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INVESTIGATION OF THE *EXO* AND *ENDO* ISOMERS OF DIOXOLANE-TYPE BENZYLIDENE DERIVATIVES OF CARBOHYDRATES BY ^{13}C NMR SPECTROSCOPY

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Abstract—The absolute configurations of nine 2,3-O-benzylidene-α-L-rhamno- and α-D-mannopyranoside diasteteomeric pairs were determined and the ^{13}C NMR spectra of further thirteen α-L-rhamno- and α-D-mannopyranosides, having various substituents, were completely assigned.

Four ^{13}C shifts were found suitable for the determination of the absolute configuration of the dioxolane skeleton. (1) The chemical shift of the acetal carbon in the *endo* isomers is between 103.9 and 104.7 ppm whereas for the *exo* isomers this region extends from 102.8 to 103.4 ppm; (2) The formation of the dioxolane ring causes a deshielding effect for the bridgehead carbons, in the *exo* isomers this effect is more pronounced for C-3 whereas in the *endo* isomers for C-2. For C-4, shielding effect was found in the *exo* isomers and deshielding effect in the *endo* ones; (3) The chemical shift of the quaternary carbon of the phenyl group is greater in the *exo* isomers than in the *endo* ones; (4) The difference between the shift of the acetal carbon and that of the quaternary carbon of the phenyl group in the *exo* isomers is greater than 35.4 ppm, in the *endo* isomers is less than 33.7 ppm.

During the structural investigation of the lipopolysaccharide functioning as the antigen of *Escherichia coli* 08, the trisaccharides O-α-D-Manp-(1→2)-O-α-D-Manp-(1→2)-D-Man and O-α-D-Manp-(1→3)-O-α-D-Manp-(1→2)-D-Man were isolated, among other degradation products.[1] In the course of the synthesis of these trisaccharides, both the *exo* and the *endo* isomers of benzyl 3-O-benzyl-4,6-O-benzylidene-2-O-(2,3 : 4,6-di-O-benzylidene-α-D-mannopyranosyl)-α-D-mannopyranoside[2] (4 *exo* and 4 *endo*) were prepared. The absolute configuration of the dioxolane-type benzylidene ring in 4 *exo* and 4 *endo* could be determined with certainty on the basis of their ^1H NMR spectra, using the earlier observation of Baggett *et al.*[3] according to which the benzylidene proton in the *exo* isomers always resonates at a lower field than that of the corresponding *endo* isomers. In our case, the skeletal protons and H-1′ characteristic of the anomeric configuration of the interglycosidic linkage, gave higher-order multiplets and could not be assigned in a first-order analysis. ^1H NMR was, therefore, not suitable for the determination of the anomeric configuration of the interglycosidic linkage and of the configuration of the dibenzylidene-mannopyranosyl part, although even the latter may be questionable as pointed out by Freestone *et al.*[4] in case of 7-(2,3:4,6-di-O-benzylidene-α-D-mannopyranosyl)-theophyllin.

Recently we reported the determination of the absolute configuration of several dioxolane-type benzylidene derivatives of carbohydrates by ^{13}C NMR spectroscopy.[5] Complete assignments of the compounds studied are now presented.

RESULTS AND DISCUSSION

^{13}C NMR spectra of the following compounds, shown in Tables 1 and 2, were recorded and assigned:

Benzyl 3-O-benzyl-4, 6-O-benzylidene-2-O-(2, 3, 4, 6-tetra-O-acetyl-α-D-mannopyranosyl)-α-D-mannopyranoside[2] (1),

Methyl 2, 3, 4, 6-tetra-O-acetyl-α-D-mannopyranoside[6] (2),

Methyl 2, 3, 4, 6-tetra-O-acetyl-β-D-mannopyranoside[6] (3),

exo and *endo* Isomers of benzyl 3-O-benzyl-4, 6-O-benzylidene-2-O-(2, 3:4, 6-di-O-benzylidene-α-D-mannopyranosyl)-α-D-mannopyranoside[2] (4 *exo* and 4 *endo*),

Benzyl α-D-mannopyranoside[7] (5),

Benzyl 4, 6-O-benzylidene-α-D-mannopyranoside[8] (6),

Benzyl 3-O-benzyl-4, 6-O-benzylidene-α-D-mannopyranoside[9] (7),

Benzyl 3-O-benzyl-4, 6-O-benzylidene-2-O-methyl-α-D-mannopyranoside[9] (8),

Methyl 3-O-benzyl-4, 6-O-benzylidene-α-D-mannopyranoside[10] (9),

exo[11] and *endo*[9] Isomers of benzyl 2, 3:4, 6-di-O-benzylidene-α-D-mannopyranoside (10 *exo* and 10 *endo*),

exo[12] and *endo*[12] Isomers of methyl 2, 3:4, 6-di-O-benzylidene-α-D-mannopyranoside (11 *exo* and 11 *endo*),

Benzyl α-L-rhamnopyranoside[13] (12),

Benzyl 2, 3-O-isopropylidene-α-L-rhamnopyranoside[13] (13),

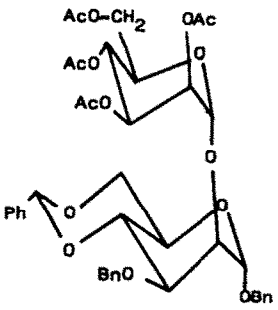
Benzyl 4-O-benzyl-2, 3-O-isopropylidene-α-L-rhamnopyranoside[14] (14),

Benzyl 4-O-acetyl-2, 3-O-isopropylidene-α-L-rhamnopyranoside[15] (15),

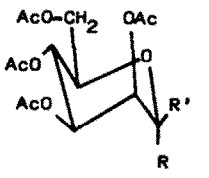
Benzyl 2, 3-O-isopropylidene-4-O-methyl-α-L-rhamnopyranoside (16),

exo[16] and *endo*[16] Isomers of benzyl 2, 3-O-benzylidene-α-L-rhamnopyranoside (17 *exo* and 17 *endo*),

THE STRUCTURE OF COMPOUNDS INVESTIGATED

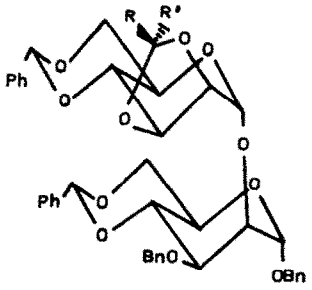


1



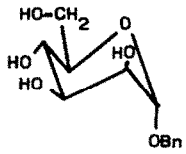
2 R = OCH_3; R' = H

3 R = H; R' = OCH_3

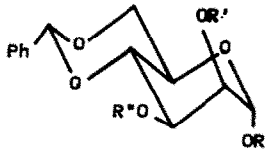


4_{exo} R = Ph; R' = H

4_{endo} R = H; R' = Ph



5

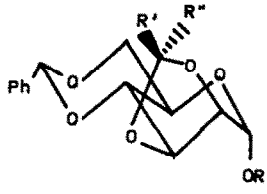


6 R = Bn; R' = R" = H

7 R = R" = Bn; R' = H

8 R = R" = Bn; R' = CH_3

9 R = CH_3; R' = H; R" = Bn

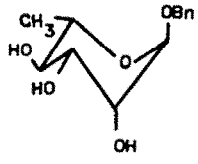


10_{exo} R = Bn; R' = Ph; R" = H

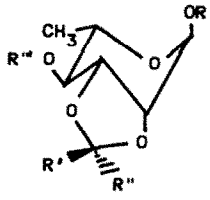
10_{endo} R = Bn; R' = H; R" = Ph

11_{exo} R = CH_3; R' = Ph; R" = H

11_{endo} R = CH_3; R' = H; R" = Ph



12



13 R = Bn; R' = R" = CH_3; R"' = H

14 R = R"' = Bn; R' = R" = CH_3

16 R = Bn; R' = R" = CH_3; R"' = CH_3-CO

16 R = Bn; R' = R" = R"' = CH_3

17_{exo} R = Bn; R' = Ph; R" = R"' = H

17_{endo} R = Bn; R' = R"' = H; R" = Ph

18_{exo} R = R"' = Bn; R' = Ph; R" = H

18_{endo} R = R"' = Bn; R' = H; R" = Ph

19_{exo} R = Bn; R' = Ph; R" = H; R"' = CH_3-CO

19_{endo} R = Bn; R' = H; R" = Ph; R"' = CH_3-CO

20_{exo} R = CH_3; R' = Ph; R" = R"' = H

20_{endo} R = CH_3; R' = R"' = H; R" = Ph

21_{exo} R = CH_3; R' = Ph; R" = H; R"' = Bn

21_{endo} R = CH_3; R' = H; R" = Ph; R"' = Bn

22_{exo} R = CH_3; R' = Ph; R" = H; R"' = CH_3-CO

22_{endo} R = CH_3; R' = H; R" = Ph; R"' = CH_3-CO

exo[15] and *endo*[15] Isomers of benzyl 4-O-benzyl-2, 3-O-benzylidene-α-L-rhamnopyranoside (**18** *exo* and **18** *endo*),
exo[15] and *endo*[15] Isomers of benzyl 4-O-acetyl-2,3-O-benzylidene-α-L-rhamnopyranoside (**19** *exo* and **19** *endo*),
exo[17] and *endo*[17] Isomers of methyl 2, 3-O-benzylidene-α-L-rhamnopyranoside (**20** *exo* and **20** *endo*),
exo[18] and *endo*[18] Isomers of methyl 4-O-benzyl-2, 3-O-benzylidene-α-L-rhamnopyranoside (**21** *exo* and **21** *endo*),
exo[17] and *endo*[17] Isomers of methyl 4-O-acetyl-2, 3-O-benzylidene-α-L-rhamnopyranoside (**22** *exo* and **22** *endo*).

The anomeric configuration of the interglycosidic linkage in **1** was unequivocally assigned as being α with reference to the carbon chemical shifts of the tetra-O-acetyl-mannopyranosyl unit and its $^1J_{CH}$ = 172 Hz coupling constant.[19] In **3** the value of the $^1J_{CH}$ coupling constant is 158 Hz.

The resonances of the "reducing" end of **1** were assigned with reference to the chemical shifts of **7** and **8**.

The assignment of the ^{13}C NMR spectra of **4** *exo* and **4** *endo* is based on the study of suitably substituted D-mannopyranosyl and L-rhamnopyranosyl derivatives, as model compounds. Complete assignment of the spectra of compounds investigated is shown in Tables 1 and 2.

The chemical shifts of carbons of **5**, except that of C-1 (100.2 ppm) are practically identical with those reported by Voelter[20] for methyl α-D-mannopyranoside (C-1: 102.0 ppm). The difference can be interpreted by the smaller "alkylation shift" of benzyl groups as compared to the well-known methylation shift. For the assignment of **6**, **7** and **9**, the known shifts[21] of methyl 4, 6-O-benzylidene-α-D-mannopyranoside were taken into account. At the same time, the investigation of **9** made possible differentiation between the methylene carbons of C_1-O-benzyl and C_3-O-benzyl group, respectively (69.3 and 73.3 ppm). Benzylation of HO-3 results, generally, in a downfield shift of +6 ppm for C-3 whereas a slight β-upfield shift (−1.2 ppm) is found in case of C-2. In **8** a downfield shift for C-2 of +9.6 ppm typical methylation shift[22] and a β shift for C-1 are observed. Complete assignments of the "reducing" unit of **1**, **4** *exo*, and **4** *endo* were enabled by the assignation of **8** and mainly **7**. Glycosylation shifts for C-2 of +6.9 ppm and +5.9 ppm were found in **1** and in both **4** *exo* and **4** *endo*, respectively, as compared to **7**. These data are in agreement with the literature values.[23–25] Assignment of the "non-reducing" residue and the complete analyses of **10** *exo*, **10** *endo*, **11** *exo* and **11** *endo* were made with reference to the data obtained for the benzyl α-L-rhamnopyranoside derivatives.

Our assignments of the resonances of **12** are similar to those given by Gorin *et al.*[26] for methyl α-L-rhamnopyranoside. The only difference is an upfield shift of −1.5 ppm for C-1, similar to that found in case of **5** for the methyl→ benzyl change. In **13** the isopropylidene ketal on the C-2 and C-3 oxygens produces an upfield shift of −3.8 ppm for C-1. Of the bridgehead carbons, a larger (+6.9 ppm) shift was found for C-3, having an equatorial oxygen, than for C-2 (+4.7 ppm) having an axial one. Both the direction and magnitude of these shifts are in very good agreement with the chemical shifts of the isopropylidene derivatives of 1,6-anhydro-hexopyranoses found by Paulsen *et al.*[27] and Perlin *et al.*[28] The dioxolane skeleton induces significant shifts of all skeletal carbons of **13** which could possibly originate in a change of the molecular geometry. This change is also indicated by the ^1H NMR spectrum of **13** revealing the alteration of the dihedral angle between the bridgehead hydrogens.

In the spectra of the benzylated **14**, acetylated **15**, and methylated **16** derivatives of **13**, mainly the shielding of C-4 can be observed as a result of the α alkylation and acetylation shifts but also small β shifts were found in all cases (Tables 3 and 4). The assignments of C-2, C-3 and C-4 of **13** and C-4 of **14**, **15**, and **16** were confirmed by $^{13}C\{^1H\}$ selective heteronuclear decoupling.

The assignment of the resonances of **17** *exo* was made considerably easier by the knowledge of the assignment of the signals of **13**. The assignment was further supported by the investigation of the spectra of **18** *exo* and **19** *exo* in which the chemical shift of C-2 agrees with the δ values found in **17** *exo*. As far the C-3 is concerned, slight alkylation or acylation β upfield shifts were observed in both the benzylated and acetylated derivatives. In **18** *exo* benzylation caused for C-4 an alkylation shift of +5.8 ppm whereas in **19** *exo* acetylation induced an upfield shift of −0.5 ppm.

In **17** *endo*, contrary to **17** *exo*, the introduction of an acetal ring induces approximately identical shifts for both the C-2 and the C-3 bridgehead atoms (~+7 ppm) while C-4 shows only a slight downfield shift as compared to C-4 of **12**. The differentiation between C-2 and C-3 was made possible by the analysis of the spectra of **18** *endo* and **19** *endo*. In the former one, benzylation at C-4 induces slight downfield shifts for C-2 and the neighbouring C-3 (+0.2 ppm and +0.5 ppm, respectively) while a +6.9 ppm alkylation shift for C-4 itself. In the 4-O-acetyl derivative (**19** *endo*) the position of C-2 is not changed whereas for C-3 an upfield shift of −2.9 ppm[29–34] and for C-4 a +1.1 ppm downfield shift is observed.

The shifts in the benzylidene derivatives of methyl α-L-rhamnopyranoside were similar in terms of both direction and magnitude. The investigation of these compounds was undertaken in order to determine the dependence of the chemical shift of the quaternary carbon of the benzylidene group on the spatial position of the phenyl group (*vide infra*).

The chemical shift differences between benzyl α-L-rhamnopyranoside (**12**) and its derivatives (**13**, **14**, **15**, **16**, **17** *exo*, **17** *endo*, **18** *exo*, **18** *endo*, **19** *exo*, **19** *endo*) moreover those between methyl α-L-rhamnopyranoside and its derivatives (**20** *exo*, **20** *endo*, **21** *exo*, **21** *endo*, **22** *exo*, **22** *endo*) are summarized in Table 5.

Complete analyses of **4** *exo*, **4** *endo*, **10** *exo*, **10** *endo*, **11** *exo* and **11** *endo* were made possible by the regularities observed in the spectra of 2,3-O-benzylidene-L-rhamnopyranosides: (1) In the *exo* isomers, similarly to the isopropylidene derivatives, C-3, having an equatorial O atom, is more shielded (+8 ppm) than C-2 having an axial oxygen (+5 ppm); (2) In the *endo* isomers the shifts of C-2 and C-3 are nearly identical, the positive shift of C-2 having an axial O atom is 0.5–1.0 ppm higher than that having an equatorial oxygen.

In **4** *exo*, **4** *endo*, **10** *exo*, **10** *endo*, **11** *exo* and **11** *endo* the formation of the dioxolane skeleton induces a 2–3 ppm upfield shift for C-5 relative to **6**. In the *exo* isomers, C-4 undergoes an upfield shift of 3.3–3.6 ppm whereas a downfield shift of 1.5 ppm occurs in the *endo* isomers. In the *exo* isomers, similarly to the rhamnose

Table 1. ^{13}C chemical shifts of α-D-mannopyranoside derivatives

Carbon	Compound	1	2	3	4 exo	4 endo	5	6	7	8	9	10 exo	10 endo	11 exo	11 endo
1		99.2			100.1	100.1	100.2	100.0	99.5	98.3	100.8				
	1'	99.6 /172/	98.8 /172.5/	100.0 /158/	99.1	99.2						97.5	96.9	99.1	98.8
2		77.0			76.0	76.0	71.7	71.1	70.1	79.7	69.2				
	2'	69.3	69.3	71.4	75.5	78.4						75.5	78.4	75.6	78.3
3		75.9			76.6	76.6	71.1	69.7	75.9	76.5	75.2				
	3'	68.7	68.8	69.0	77.6	74.1						77.6	74.1	77.7	74.2
4		79.4			79.3	79.4	67.7	79.1	79.0	79.2	78.2				
	4'	66.6	66.6	66.7	75.5	80.6						75.8	80.5	75.8	80.6
5		64.5			64.4	64.4	73.7	63.6	63.7	64.5	62.8				
	5'	69.4	69.8	72.8	61.0	61.0						60.8	60.6	60.5	60.5
6		69.3			69.2	69.2	61.8	68.9	68.9	68.9	68.2				
	6'	62.7	62.8	62.8	68.9	68.9						68.9	68.7	69.0	68.8
1-O Benzyl	CH_2	69.4			69.2	69.2	70.0	69.7	69.4	69.3		69.8	69.5		
	q	137.1			137.0	137.0	137.9	137.1	137.1	137.1		137.0	136.9		
1-O-Methyl	CH_3			57.2							54.0			55.0	54.8
2,3-O-Benzylidene															
	CH				103.1	104.1						103.0	103.9	103.0	103.9
	q				139.1	137.6						138.9	137.2	138.9	137.5
3-O-Benzyl	CH_2	73.3			73.4	73.4			73.1	73.3	72.2				
	q	138.7			138.8	138.8			138.1	138.8	137.7				
4,6-O-Benzylidene															
	CH	101.6			101.7	101.8		102.4	101.6	101.5	101.1	102.0	101.6	102.0	101.7
	q	138.0			102.0 138.0 137.6	101.8 137.9 137.5		137.5	137.7	137.8	137.2	137.5	137.3	137.5	137.5

Table 2. ^{13}C chemical shifts of α-L-rhamnopyranoside derivatives

Compound / Carbon	12	13	14	15	16	17		18		19		20		21		22	
						exo	endo	exo	endo	exo	endo	exo	endo	exo	endo	exo	endo
1	100.4	96.6	96.5	96.6	96.9	96.6	96.3	96.5	96.3	96.5	96.3	96.2	98.1	98.2	98.0	98.0	97.8
2	71.4	76.1	76.3	76.3	76.5	75.6	78.3	75.8	78.5	75.8	78.3	75.4	78.5	75.7	78.3	75.5	77.9
3	71.7	78.6	78.8	77.1	78.6	79.8	78.1	79.9	78.6	77.3	75.2	79.9	78.1	79.7	78.3	76.9	75.0
4	73.2	74.6	81.4	76.0	84.0	72.2	74.6	78.0	81.5	71.7	75.7	71.9	74.6	78.0	81.2	71.6	75.4
5	70.0	66.3	64.9	64.4	65.2	65.9	66.4	64.6	64.8	64.0	64.3	65.4	65.9	64.2	64.3	63.4	63.6
6	17.9	17.5	17.9	17.1	17.8	17.5	17.5	17.9	17.9	17.1	17.1	17.4	17.4	17.9	17.8	16.8	16.8
1-O benzyl CH_2	69.6	69.3	69.2	69.4	69.4	69.4	69.4	69.3	69.3	69.5	69.4						
q	138.1	137.3	137.4	137.3	137.7	137.2	137.2	137.2	137.3	137.1	137.1						
1-O-Methyl CH_3												54.8	54.7	54.7	54.5	54.5	54.4
2,3-O-Benzylidene																	
CH						103.1	104.1	102.9	104.0	103.1	104.7	102.9	104.1	102.9	103.9	102.8	104.3
q						138.8	137.2	138.8	137.6	138.5	136.7	138.8	137.3	139.0	137.6	138.5	136.7
2,3-O-Iso- C		109.6	109.2	109.8	109.6												
propylidene CH_3		28.0	28.0	27.7	28.1												
CH_3		26.2	26.4	26.5	26.3												
4-O-Benzyl CH_2			73.0					73.0	72.8					72.8	72.5		
q			138.6					138.2	138.4					138.3	138.3		
4-O-Methyl CH_3					59.2												
4-O-Acetyl CH_3				20.8						20.9	20.9					20.4	20.4
CO				169.7						170.0	169.8					169.6	169.4

Table 3. Relative chemical shifts of 2,3-di-O-substituted α-L-rhamnopyranosides upon benzylation of the 4-OH group

Compound / Carbon	14	18 exo	18 endo	21 exo	21 endo
C-1	-0.1	-0.1	0	0	-0.1
C-2	+0.2	+0.2	+0.2	+0.3	-0.2
C-3	+0.2	+0.1	+0.5	-0.2	+0.2
C-4	+6.8	+5.8	+6.9	+6.1	+6.6
C-5	-1.4	-1.3	-1.6	-1.2	-1.6
C-6	+0.4	+0.4	+0.4	+0.5	+0.4
Ph-CH		-0.2	-0.1	0	-0.2
Cq		0	+0.4	+0.2	+0.3

Table 4. Relative chemical shifts of 2,3-di-O-substituted α-L-rhamnopyranosides upon acetylation of the 4-OH group

Compound / Carbon	15	19 exo	19 endo	22 exo	22 endo
C-1	0	-0.1	0	-0.2	-0.3
C-2	+0.2	+0.2	0	+0.1	-0.6
C-3	-1.5	-2.5	-2.9	-3.0	-3.1
C-4	+1.4	-0.5	+1.1	-0.3	+0.8
C-5	-1.9	-1.9	-2.1	-2.0	-2.3
C-6	-0.4	-0.4	-0.4	-0.6	-0.6
Ph-CH		0	+0.6	-0.1	+0.2
Cq		-0.3	-0.5	-0.3	-0.6

derivatives, C-3 is more shielded (+7.9 ppm) than C-2 (+4.2 ppm). In the *endo* isomers the difference between the shielding of C-2 and C-3 is smaller than in the *exo* isomers, the shielding of C-2, having an axial oxygen being greater (Table 6).

In both L-rhamno- and D-mannopyranosides, the shielding of C-2 and C-4 in case of *endo* isomers and the shielding of C-3 in case of *exo* isomers is a more pronounced and consequent phenomenon.

The dependence of the chemical shift of the dioxolane acetal carbon benzylidene carbon on the configuration[5] in all compounds studied should be emphasized. This shielding is stronger in the *endo* isomers than in the *exo* isomers. This resonance occurs in the range of 103.9–104.7 ppm whereas the upper limit for *exo* isomers is 103.1 ppm. In the *exo* isomers the chemical shift of the acetal carbon is insensitive to substitution in the molecule whereas in the *endo* isomers acetylation induces a shift of +0.6 ppm.

^{13}C NMR spectroscopy is a good tool for the differentiation between the dioxane- and dioxolanetype benzylidene skeletons, as the acetal carbons of the former resonate below 102 ppm.

For the determination of the absolute configuration of the dioxolane-type acetal carbon a further possibility is provided by our observation that the chemical shift of the aromatic quaternary carbon, linked to the acetal carbon, depends on the configuration of the acetal carbon atom. This dependence is especially striking in the isomeric pairs **20** *exo* – **20** *endo* and **22** *exo* – **22** *endo*, having only one quaternary C atom. This atom resonates above 138.5 ppm in the *exo* isomers whereas under 137.6 ppm in the *endo* isomers. This latter resonance practically coincides with that of the quaternary carbon of the phenyl group in the 4,6-O-benzylidene derivatives.

The determination of the absolute configuration is made especially easy by the calculation of the difference ($\Delta\delta$) between the chemical shift of the acetal carbon and that of the quaternary carbon (Table 7). In *exo* isomers this difference is greater than 35.4 ppm and in the *endo* isomers is less than 33.7 ppm.

Our study enables the determination by ^{13}C NMR spectroscopy of the absolute configuration of the 2,3-O-benzylidene derivatives of pyranosides even if only one member of the isomeric pair is available, considering the chemical shifts of the acetal and quaternary carbons of the phenyl group and the difference between these shifts.

Table 5. ^{13}C shielding differences (ppm) between benzyl α-L-rhamnopyranoside (12) or methyl α-L-rhamnopyranoside and their dioxolane derivatives

Compound	benzyl α-L-rhamnopyranoside derivatives										methyl α-L-rhamnopyranoside derivatives					
Carbon	2,3-O-isopropylidene				exo-2,3-O-benzylidene			endo-2,3-O-benzylidene			exo-2,3-O-benzylidene			endo-2,3-O-benzylidene		
	4-OH 13	4-O-Bz 14	4-OAc 15	4-OCH_3 16	4-OH 17	4-OBz 18	4-OAc 19	4-OH 17	4-OBz 18	4-OAc 19	4-OH 20	4-OBz 21	4-OAc 22	4-OH 20	4-OBz 21	4-OAc 22
1	-3.8	-3.9	-3.8	-3.5	-3.8	-3.9	-3.9	-4.1	-4.1	-4.1	-3.7	-3.7	-3.9	-3.8	-3.9	-4.1
2	+4.7	+4.9	+4.9	+5.1	+4.2	+4.4	+4.4	+6.9	+7.1	+6.9	+4.7	+4.7	+4.5	+7.5	+7.3	+6.9
3	+6.9	+7.1	+5.4	+6.9	+8.1	+8.2	+5.6	+6.4	+6.9	+3.5	+8.6	+8.4	+5.6	+6.8	+7.0	+3.7
4	+1.4	+8.2	+2.8	+10.8	-1.0	+4.8	-1.5	+1.4	+8.3	+2.5	-1.2	+4.9	+1.5	+1.5	+5.1	+2.3
5	-3.7	-5.1	-5.6	-4.8	-4.1	-5.4	-6.0	-3.6	-5.2	-5.7	-4.0	-5.2	-6.0	-3.5	-5.1	-5.8
6	-0.4	0	-0.8	-0.1	-0.4	0	-0.8	-0.4	0	-0.8	-0.3	+0.2	-0.9	-0.3	+0.1	-0.9

Chemical shifts for methyl α-L-rhamnopyranoside are as follows[25] : 101.9 /C-1/, 71.0 /C-2/, 71.3 /C-3/, 73.1 /C-4/, 69-4 /C-5/, 17.7 /C-6/

Table 6. ^{13}C shielding differences (ppm) between benzyl 4,6-O-benzylidene-α-D-manopyranoside and the di-O-benzylidene mannopyranoside derivatives

Carbon \ Compound	4 exo	4 endo	10 exo	10 endo	11 exo	11 endo
1'	-0.9	-0.8	-2.5	-3.1	-0.9	-1.2
2'	+4.2	+7.1	+4.2	+7.1	+4.3	+7.0
3'	+7.9	+4.4	+7.9	+4.4	+8.0	+4,5
4'	-3.6	+1.5	-3.3	+1.4	-3.3	+1.5
5'	-2.6	-2.6	-2.8	-3.0	-3.1	-3.1
6'	0	0	0	-0.2	+0.1	-0.1

Table 7. Difference ($\Delta\delta$) between the chemical shifts of the quaternary and the acetal carbon atoms of benzylidene groups

Compound	$\Delta\delta = \delta_C$ quat. - δ_C acetal	
	exo	endo
4	36.0	33.5
10	35.9	33.3
11	35.9	33.6
17	35.7	33.1
18	35.9	33.6
19	35.4	32.0
20	35.9	33.2
21	36.1	33.7
22	35.7	32.4

EXPERIMENTAL

Natural-abundance, proton decoupled ^{13}C NMR spectra were obtained with a Varian XL-100-15 F.T. spectrometer (25.16 MHz), using 8K data points. All spectra were measured at 55° for 25% solutions in $CDCl_3$. $^1J_{CH}$ coupling constants were determined from natural-abundance proton coupled spectra measured by the gated decoupling technique.

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