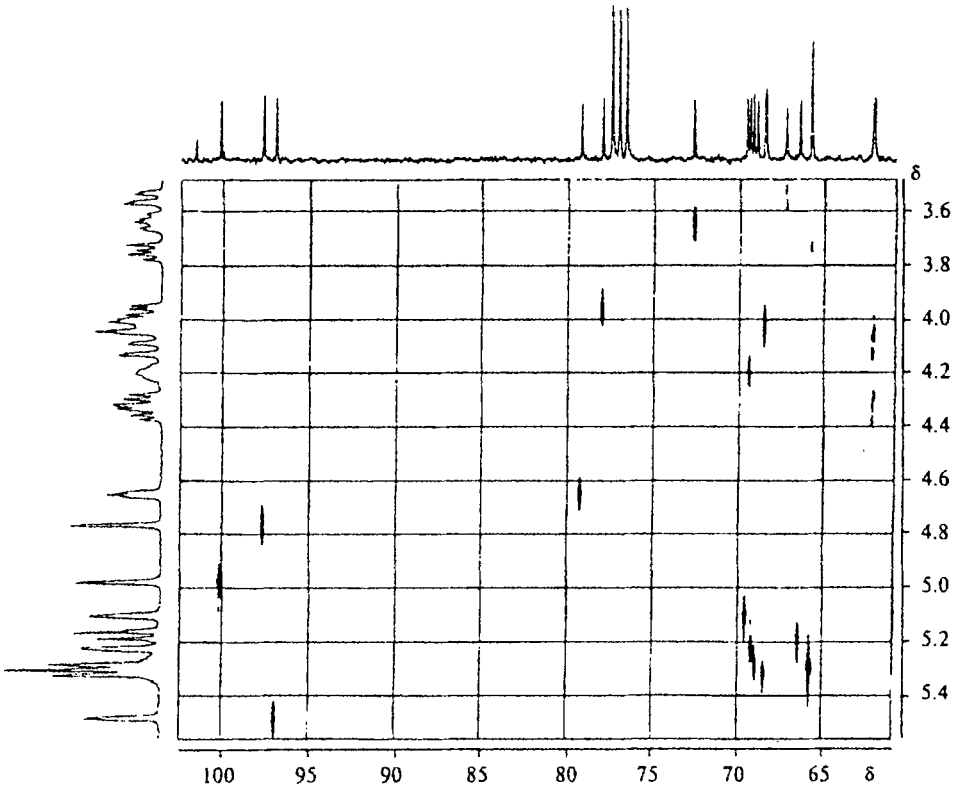


Fig. 1. HMQC spectrum of cyanoethylidene derivative **5** ($CDCl_3$, Bruker DRX-500, 500 MHz).

unambiguously assigned from 2D-spectra taking into account the data for the parent compound **4** (see Table 1). As expected, the H-4B signal of the acetate **5** was shifted to lower field relative to its position in the spectrum of the OH-derivative **4**. Complete assigmnent of the signals in the ^1H NMR spectrum was accomplished from the data of NOE, COSY, and COSYRCT spectra. In particular, pre-irradiation of a signal for H-5 at δ 4.17 gave a response for H-3 at δ 5.27.

Assignment of the signals in the ^{13}C NMR spectrum was carried out using HMQC spectroscopy (Fig. 1), and the position of the CN group, the "central" carbon atom of the cyanoethylidene group, and CH_2-groups was additionally established from the APT spectrum[22] (see Table 2).

The known examples of glycosylation by cyanoethylidene derivatives of disaccharides[23–25] and a linear tetrasaccharide[26] have shown that their efficiency did not differ from that of monosaccharide derivatives. One could expect that the CED of a branched trisaccharide, compound **5**, would also be an efficient glycosyl donor.

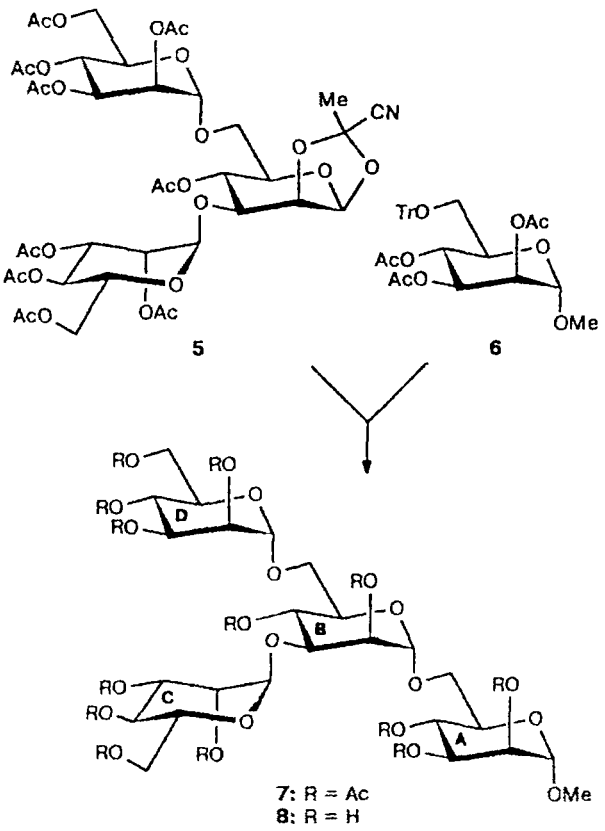
To check this, methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-mannopyranoside **6** [27] was chosen as the model glycosyl acceptor, and it was glycosylated with **5** under standard conditions of trityl-cyanoethylidene condensation, *viz.*, in CH_2Cl_2 in the presence of triphenylmethylium perchlorate ($TrClO_4$) as the catalyst using a high-vacuum technique[11] (Scheme 2).

The structure of the fully protected tetrasaccharide derivative **7**, which was isolated in 56% yield, followed from the 1D- and 2D-NMR spectral data (see Tables 1 and 2). Assignment of the proton signals to particular monosaccharide residues was carried out using COSY and COSYRCT spectroscopies. All of the α-D-mannopyranose residues in the oligosaccharide **7** have the usual $^4C_1$ conformation, which followed from the "standard" values of the spin-spin coupling constants of vicinal protons: $J_{1,2} \approx 1.5$—2; $J_{2,3} \approx 3$—3.5; $J_{3,4} \approx J_{4,5} \approx 10$; $J_{5,6} \approx 6$; $J_{5,6'} \approx 2$; and $J_{6,6'} \approx 10$—12 Hz.

The regions of resonances of the anomeric protons and the carbon atoms in the ^1H and ^{13}C NMR spectra contained 4 signals. Two signals of the CH_2O-groups were present in a relatively high field (δ_C 62.0 and 62.3), and the other two, in a relatively low field (δ_C 65.8 and 66.7, APT spectrum). The signals of protons of the CH_2O-groups in the ^1H NMR spectrum were also found both in the higher field (δ_H 3.50 and 3.72, unit **A**; δ_H 3.47 and 3.72, unit **B**) and in the lower field (δ_H 4.05 and 4.23, unit **D**; δ_H 4.05 and 4.25, unit **C**). The high-field signal H-3B in the ^1H NMR spectrum (δ 4.15) correlates with a low-field signal of C-3B (δ 74.8) in the ^{13}C NMR spectrum. These data altogether show that the tetrasaccharide contains one 1→3- and two 1→6-glycosidic bonds and two nonreducing termini.

An additional proof of the branched structure of the tetrasaccharide **7** with unit **B** as the 3,6-branching point

Scheme 2



was obtained from analysis of the ROESY spectrum, which contained H-1A/OMe, H-1B/H-6A, H-1D/H-6B, and H-1C/H-3B correlations.

Deprotection of **7** yielded the free methyl tetraoside **8**. ^1H and ^{13}C NMR spectral data of this compound (see Tables 1 and 2) corroborate its structure. In compounds **7** and **8**, as in cyanoethylidene derivatives **4** and **5**, the signals for H(C)-1C (1→3-bond) are shifted downfield as compared to those for H(C)-1B and H(C)-1D (1→6-bonds) and are in good agreement with the published data for linear and branched oligomannosides.[21] The $^1J_{C\text{-}1,H\text{-}1}$ coupling constants are in the range 171—173 Hz, which corresponds to the α-configuration of glycosidic linkages of all of the monosaccharide residues.

Thus, trityl-cyanoethylidene condensation with trisaccharide cyanoethylidene derivative **5** as the glycosyl donor is promising for the directed synthesis of highly branched manno-oligosaccharides.

Experimental

Melting points were determined on a Kofler hot stage. Optical rotations were measured using a Jasco DIP-360 polarimeter at *ca.* 20 °C in $CHCl_3$. ^1H and ^{13}C NMR spectra were recorded on Bruker WM-250, AM-300, and DRX-500 instruments in $CDCl_3$ for compounds **4**, **5**, and **7** (with Me_4Si as the internal standard) and in D_2O (methyl tetraoside **8**, acetone as the internal standard; δ_H 2.225, δ_C 31.45). 2D spectra were obtained using standard Bruker software for Aspect 2000 and 3000 (COSY, COSYRCT, ROESY, HMQC). Column chromatography was carried out using Silpearl silica gel. Thin-layer chromatography (TLC) was carried out on Merck DC-Alufolien Kieselgel 60 F 254; spots were visualized by spraying with dilute H_2SO_4 and subsequent heating at *ca.* 150 °C. $TrClO_4$ was prepared according to a literature procedure[28] and reprecipitated with anhydrous ether from nitromethane as described earlier.[29] Pyridine was distilled from KOH. Dichloromethane and acetonitrile were distilled from P_2O_5 and CaH_2 (nitromethane, from CaH_2) and stored over 3 Å molecular sieves. The solvents used in the trityl-cyanoethylidene condensation (benzene, dichloromethane) were degassed and distilled over CaH_2 in a high-vacuum system. Solutions were concentrated at 40 °C on a rotary evaporator.

1,2-*O*-[1-(*exo*-Cyano)ethylidene]-3,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-β-D-mannopyranose (4). A mixture of 1,2-*O*-[1-(*exo*-cyano)ethylidene]-β-D-mannopyranose **2** [16] (1.95 g, 8.44 mmol), $Hg(CN)_2$ (7.60 g, 30 mmol), and $HgBr_2$ (1.08 g, 3.0 mmol) was dried *in vacuo* (oil pump) for 2 h, MeCN (10 mL) was added, and then a solution of 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide[13] (12.33 g, 30 mmol) in MeCN (15 mL) was added dropwise with stirring over *ca.* 1 h. Stirring was continued for *ca.* 16 h at ambient temperature, and the reaction mixture was concentrated *in vacuo*. The residue was partitioned between $CHCl_3$ and aq. NaI (*ca.* 100 mL each), and the organic layer was washed with water and concentrated. Column chromatography of the residue (toluene—AcOEt, 1 : 1) afforded the product **4** (4.7 g, 62%), $[\alpha]_D$ +35.4° (*c* 0.88). Found (%): C, 49.92; H, 5.62; N, 1.50. $C_{37}H_{49}NO_{24}$. Mol. weight 891.8. Calculated (%): C, 49.83; H, 5.53; N, 1.57.

4-*O*-Acetyl-1,2-*O*-[1-(*exo*-cyano)ethylidene]-3,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-β-D-mannopyranose (5). Monohydroxy derivative **4** (1 g) was acetylated with Ac_2O (2 mL) in Py (1 mL) in the presence of a catalytic amount of DMAP at *ca.* 20 °C for 16 h. Several drops of water were added to the mixture on cooling, which was then diluted with $CHCl_3$. The solution was washed with water, dilute HCl, and aq. $NaHCO_3$, and concentrated. Crystallization of the residue from MeOH gave the title compound (yield 0.84 g, 80 %), m.p. 154—159 °C, $[\alpha]_D$ +27.3° (*c* 0.9). Found (%): C, 50.31; H, 5.17; N, 1.25. $C_{39}H_{51}NO_{25}$ Mol. weight 933.8. Calculated (%): C, 50.16; H, 5.50; N, 1.50.

Methyl 2,3,4-tri-*O*-acetyl-6-*O*-[2,4-di-*O*-acetyl-3,6-di-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-α-D-mannopyranosyl]-α-D-mannopyranoside (7). Glycosylation of the trityl ether **6** [27] with the cyanoethylidene derivative **5** was carried out according to the usual procedure.[11] A solution of methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-mannopyranoside **6** (0.145 g, 0.26 mmol) and cyanoethylidene derivative **5** (0.241 g, 0.26 mmol) in benzene (2 mL) was placed in one limb of a tuning fork-shaped tube A, and a solution of $TrClO_4$ (0.009 g, 0.026 mmol) in dry $MeNO_2$ (0.2 mL), in the other. The tube was connected to a vacuum line ($(3—4)\cdot10^{-3}$ Torr), and the solutions were freeze-dried. Then benzene (2 mL) was distilled to the limb with the reagents, the solution that formed was freeze-dried again, and the residue was dried at 30—40 °C for *ca.* 30 min. CH_2Cl_2 (2 mL) was distilled into the tube; the solutions of the reagents and the catalyst were mixed and left overnight at *ca.* 20 °C. A drop of pyridine was added to the bright-yellow solution, which became colorless. It was diluted with $CHCl_3$, washed with water, and concentrated. Column

chromatography (benzene—AcOEt, 1 : 1) afforded tetrasaccharide 7 (0.171 g, 56%), $[\alpha]_D$ + 47.9° (*c* 0.86). Found (%): C, 49.89; H, 5.76. $C_{51}H_{70}O_{34}$. Mol. weight 1227.0. Calculated (%): C, 49.92; H, 5.75.

Methyl 6-*O*-[3,6-di-*O*-(α-D-mannopyranosyl)-α-D-mannopyranosyl]-α-D-mannopyranoside (8). Methanolic MeONa (0.5 mol L^{-1}, 0.1 mL) was added to a solution of the acetate 7 (120 mg) in MeOH (2 mL) and C_5H_5N (1 mL), and the reaction mixture was left overnight at *ca.* 20 °C. This was neutralized with a cation-exchange resin KU-2 (H^+) prewashed with methanol, the resin was filtered off, and the filtrate was concentrated to give methyl tetraoside **8** in virtually quantitative yield, $[\alpha]_D$ + 70.3° (*c* 2.27 in H_2O).

This research was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-34354a).

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Received March 17, 1998