MAGNETIC RESONANCE IN CHEMISTRY, VOL. 35, 414–419 (1997)

NOTE

^{1}H and ^{13}C NMR Data for 3-*O*-, 4-*O*- and 3,4-Di-*O*-glycosylated Methyl α-L-Rhamnopyranosides†

Elena A. Khatuntseva, Alexander S. Shashkov* and Nikolay E. Nifant'ev
N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, 117913 Moscow B-334, Russia

^{1}H and ^{13}C NMR data for a series of 3-*O*-, 4-*O*- and 3,4-di-*O*-glycosylated methyl α-L-rhamnopyranosides are presented. The glycosylation effects on the spectra of disaccharides and the deviation from additivity values in the spectra of trisaccharides were determined.

Magn. Reson. Chem. **35**, 414–419 (1997) No. of Figures: 0 No. of Tables: 4 No. of References: 21

Keywords: NMR; ^{1}HNMR; ^{13}CNMR; disaccharide; branched trisaccharide; glycosylation effect; deviation from additivity; diequatorial branching

Received 13 June 1996; revised 21 September 1996; accepted 17 October 1996

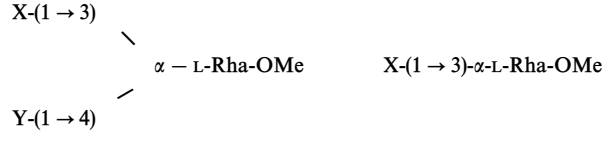
INTRODUCTION

To develop a computerized approach for the structural elucidation of regular branched polysaccharides,[2,3] series of different branched trisaccharides need to be studied.[4] This examination is necessary for the elucidation of both glycosylation effect databases and deviations from additivity, which are used in computational calculations.[3] Previously, series of 2,3-di-*O*-glycosyl derivatives of methyl α-L-rhamnopyranoside,[5-7] methyl a-D-mannopyranoside,[5] 3,4-di-*O*-glycosylated methyl α-[8,9] and β-D-galactopyranosides[10] were studied as models with 2,3- and 4,3-axial-equatorial branching points, respectively, and series of 2,3-di-*O*-glycosylated methyl α- and β-D-glucopyranosides[11-13] and β-D-galactopyranosides[12,13] were investigated as models with 2,3-di-equatorial branching. To develop a database for structures with 3,4-di-equatorial branching points we examined ^{13}C NMR spectra of the 3,4-di-*O*-glycosyl derivatives of methyl α-L-rhamnopyranoside (**1-16**) that have monosaccharide substituents with the α-D-, β-D-, α-L- and β-L-configurations. Together with trisaccharides **1-16** respective consistent disaccharides (**17-24**) were also studied. An NMR study of the trisaccharides **1-16** and the disaccharides **17-24** is described in this paper.

RESULTS AND DISCUSSION

Tables 1 and 2 give the ^{1}H NMR and ^{13}C NMR chemical shifts for compounds **1–24**. The assignments of the signals in the spectra for disaccharides **17** and **20** were taken from Ref. 4, for **18** from Ref. 14 and for **19** from Ref. 6. The ^{13}C data obtained for **22** and **23** are in good agreement with the published values.[14,15] For other compounds (**1–16**, **21** and **24**), ^{1}H NMR and ^{13}C NMR spectra were recorded and assigned. Assignments of the ^{1}H NMR spectra (Table 1) of these compounds were made[4,6] using a combination of COSY and relayed and double-relayed coherence transfer COSY 2D experiments, in addition to 1D double resonance in the difference mode as described.[16] Assignments of the ^{13}C NMR spectra (Table 2) were made[4,6] by using 2D ^{1}H–^{13}C correlation spectroscopy and ^{13}C NMR data for the corresponding methyl glycosides in cases of glycosylating sugar residues.

The glycosylation effects[18] in the ^{13}C NMR spectra of disaccharides, which are the differences in chemical



	X	Y
1	α-D-Man	α-D-Man
2	α-D-Man	β-D-Glc
3	α-D-Man	α-L-Rha
4	α-D-Man	β-L-Fuc
5	β-D-Glc	α-D-Man
6	β-D-Glc	β-D-Glc
7	β-D-Glc	α-L-Rha
8	β-D-Glc	β-L-Fuc
9	α-L-Rha	α-D-Man
10	α-L-Rha	β-D-Glc
11	α-L-Rha	α-L-Rha
12	α-L-Rha	β-L-Fuc
13	β-L-Fuc	α-D-Man
14	β-L-Fuc	β-D-Glc
15	β-L-Fuc	α-L-Rha
16	β-L-Fuc	β-L-Fuc

	X
17	α-D-Man
18	β-D-Glc
19	α-L-Rha
20	β-L-Fuc

Y-(1 → 4)-α-L-Rha-OMe

	Y
21	α-D-Man
22	β-D-Glc
23	α-L-Rha
24	β-L-Fuc

* *Correspondence to*: A. S. Shashkov.

† Synthesis, NMR and Conformational Studies of Branched Oligosaccharides. Part 17. For Part 16, see Ref. 1.

Contract grant sponsor: RFFI, *Contract grant number*: 93-03-18196.

CCC 0749–1581/97/060414–06 $17.50

Table 1. ^{1}H NMR data (D_2O, δ in ppm, J in Hz) for oligosaccharides 1–16, 21 and 24

Compound	Residue	H-1	H-2	H-3	H-4	H-5	H-6a	H-6b	OMe	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6a}$	$J_{5,6b}$	$J_{6a,6b}$
1	α-D-Man-(1→3)-	5.06	4.00	3.87	3.65					1.9	3.0	9.0	9.0			
	α-D-Man-(1→4)-	5.10	3.99	3.81	3.67					1.9	3.5	9.5	9.5			
	α-L-Rha-OMe	4.74	4.20	4.02	3.75	3.85	1.36		3.41	2.5	2.5	8.5	8.5	6.0		
2	α-D-Man-(1→3)-	5.07	3.98	3.90	3.67	[a]	3.87	[a]		2.0	3.5	9.5	9.5			
	β-D-Glc-(1→4)-	4.66	3.26	[b]	[b]	[b]	3.90	3.74		7.5	8.5					
	α-L-Rha-OMe	4.73	4.19	4.04	3.91		1.35	—	3.40	2.5	2.5	8.5	8.5	6.0		
3	α-D-Man-(1→3)-	5.08	4.00	3.79	3.71	3.60	3.92	3.77		1.9				2.5		12.5
	α-L-Rha-(1→4)-	5.15	4.03	3.73	3.49	3.81	1.31			1.5		9.6	9.6	6.5		
	α-L-Rha-OMe	4.75	4.24	4.02	3.72	3.83	1.37	—	3.41	2.2	2.2	9.6	9.6	6.0		
4	α-D-Man-(1→3)-	4.98	3.95	4.17	3.63	4.31	3.85	3.77		2.0	3.5	10.0	10.0	2.5	5.0	12.5
	β-L-Fuc-(1→4)-	4.45	3.36	3.61	3.71	3.74	1.30			8.0	10.0	3.5	<1	6.5		
	α-L-Rha-OMe	4.73	4.14	3.94	3.70	3.82	1.37		3.40	2.0	2.0	9.5	9.5	6.0		
5	β-D-Glc-(1→3)-	4.64	3.34	[b]	[b]	[b]	3.88	3.73		7.5						
	α-D-Man-(1→4)-	5.11	3.99	3.84	3.68	4.02	[c]	[c]		2.0	3.0	9.5	9.5			
	α-L-Rha-OMe	4.70	4.22	4.03	3.88	3.83	1.36		3.40	2.5	2.5	8.0	8.0	6.0		
6	β-D-Glc-(1→3)-	4.67	3.35				3.88	3.74		7.5				2.1	6.5	13.0
	β-D-Glc-(1→4)-	4.77	3.24	[d]	[d]	[d]	3.90	3.72		8.0	8.0			1.5	4.5	12.5
	α-L-Rha-OMe	4.68	4.16	4.01	3.81	3.75	1.35		3.39	1.9	3.2	9.0		6.0		
7	β-D-Glc-(1→3)-	4.61	3.35	3.51	[b]	[b]	3.90	3.73		8.0				<1	8.0	11.8
	α-L-Rha-(1→4)-	5.24	4.10	3.72	3.48	3.80	1.30			2.0	3.2	9.5	9.5	6.2		
	α-L-Rha-OMe	4.70	4.21	4.00	3.68	3.82	1.36		3.41	2.0	3.0	9.0	9.0	6.0		
8	β-D-Glc-(1→3)-	4.53	3.34	3.49	[b]	[b]	3.89	3.73		7.5	9.0	7.5		<1	5.0	12.5
	β-L-Fuc-(1→4)-	4.48	3.49	3.65	3.74	3.78	1.29			7.5	9.5	3.5		6.5		
	α-L-Rha-OMe	4.69	4.16	3.89	3.71	3.84	1.39		3.40	2.0	3.0	9.0	9.0	6.0		
9	α-L-Rha-(1→3)-	5.01	4.10	3.81	3.46	[e]	1.35			<1	3.0	9.5	9.5	6.0		
	α-D-Man-(1→4)-	5.05	3.97	3.81	3.68	[e]	[e]	[e]		2.0	2.0	9.0	9.0	—		
	α-L-Rha-OMe	4.65	4.00	3.90	3.68	[e]	1.28		3.40	2.0	2.0	9.0	9.0	6.0		
10	β-L-Rha-(1→3)-	4.96	4.04	3.74	4.39	3.74	1.21[h]			1.5	3.0	9.5	9.5	6.5		
	β-D-Glc-(1→4)-	4.55	3.21	[f]	[f]	[f]	3.84	3.68		8.0	9.0			2.0		12.5
	α-L-Rha-OMe	4.59	3.92	3.89	[g]	[g]	1.28[h]		3.33	2.0	3.0			6.0		
11	α-L-Rha-(1→3)-	4.97	3.96	3.84	3.46	3.85	1.28			1.5	3.0	9.5	9.5	6.3		
	α-L-Rha-(1→4)-	5.05	3.91	3.72	3.48	3.81	1.30			1.5	2.5	9.5	9.5	6.0		
	α-L-Rha-OMe	4.66	4.02	3.93	3.63	3.82	1.35		3.40	2.0	3.0	9.5	9.5	6.0		
12	α-L-Rha-(1→3)-	5.12	4.14	3.80	3.44		1.27			1.8	3.5	9.5	9.5	6.5		
	β-L-Fuc-(1→4)-	4.43	3.43	3.64	3.72	3.76	1.37			7.5	10.0	3.5	<1	6.0		
	α-L-Rha-OMe	4.65	3.98	3.88	3.69		1.27		3.39	2.0	3.0	9.0	9.0	6.5		
13	β-L-Fuc-(1→3)-	4.42	3.46	3.62	3.72	3.74	1.27			7.5	9.5	3.5	<1	6.5		
	α-D-Man-(1→4)-	5.01	3.96	3.93	3.65	4.40	3.87	3.78		<1						
	α-L-Rha-OMe	4.72	4.11	3.97	3.75	3.79	1.35		3.40	2.0	3.0			5.5		
14	β-L-Fuc-(1→3)-	4.49	3.56	3.68	3.78	3.82	1.30			8.0	10.0	3.4		6.6		
	β-D-Glc-(1→4)-	4.67	3.30	3.54	[d]	[d]	3.94	3.76		8.0	11.0			2.0		12.5
	α-L-Rha-OMe	4.76	4.15	4.08	[c]	[c]	1.44		3.43	2.0	3.2					
15	β-L-Fuc-(1→3)-	4.43	3.55	3.68	3.77	3.80	1.31			7.5	11.0	3.5	4.0	6.5		
	α-L-Rha-(1→4)-	5.26	4.24	3.75	3.50	3.81	1.33			1.5	3.5	9.5	9.5	6.0		
	α-L-Rha-OMe	4.76	4.12	4.06	3.71	3.81	1.39		3.44	1.5	3.0	8.5	9.5	6.0		
16	β-L-Fuc-(1→3)-	4.53	3.61	3.67	[c]	[c]	1.29			7.0	9.5	3.0		6.0		
	β-L-Fuc-(1→4)-	4.56	3.53	3.64	[c]	[c]	1.29			7.5	9.5	3.0		6.0		
	α-L-Rha-OMe	4.73	4.10	4.16	[i]	[i]	1.40		3.43	2.5	2.5	8.0		6.0		
21	α-D-Man-(1→4)-	4.98	4.01	3.82	3.71	3.92	3.81	3.79		2.0	3.0	9.8	9.8			
	α-L-Rha-OMe	4.70	3.94	3.80	3.53	3.77	1.33		3.40	1.8	3.5	9.5	9.5	6.2		
24	β-L-Fuc-(1→4)-	4.47	3.53	3.69	3.80	3.88	1.30			8.0	10.0	3.5	<1	6.5		
	α-L-Rha-OMe	4.74	4.04	3.83	3.58	3.84	1.40		3.43	1.5	3.5	9.5	9.5	6.0		

[a] 3.74–3.82 (m. 2H: H-5, −6b-Man).
[b] 3.41–3.54 (m. 3H: H-3, −4, −5-Glc in **2** and **5**; m. 2H: H-4, −5-Glc in **7** and **8**).
[c] 3.72–3.86 (m. 2H: H-6a, −6b-Man in **5**; m. 2H: H-4, −5-Rha in **14**; m. 4H: H-4, −5-Fuc. H-4, −5-Fuc′ in **16**).
[d] 3.39–3.50 (m. 3H: H-3, −4, −5-Glc in **6**; m. 2H: H-4, −5-Glc in **14**).
[e] 3.77–3.92 (m. 5H: H-5-Rha. H-5-Rha′. H-5, −6a, −6b-Man).
[f] 3.34–3.47 (m. 3H: H-3, −4, −5-Glc).
[g] 3.65–3.72 (m. 2H: H-4, −5-Rha)
[h] The assignments may be interchanged.
[i] 3.80–3.91 (m. 2H: H-4, −5-Rha).

Table 2. ^{13}C NMR data (D_2O, δ in ppm, 60–70 °C) for oligosaccharides 1–24, methyl rhamnoside 25 and hexopyranoses 26–29

Compound	Residue	C-1	C-2	C-3	C-4	C-5	C-6	OMe
1	α-D-Man-(1 → 3)-	97.8	71.3	71.7	68.1	74.8	62.3	
	α-D-Man-(1 → 4)-	101.6	70.9	71.8	68.2	74.8	62.3	
	α-L-Rha-OMe	101.5	67.25	74.5	77.5	69.45	18.7	56.2
2	α-D-Man-(1 → 3)-	97.4	71.5	72.1	68.9	74.3	62.3[b]	
	β-D-Glc-(1 → 4)-	103.5	75.0[a]	77.6	71.2	77.3	62.1[b]	
	α-L-Rha-OMe	101.9	67.0	75.3[a]	77.3	68.2	18.3	56.3
3	α-D-Man-(1 → 3)-	96.5	71.1	71.8	67.6	74.8	62.1	
	α-L-Rha-(1 → 4)-	102.7	71.8	71.4	72.7	70.9	17.55[a]	
	α-L-Rha-OMe	101.7	66.3	75.2	78.3	68.2	18.7[a]	56.0
4	α-D-Man-(1 → 3)-	97.1	71.6	71.4	68.6	73.4	62.3	
	β-L-Fuc-(1 → 4)-	104.3	73.0[a]	74.3	73.2	71.7	17.0	
	α-L-Rha-OMe	101.8	67.6	72.8[a]	78.5	69.6	18.1	56.2
5	β-D-Glc-(1 → 3)-	104.1	74.7	77.4	70.8	77.2	62.1	
	α-D-Man-(1 → 4)-	101.6	71.3	71.6	68.1	74.7	62.3	
	α-L-Rha-OMe	101.6	70.8	80.8	78.6	69.0	18.75	56.2
6	β-D-Glc-(1 → 3)-	104.7	74.9	77.6[b]	71.0[a]	77.3[b]	62.3[c]	
	β-D-Glc-(1 → 4)-	103.8	75.2	77.4[b]	71.3[a]	77.3[b]	62.1[c]	
	α-L-Rha-OMe	101.8	71.3	81.8	79.45	68.6	18.4	56.2
7	β-D-Glc-(1 → 3)-	104.8	74.65	77.5	70.9	77.2	62.1	
	α-L-Rha-(1 → 4)-	102.7	71.6	71.6	73.4	70.7	17.8[a]	
	α-L-Rha-OMe	101.75	71.4	82.2	79.1	68.5	18.9[a]	56.1
8	β-D-Glc-(1 → 3)-	105.75	74.7	76.5	70.9	77.1	62.1	
	β-L-Fuc-(1 → 4)-	104.6	72.3[a]	74.3	72.4[a]	72.3[a]	16.4	
	α-L-Rha-OMe	101.6	71.15	81.0	80.4	69.2	18.0	56.0
9	α-L-Rha-(1 → 3)-	103.7	71.7[a]	71.6[a]	73.4	70.4	18.7	
	α-D-Man-(1 → 4)-	102.1	71.4[a]	71.6[a]	67.9	74.8	62.4	
	α-L-Rha-OMe	101.8	71.6[a]	79.9	78.9	69.2	17.8	56.1
10	α-L-Rha-(1 → 3)-	103.7	71.5	71.7	73.4	70.4	17.8	
	β-D-Glc-(1 → 4)-	103.9	74.7	77.25[a]	71.2	77.1[a]	62.2	
	α-L-Rha-OMe	101.95	71.2	80.5	78.7	68.7	18.35	56.2
11	α-L-Rha-(1 → 3)-	103.8	72.1[a]	72.0[a]	73.5	70.6	18.0	
	α-L-Rha-(1 → 4)-	103.2	72.1[a]	71.9[a]	73.3	70.9	17.8	
	α-L-Rha-OMe	102.1	71.4	81.5	80.1	68.8	18.7	56.3
12	α-L-Rha-(1 → 3)-	102.8	71.3[a]	71.6[a]	73.5	70.3	17.9	
	β-L-Fuc-(1 → 4)-	104.8	72.6	74.3	72.0	72.8	16.9	
	α-L-Rha-OMe	101.8	71.3[a]	76.5	81.4	69.3	18.1	56.1
13	β-L-Fuc-(1 → 3)-	101.6	72.1	73.7	72.9	71.95	16.8	
	α-D-Man-(1 → 4)-	101.3	71.5	71.5	68.4	74.3	62.6	
	α-L-Rha-OMe	101.5	69.5	77.0	76.6	68.9	18.5	56.1
14	β-L-Fuc-(1 → 3)-	102.3	71.8	74.3	72.5	72.6	16.6	
	β-D-Glc-(1 → 4)-	105.1	75.25	77.2	71.0	77.2	62.1	
	α-L-Rha-OMe	101.6	68.9	79.0	80.9	68.9	18.3	56.1
15	β-L-Fuc-(1 → 3)-	101.9	72.1	74.3	72.8	72.1	16.7	
	α-L-Rha-(1 → 4)-	102.8	71.45	71.6	73.3	70.7	17.8	
	α-L-Rha-OMe	101.7	68.9	79.25	78.3	68.4	18.7	56.1
16	β-L-Fuc-(1 → 3)-	101.9	71.5	74.3	72.6	72.2	16.7	
	β-L-Fuc-(1 → 4)-	103.5	72.0	74.3	72.6	72.4	16.7	
	α-L-Rha-OMe	101.6	69.45	76.1	79.3	69.55	18.5	56.2
17[4]	α-D-Man-(1 → 3)-	97.5	71.6	71.75	67.85	73.9	62.1	
	α-L-Rha-OMe	102.05	67.2	75.45	71.6	69.75	18.05	56.1
18[15]	β-D-Glc-(1 → 3)-	105.0	74.9	77.3	71.1	77.2	62.2	
	α-L-Rha-OMe	102.0	71.2	81.5	72.5	69.7	18.2	56.1
19[6]	α-L-Rha-(1 → 3)-	103.3	71.1	71.1	73.0	70.0	17.6	
	α-L-Rha-OMe	101.8	70.8	79.0	72.4	69.6	17.6	56.1
20[4]	β-L-Fuc-(1 → 3)-	102.35	71.9	74.2	72.7	72.4	16.8	
	α-L-Rha-OMe	101.95	69.2	79.7	71.9	69.65	18.15	56.15
21	α-D-Man-(1 → 4)-	102.7	71.8[a]	71.7[a]	68.2	74.6	62.3	
	α-L-Rha-OMe	102.0	72.0[a]	70.7	82.7	68.75	18.3	56.1
22	β-D-Glc-(1 → 4)-	104.6	75.4	77.3	71.15	77.3	62.3	
	α-L-Rha-OMe	102.1	71.5	71.75	82.6	68.4	18.2	56.2
23	α-L-Rha-(1 → 4)-	102.8	71.8	72.3	73.3	70.6	17.8	
	α-L-Rha-OMe	102.1	71.7	71.9	81.1	68.3	18.6	56.1

Table 2. *Continued*

Compound	Residue	C-1	C-2	C-3	C-4	C-5	C-6	OMe
24	β-L-Fuc-(1 → 4)-	104.5	72.2	74.3	72.6	72.3	16.6	
	α-L-Rha-OMe	102.0	70.9	70.6	83.7	68.4	18.0	56.2
25[17]	α-L-Rha-OMe	102.1	71.3	71.6	73.3	69.6	17.8	55.9
26[18]	α-D-Man-OH	95.3	72.0	71.5	68.2	73.7	62.3	
27[19]	β-D-Glc-OH	97.1	75.4	77.0	70.9	77.2	62.1	
28[18]	α-L-Rha-OH	95.2	72.1	71.3	73.5	69.5	18.0	
29[20]	β-L-Fuc-OH	97.3	72.8	74.0	72.5	71.9	16.7	

[a,b,c] Assignments may be interchanged.

shifts of the respective carbon atoms in the monosaccharide fragments of disaccharide and in corresponding monosaccharides (the ^{13}C NMR data for the respective monosaccharides **25**–**29** are also included in Table 2), are summarized in Table 3. These data are in good agreement with a previously published[18] glycosylation effect database and supplement it.

The deviation from additivity values (ΔΔ), which were observed in the case of branched trisaccharides **1**–**16** are presented in Table 4. These values represent the deviation between experimental and calculated chemical shift values for the respective carbons C-1–C-6 of the bisglycosylated unit and for C-1′ and C-1″ [anomeric carbons of the 3- and 4-substituents; the numbering of the carbon atoms is shown on the formula of the trisaccharide (**1**)], which are used in computational calculations.[2,3]

The ΔΔ values for carbon atoms in the methyl α-L-rhamnopyranoside fragment, for example for C-*i*, were calculated using Eqn (1) and for C-1′ and C-1″ using Eqns (2) and (3), respectively.

$$\Delta\Delta\delta\text{C-}i = \delta\text{C-}i_{\text{TS}} - \delta\text{C-}i_{(1\rightarrow3)} - \delta\text{C-}i_{(1\rightarrow4)} + \delta\text{C-}i_{\alpha\text{-L-Rha}p\text{-OMe}} \quad (1)$$

$$\Delta\Delta\delta\text{C-}1' = \delta\text{C-}1'_{\text{TS}} - \delta\text{C-}1'_{(1\rightarrow3)} \quad (2)$$

$$\Delta\Delta\delta\text{C-}1'' = \delta\text{C-}1''_{\text{TS}} - \delta\text{C-}1''_{(1\rightarrow4)} \quad (3)$$

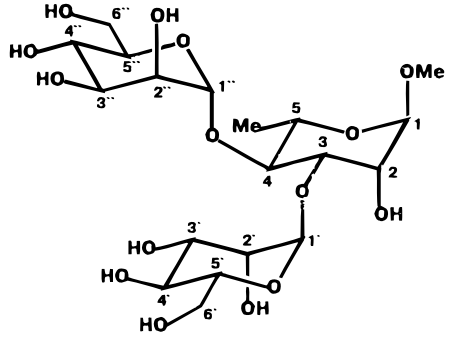
In Eqn (1), δC-i_{TS}, δC-$i_{(1\rightarrow3)}$, δC-$i_{(1\rightarrow4)}$ and δC-$i_{\alpha\text{-L-Rha}p\text{-OMe}}$ are the chemical shifts of C-*i* in ^{13}C NMR

Table 3. Effects of glycosylation on the chemical shifts (ppm)of the ^{13}C resonances in disaccharides 17–24

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-2′	C-5′
17	−0.05	−4.1	3.85	−1.7	0.15	0.25	2.2	−0.4	0.2
18	−0.1	−0.1	9.9	−0.8	0.1	0.4	7.9	−0.5	0
19	−0.3	−0.5	7.4	−0.9	0	−0.2	8.1	−1.0	0.5
20	−0.15	−2.1	8.1	−1.4	0.05	0.35	5.05	−0.9	0.5
21	−0.1	0.7	−0.9	9.4	−0.85	0.5	7.4	−0.2	0.9
22	0	0.2	0.15	9.3	−1.2	0.4	7.5	0	0.1
23	0	0.4	0.3	7.8	−1.3	0.8	7.6	−0.3	1.1
24	−0.1	−0.4	−1.0	10.4	−1.2	0.2	7.2	−0.6	0.4

Table 4. Deviations from additivity in ^{13}C NMR spectra of trisaccharides 1–16 (ppm)

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-1′	C-1″
1	−0.45	−0.65	−0.05	−3.5	0.55	0.15	0.3	−1.1
2	−0.15	−0.4	−0.3	−3.6	−0.35	−0.15	−0.1	−1.1
3	−0.35	−1.3	−0.55	−1.1	−0.25	−0.15	−1.0	−0.1
4	−0.15	0.8	−1.65	−3.5	1.05	−0.15	−0.4	−0.2
5	−0.3	−1.1	0.2	3.3	0.15	0.05	−0.9	−1.1
6	−0.2	−0.1	0.15	−2.35	0.1	−0.2	−0.3	−0.8
7	−0.25	−0.2	0.4	−1.2	0.1	−0.1	−0.2	−0.1
8	−0.3	0.35	0.5	−2.5	0.7	−0.4	0.75	0.1
9	0.1	0.1	1.8	−2.9	0.45	−0.3	0.4	−0.6
10	0.15	0.2	1.35	−3.0	0.3	0.35	0.4	−0.7
11	0.3	0.2	2.2	−0.1	0.5	0.3	0.5	0.4
12	0.1	0.9	−1.5	−1.4	0.9	0.3	−0.5	0.3
13	−0.35	−0.4	−1.8	−4.7	0.1	−0.15	−0.75	−1.4
14	−0.35	−0.5	−0.85	−0.3	0.45	−0.25	−0.05	0.5
15	−0.25	−0.7	−0.75	−1.4	0.05	−0.25	−0.45	0
16	−0.25	0.65	−2.6	−3.0	1.1	0.15	−0.45	−1.0



1

spectra of the examined trisaccharide, $(1 \rightarrow 3)$- and $(1 \rightarrow 4)$-linked disaccharides and methyl α-L-rhamnopyranoside (**25**), respectively.

The data from the Table 4 show that almost all trisaccharides display significant ΔΔ values, especially for glycosylated C-3 and C-4 of the branched rhamnose moiety (from −4.7 up to 2.2). Also, the anomeric carbons in monosaccharide substituents have considerable ΔΔ values (from −1.4 up to 0.75). This situation is different from that observed in a study of series of 2,3-di-*O*-glycosylated α-D-glucosides[11,12] and β-D-galactosides[12,13] with 2,3-diequatorial branching, which included compounds with three different types of ΔΔ values: significant ($|\Delta| > 2$ ppm), moderate ($1 < |\Delta\Delta| < 2$ ppm) and small ($|\Delta\Delta| < 1$ ppm). Comparison of the ΔΔ values for these series indicates that there are significant differences between the oligosaccharides with similar types of branching but with different character and orientation of substituents neighboring the branching point. Thus, the conclusion can be drawn that the transfer of ΔΔ values from trisaccharides with 2,3-diequatorial branching to stereochemically similar structures with 3,4-diequatorial branching[8,9] is not correct. This is the reason why ΔΔ values obtained for model trisaccharides with similar character and orientation of neighboring substituents should be used when performing computer-based calculations of the spectra of branched polysaccharides.

The correlation between the deviations from additivity in the ^{13}C NMR spectra of branched trisaccharides **1**–**16** and their stereochemical properties together with a detailed comparative analysis of the data for diequatorially branched oligosaccharides with different positions of the branch point, including 2,3-di-*O*-glycosylated α-D-glucosides and β-D-galactosides and 3,4-di-*O*-glycosylated α-D-glucosides and α-L-rhamnosides will be considered in a further paper in this series.[21]

EXPERIMENTAL

The 1D and 2D NMR experiments were performed[12] on solutions (2–5%) in D_2O at 60–70 °C using Bruker WM-250 (for ^1H) and AM-300 (for ^{13}C) spectrometers with acetone as the reference (^1H 2.225 ppm; ^{13}C 31.45 ppm). Assignments of the ^1H NMR spectra (Table 1) were made[4,6] using a combination of COSY and relayed and double-relayed coherence transfer COSY 2D experiments, and also 1D double resonance in the difference mode as described[16] (standard Bruker software for ASPECT-2000). The HDO signal was suppressed during relaxation delay (1 s). D_2 was 33 ms (0.25 J; $J = 7.5$ Hz). The spectral windows were *ca* 500 Hz (the region of the pyranose ring protons only). Data sets consisting of 256 t_1 experiments each with 512 data points were zero-filled to 512 data points. Prior to Fourier transformation, the FIDs were multiplied with a sine-bell window function (not shifted).

Assignments of the ^{13}C NMR spectra (Table 2) were made[4,6] by using 2D ^1H–^{13}C correlated spectroscopy. The typical spectral window was 500 Hz for ^1H and 5000 Hz for ^{13}C (the regions of pyranose ring protons and carbon atoms only). Data sets consisting of 256 t_1 experiments each with 2K data points were zero-filled to 512 data points. For detection of ^1J correlations, D_3 was set to 3.2 ms and D_4 to 1.6 ms (0.5 and 0.25 J, respectively; $J = 155$ Hz). FIDs were multiplied with a square sine-bell window function (shifted by p/2) in both directions, prior to Fourier transformation.

The syntheses of compounds **1**–**24** have been published previously.[1,4,15]

Acknowledgements

RFFI is gratefully acknowledged for financial support (Grant 93-03-18196). E.A.K. thanks the International Science Foundation for financial support (Grant No. a863-x).

REFERENCES

1. E. A. Khatuntseva, A. S. Shashkov and N. E. Nifant'ev, *Bioorg. Khim.* **22**, 376 (1996).
2. G. M. Lipkind, A. S. Shashkov and N. K. Kochetkov, *Carbohydr. Res.* **198**, 399 (1992).
3. G. M. Lipkind, A. S. Shashkov, N. E. Nifant'ev and N. K. Kochetkov, *Carbohydr. Res.* **237**, 11 (1992).
4. N. E. Nifant'ev, L. V. Backinovsky, G. M. Lipkind, A. S. Shashkov and N. K. Kochetkov, *Bioorg. Khim.* **17**, 517 (1991).
5. N. E. Nifant'ev, A. S. Shashkov, G. M. Lipkind and N. K. Kochetkov, *Carbohydr. Res.* **237**, 95 (1992).
6. G. M. Lipkind, N. E. Nifant'ev, A. S. Shashkov and N. K. Kochetkov, *Can. J. Chem.* **68**, 1238 (1990).
7. N. K. Kochetkov, G. M. Lipkind, A. S. Shashkov and N. E. Nifant'ev, *Carbohydr. Res.* **221**, 145 (1991).
8. H. Baumann, B. Erbing, P.-E. Jansson and L. Kenne, *J. Chem. Soc., Perkin Trans. 1* 2153 (1989).
9. H. Baumann, B. Erbing, P.-E. Jansson and L. Kenne, *J. Chem. Soc., Perkin Trans. 1* 2167 (1989).
10. G. M. Lipkind, A. S. Shashkov, O. A. Nechaev, V. I. Torgov, V. N. Shibaev and N. K. Kochetkov, *Bioorg. Khim.* **15**, 1366 (1989).
11. N. E. Nifant'ev, V. Yu. Amochaeva, A. S. Shashkov and N. K. Kochetkov, *Carbohydr. Res.* **250**, 211 (1993).
12. A. S. Shashkov, N. E. Nifant'ev V. Yu. Amochaeva and N. K. Kochetkov, *Magn. Reson. Chem.* **31**, 599 (1993).
13. A. S. Shashkov, N. E. Nifant'ev, V. Yu. Amochaeva and N. K. Kochetkov, *Bioorg. Khim.* **19**, 633 (1993).
14. N. K. Kochetkov, B. A. Dmitriev, A. V. Nikolaev, N. E. Bayramova and A. S. Shashkov, *Bioorg. Khim.* **5**, 64 (1979).
15. S. S. Mamyan, G. M. Lipkind, A. S. Shashkov, N. E. Bairamova, N. E. Nikolaev and N. K. Kochetkov, *Bioorg. Khim.* **14**, 205 (1988).

16. N. A. Kocharova, Y. A. Knirel, A. S. Shashkov, N. K. Kochetkov and G. B. Pier, *J. Biol. Chem.* **263**, 11291–5 (1988).
17. N. E. Nifant'ev, A. S. Shashkov, G. M. Lipkind and N. K. Kochetkov, *Carbohydr. Res.* **237**, 95 (1992).
18. G. M. Lipkind, A. S. Shashkov, Y. A. Knirel, E. V. Vinogradov and N. K. Kochetkov, *Carbohydr. Res.* **175**, 59 (1988).
19. P. A. J. Gorin, *Adv. Carbohydr. Chem. Biochem.* **38**, 13 (1980).
20. K. Bock and C. Pedersen, *Adv. Carbohydr. Chem. Biochem.* **41**, 27 (1983).
21. A. S. Shashkov, E. A. Khatuntseva and N. E. Nifant'ev, in preparation.