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^{13}C-NMR STUDY OF METHYL- AND BENZYL ETHERS OF L-ARABINOSE AND OLIGOSACCHARIDES HAVING L-ARABINOSE AT THE REDUCING END. SYNTHESIS OF 2-O-β-D-GLUCOPYRANOSYL-, 2-O-α-L-RHAMNOPYRANOSYL-, 3-O-β-D-GLUCOPYRANOSYL-2-O-α-L-RHAMNOPYRANOSYL- AND 4-O-β-D-GLUCOPYRANOSYL-2-O-α-L-RHAMNOPYRANOSYL-L-ARABINOSE

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Abstract—The reaction of benzyl *exo*-3,4-O-benzylidene-β-L-arabinopyranoside **1** with α-acetobromo-D-glucose **3** resulted in a mixture of two disaccharides, **5** and **6**, in which the configuration of the acetal ring was different. The reaction of **1** with α-acetobromo-L-rhamnose **4** gave the desired disaccharide **7** without isomerisation of the dioxolane-type benzylidene ring. The reason for the isomerisation, occuring during the Koenigs–Knorr reaction, is discussed. Similar treatment of benzyl *endo*-3,4-O-benzylidene-β-L-arabinopyranoside **2** with **4** yielded **8**. Compounds **6**, **7** and **8** were deacetylated and benzylated to obtain **9**, **10** and **11**. Hydrogenolysis ($LiAlH_4$–$AlCl_3$) of all fully protected disaccharides afforded derivatives with a free OH-3 (**9**→**13** and **11**→**15**). Hydrogenolysis of **10** also resulted in **15**, and the desired **14** with a free OH-4 was only the minor product of the reaction. Glucosylation of compounds **14** and **15** resulted in the two trisaccharide derivatives in protected form (**16** and **17**). Deprotection of **6**, **7**, **16** and **17** gave the four title compounds (**22**, **23**, **18** and **19**).

The synthesized compounds were studied by ^{1}H- and ^{13}C-NMR spectroscopic methods. In disaccharides having (1→2) bonds and in trisaccharide **19** having (1→2) and (1→3) bonds the arabinose moiety is present in pyranose and furanose forms. The complex spectra of these derivatives were assigned using the methyl ethers of L-arabinose (**24**–**29**) as model compounds. The ^{13}C-NMR spectrum of **18** was assigned with the aid of 4-O-β-D-glucopyranosyl-L-arabinopyranose. For comparisons, the spectra of all mono-and dibenzyl ethers of benzyl β-L-arabinopyranoside were also recorded and assigned.

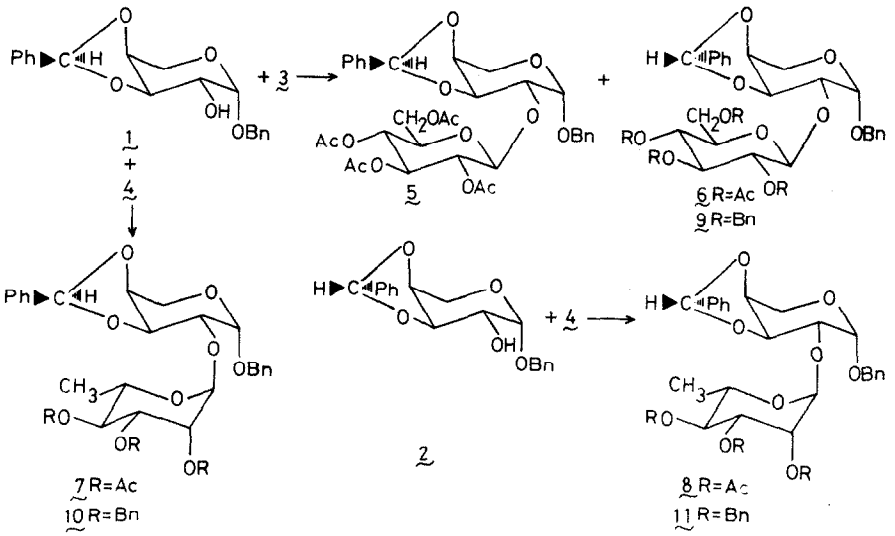
In nature both the D- and L-arabinose derivatives are very abundant compounds as the building blocks of polysaccharides[1] or as constituents of glycosides, mainly of saponine glycosides.[2–4] There are some studies on the synthesis of disaccharides containing a D- or L-arabinose moiety,[5] however the synthesis of higher oligosaccharides has not been reported. The acid reversion of D- or L-arabinose to oligosaccharides can not be taken into consideration as definitive synthesis.[6] The difficulties of such syntheses may be explained by the lack of suitably protected arabinose derivatives. We have shown that the reductive cleavage of the benzylidene ring is a suitable method for the preparation of different benzyl ethers even in the case of D- and L-arabinopyranosides.[7,8] Furthermore, it has been demonstrated that the benzylidene group can serve as a "temporary" blocking group for the preparation of higher oligosaccharides having branched structure.[9,10] Both disaccharides[2] and 4-O-β-D-glucopyranosyl-2-O-α-L-rhamnopyranosyl-L-arabinose reported here are sugar components of saponine glycosides.[3]

RESULTS AND DISCUSSION

The reaction of benzyl *exo*-3,4-O-benzylidene-β-L-arabinopyranoside[8] **1** with α-acetobromo-D-glucose **3** (2,3,4,6,-tetra-*O*-acetyl-α-D-glucosyl bromide) using the Helferich procedure resulted in two disaccharide derivatives (**5** and **6**) in a ratio of 53:47 (GLC). Examination of this mixture showed clearly that isomerization of the dioxolane ring had taken place and compound **5** proved to be benzyl *exo*-3,4-*O*-benzylidene-2-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl) -β -L-arabinopyranoside, whereas compound **6** was the *endo*-3,4-*O*-benzylidene isomer of **5**. The latter isomer **6** could be smoothly isolated by simple crystallization but the separation of **5** from the traces of the isomeric **6** proved to be unsuccessful.

The *endo*-configuration of the benzylidene ring of **6** was confirmed on the basis of ^{1}H and ^{13}C-NMR spectroscopic investigations;[11,12] the benzylidene proton resonated at 5.92 ppm, the signal of the acetalic carbon atom appeared at 103.7 ppm, whereas the benzylidene proton of the *exo*-isomer **5** was found at 6.16 ppm. These values are in good agreement with the corresponding data of compound **1** (6.18 and 103.0 ppm) and **2** (5.84 and 103.9 ppm).

The β-configuration of the interglycosidic bond in **6** was deduced from the ^{13}C-NMR chemical shift value (C-1' 100.8 ppm).



Acetal migration during the Koenigs–Knorr reaction was reported in several cases[13–17] and recently the structure of the acetal-migrated product has been determined in connection with the synthesis of laminaribiose[18] and that of an (1→6)-bonded digalactoside derivative.[19]

In the present reaction mercuric bromide catalyses the *exo*⇌*endo* isomerization and the very long time required for the glucosylation reaction (20 h) is enough to reach the equilibrium. The mechanism of this isomerization is the same as those of the acetal migration.[20]

Rhamnosylation of **1** with α-acetobromo-L-rhamnose **4** required only 30 min reaction time, in this case isomerization was not observed and crystalline benzyl *exo*-3,4-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-L-arabinopyranoside **7** was isolated. It was reported that the *endo*-benzylidene isomer of *p*-NO_2-phenyl α-L-rhamnopyranoside reacted more slowly than the *exo*-one,[21] and this observation was confirmed in the case of benzyl *endo*-3,4-*O*-benzylidene-β-L-arabinopyranoside[8] **2**, as well. The reaction of **2** with **4** required about 1 h and during this prolonged reaction time isomerization, to a small extent, took place but the presence of **7** did not affect the preparation of **8**, i.e. the isolation of benzyl *endo*-3,4-O-benzylidene-2-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl)-β-L-arabinopyranoside. The structure of the two diastereoisomeric disaccharides (**7** and **8**) was clearly proved by their ^{1}H NMR spectra; in the case of **7** the acetalic proton resonated at 6.16 ppm, and those of **8** appeared at 5.90 ppm.

Deacetylation of compounds **6**, **7** and **8**, followed by benzylation resulted in the crystalline disaccharide derivatives **9**, **10** and **11**, respectively. The ^{1}H-NMR spectra of the benzylated products showed that during the benzylation isomerization did not occur, the chemical shifts of the acetalic protons of the three disaccharides were the following: **9**: 5.84; **10**: 6.10; **11**: 5.86 ppm.

Studies on several acetal compounds have shown that the direction of the ring cleavage of the dioxolane-type benzylidene derivatives is determined by the configuration of the acetalic carbon atom.[22,23] Up to now only a few exceptions[8,24] to this rule have been found and we have assumed that these anomalies are strongly dependent on the rate of the isomerization, taking place under the conditions of the hydrogenolysis.[8,20]

Hydrogenolysis of compound **9** yielded the desired compound, i.e. benzyl 4-O-benzyl-2-O-(2,3,4,6-tetra-O-benzyl-β-D-glucopyranosyl)-β-L-arabinopyranoside **13** in crystalline form. The amount of the other, 3-O-benzyl isomer **12** was less than 5% (TLC), its presence was detected but it was not isolated.

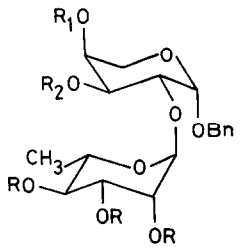
Surprisingly, the hydrogenolysis of **10** resulted in an irregular product, benzyl 4-O-benzyl-2-O-(2,3,4,-tri-O-benzyl-α-L-rhamnopyranosyl)-β-L-arabinopyranoside **15** and the amount of the expected product **14** was only 5% (TLC).

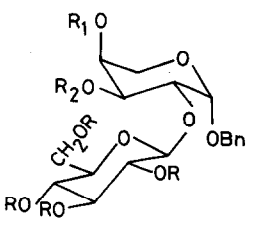
It may be assumed, that in the case of the above ring cleavage, the rate of the isomerization reaction was higher than the rate of the reduction of the oxocarbonium cation, formed from the *exo*-benzylidene ring of **10**. For this reason the quantity of $LiAlH_4$ in the "mixed-hydride" reagent[25] was increased, so it was hoped that the higher concentration of the hydride donor might increase the rate of the reduction of the oxocarbonium cation and, at the same time, the rate of the isomerization elicited by the chloroalane might be diminished. This assumption was correct, in part, and the ratio of **14** and **15** could be shifted to a value of 3:7 (TLC). Compounds **14** and **15** were separated by column chromatography.

Hydrogenolysis of **11** gave the expected product **15** and no trace of **14** could be detected by TLC.

Earlier studies have shown that the 2,4-di-O-substituted derivatives of benzyl β-L-arabinopyranoside possess higher chromatographic mobility (TLC) than the 2,3-di-O-substituted compounds.[8] Comparing the TLC behaviour of **12**, **13**, **14** and **15**, we assumed that compounds **12** and **14** were the 2,3-di-O-substituted arabinopyranoside derivatives and **13** and **15** were the 2,4,-di-O-substituted arabinopyranosides.

To get more information, compounds **13**, **14** and **15** were acetylated and the products were examined by ^{1}H-NMR. In the case of the acetate of **13** and **15** one proton shifted downfield, resonating at 5.32 and 5.14 ppm as doublet of doublets with the following coupling constants: $J_{2,3}$ 9.1 Hz, $J_{3,4}$ 3.6 Hz and $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.2 Hz, respectively. The multiplicity and the values of the couplings clearly showed that the proton, shifted





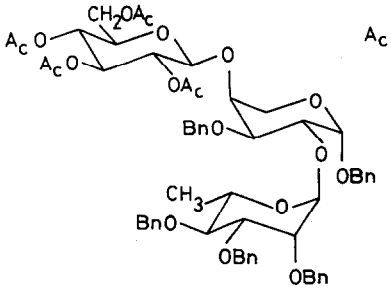
14 R_2=R = Bn i R_1=H
15 R_1=R = Bn i R_2=H
21 R_1=R_2= R = H

12 R_2=R = Bn i R_1= H
13 R_1=R = Bn i R_2= H
20 R_1=R_2=R = H

downfield, was the C_3-H in both cases, being the β-L-arabinopyranosides in Cl(L) conformation.

The spectrum of the acetate of **14** gave one proton multiplet at 5.38 ppm, originating from the coupling of H-4 with H-3 and H-5,5'.

Glycosylation of **14** and **15** with **3** according to the Helferich procedure resulted in benzyl 3-O-benzyl-4-O-(2,3,4,6 - tetra - O - acetyl - β - D - glucopyranosyl) - 2 - O - (2,3,4 - tri - O - benzyl - α - L - rhamnopyranosyl) - β - L - arabinopyranoside **16** and benzyl 4 - O - benzyl - 3 - O - (2,3,4,6 - tetra - O - acetyl - β - D - glucopyranosyl) - 2 - O - (2,3,4-tri - O - benzyl - α - L - rhamnopyranosyl) - β - L - arabinopyranoside **17**. Deacetylation of **16** and **17** and subsequent catalytic hydrogenation over Pd-on-carbon yielded the free trisaccharides **18** and **19** as amorphous solids.



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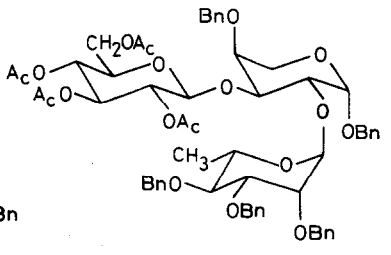


17

On removal of the O-acetyl- and benzylidene groups of **6** and **7** by Zemplén deacetylation and subsequent mild acid hydrolysis crystalline benzyl 2-O-β-D-glucopyranosyl - β - L - arabinopyranoside **20** and benzyl 2-O-α - L - rhamnopyranosyl - β - L - arabinopyranoside **21**, respectively, were obtained. Catalytic cleavage of the benzyl group of **20** and **21** resulted in crystalline 2 - O - β - D - glucopyranosyl - L - arabinose **22** and 2 - O - α - L - rhamnopyranosyl - L - arabinose **23**, respectively.

The ^{13}C-NMR spectra of compounds **20** and **21** were in good agreement with the postulated structures, the anomeric configuration of **21** was determined by measuring the $^1J_{C\text{-}1,H\text{-}1}$ coupling constant. However, both **22** and **23** showed complex ^{13}C-NMR spectra. The complex character of the spectra cannot be explained by any chemical transformation, or impurity, because compounds **22** and **23** were obtained by catalytic hydrogenolysis of **20** and **21** under very mild conditions.

Before the explanation of these spectra it is to be emphasized that ^{13}C-NMR spectroscopy is an excellent tool to determine the ring- and anomeric composition of various monosaccharides. D-Ribose was found to be the best model for showing the efficiency of this method,[26,27] and similarly, with the aid of ^{1}H-[28-29] and ^{13}C-NMR[30] spectra the composition of D-arabinose was also determined. Most recently, β-glucofuranose (0.13%) was also detected by ^{13}C-NMR spectroscopy in D_2O solution.[31] Similar investigations have been also made with several hexuloses.[32-34]

It was very obvious to assume, that the arabinose at the reducing end can exist in pyranose- and furanose forms with α- and β-anomeric configurations. Being (1→2)-bonds in the two disaccharides, the ring- and anomeric character of the reducing end is reflected at the C-1 of the gluco- and rhamnopyranosyl units.[35,36,10] This assumption was confirmed by the study of the spectra of 2-O-**24**, 3-O-**25**, 4-O-**26**, 2,3-di-O-**27**, 2,4-di-O-**28**- and 3,4-di-O-methyl-L-arabinose **29**,[37] and by the study of ring- and anomeric composition of L-arabinose in D_2O solution, where the following ratios of the isomers were found: α-*p*: 55%; β-*p*: 32%; α-*f*: 7% and β-*f*: 6%.

The detailed assignment of the methyl ethers is given in Table 1, and the following conclusions can be made in all methyl ethers in which the C_4–OH is free a considerable amount of furanoses can be found. The methylation shifts (α-shifts) are nearly 9–10 ppm, in comparison with the corresponding C atom in the arabinose unit. The β-shift values are strongly dependent on the stereo-

β-D-Glp-(1→4)
α-L-Rhp-(1→2) > L-Ara

18

β-D-Glp-(1→3)
α-L-Rhp-(1→2) > L-Ara

19

β-D-Glp-(1→2)-L-Ara

22

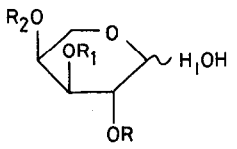
α-L-Rhp-(1→2)-L-Ara

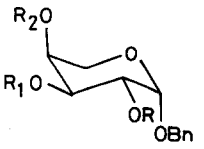
23

Table 1. ^{13}C-NMR data for L-arabinose methyl ethers (δ) in D_2O at 50°

Compounds		A		24			25			26		27			28		29	
		p	f	p	Δδ	f	p	Δδ	f	p	Δδ	p	Δδ	f	p	Δδ	p	Δδ
Carbons																		
C-1		97.5	102.0	97.2	-0.3	100.3	97.5	0	102.5	97.5	0	97.2	-0.3	100.5	97.2	-0.3	97.5	0
$^1J_{C-1,H-1}$		166.8					162.5			162								
C-2		72.7		82.4	+9.7	86.0	71.7	-4.5		73.0	+0.3	82.0	+9.3	89.6	82.7	+10.0	71.9	-0.8
C-3		73.3		72.6	-0.7		82.5	+9.2	87.1	73.0	-0.3	81.3	+8.0	85.0	72.4	-0.9	82.2	+8.9
C-4	α-anomers	69.2		69.1	-0.1		65.1	-4.1	79.9	78.8	+9.6	65.5	-3.7	83.2	78.7	+9.5	74.7	+5.8
C-5		67.0	62.1	66.7	-0.3	60.7	67.0	0	62.6	63.0	-4.0	66.7	-0.3	62.4	62.7	-4.3	62.8	-4.2
Me-2				60.7								60.6			60.8			
Me-3							57.1					57.9					57.4	
Me-4										57.8					57.8		57.4	
C-1		93.3	96.0	90.8	-2.5	94.7	93.4	+0.1	97.4	93.2	-0.1	90.7	-2.6	95.2	90.8	-2.5	93.2	-0.1
$^1J_{C-1,H-1}$		169.5					170			168								
C-2		69.4		78.6	+9.2	83.4	68.2	-1.2		69.7	+0.3	77.8	+8.4	85.4	78.9	+9.5	68.5	-0.9
C-3		69.5		68.4	-1.1		78.8	+9.3	83.5	69.1	-0.4	77.4	+7.9	84.0	68.1	-1.4	78.5	+9.0
C-4	β-anomers	69.3		69.4	-0.1		65.6	-3.7		79.0	+9.7	65.2	-4.1	81.6	79.2	+9.9	75.4	+6.1
C-5		63.2		63.0	-0.2	61.8	63.1	-0.1	63.8	59.4	-3.8	62.9	-0.3	64.0	59.1	-4.1	59.1	-4.1
Me-2				58.2								58.2			58.3			
Me-3							57.0					57.1					57.3	
Me-4										57.8					57.8		57.5	

A= L-Arabinose





24 R = CH_3 i R_1 = R_2 = H
25 R_1 = CH_3 i R = R_2 = H
26 R_2 = CH_3 i R = R_1 = H
27 R = R_1 = CH_3 i R_2 = H
28 R = R_2 = CH_3 i R_1 = H
29 R_1 = R_2 = CH_3 i R = H

30 R = Bn i R_1 = R_2 = H
31 R_1 = Bn i R = R_2 = H
32 R_2 = Bn i R = R_1 = H
33 R = R_1 = Bn i R_2 = H
34 R = R_2 = Bn i R_1 = H
35 R_1 = R_2 = Bn i R = H

chemical arrangement, their values are between −0.3 and −4.5 ppm. The introduction of a methyl group in position four results in a ~4 ppm upfield shift at C-5, and these values are nearly the same in the case of the α- and β-anomers. For this reason the C-5's are in the region of 63 ppm in the case of the α-anomers, and they resonate at 59 ppm in the β-anomers.

The resonances of the disaccharides **22** and **23** were assigned with reference to the spectrum of 2-O-methyl-L-arabinose **24**. There are three distinct sets of lines in the spectra of **22** and **23**. The first set is the anomeric region (103–93 ppm) in which eight signals can be found. In the second region the carbons of the branching points and the lines of the C-4α and C-4β of the furanose skeleton are involved. In the third region the other skeleton carbons of the disaccharides may be detected.

By comparison to the spectrum of **18** with those of the 4-O-methyl-**26** or with 2,4-di-O-methyl-L-arabinose **28**, it can be seen that the upfield shift of C-5 in the case of **18** is smaller than those of the methyl ethers.

To obtain more informations about the behaviour of substitution of arabinopyranoside derivatives on the ^{13}C-NMR spectra, a series of partially benzylated benzyl β-L-arabinopyranoside was recorded and assigned (Table 2).

The introduction of a benzyl group at a given position of benzyl β-L-arabinopyranoside results in a 8–9 ppm downfield shift, it is very similar to the values found in the case of benzylated L-rhamnopyranosides.[10] The highest magnitude of the β-shifts is about −3 ppm, and these values can also be found at position five in the case of 4-O-substituted derivatives. This β-shift value at C-5 is between the magnitude of the methylation and the glycosylation β-shift.

The chemical shift of C-5 of the arabinose moiety in **18** is very similar to those of 4-O-β-D-glucopyranosyl-L-arabinose,[38] in which the resonance lines are at 66.2 and 62.5 ppm, respectively. This finding clearly shows that the use of the chemical shift values of methyl- and benzyl ethers for the assignment of spectra of complex oligosaccharides has to be treated very carefully, and the conformation of the interglycosidic bonds might play a very decisive role in the spectral behaviour of carbohydrate oligomers.

The spectrum of compound **19** was assigned by comparison of the spectra of **22** and **23**. The arabinose moiety exists in α, β-pyranose and furanose forms, and the composition of the reducing end is strongly reflected in both monosaccharide moieties coupled to it at position C-2 and C-3. In the case of the rhamnose moiety this effect is stronger than in the case of the D-glucopyranosyl moiety, being at position 2.

It is also to be noted that the interpretation of the spectra of higher oligosaccharides having an equilibrium at the reducing end between the forms of α, β-pyranose and -furanose may be very difficult, particularly in the case of compounds having (1→2)-bond. In these cases it is most useful to study the spectra of a glycoside deriva-

Table 2. ^{13}C-NMR data for mono- and di-O-benzyl ethers of benzyl β-L-arabinopyranoside (δ)

Compounds	A	30		31		32		33		34		35	
Carbons													
C-1	99.0	97.2	-1.8	99.5	+0.5	99.3	+0.3	97.0	-2.0	97.1	-1.9	99.2	+0.2
$^1J_{C-1,H-1}$	166.1			166.0		166.0				166.0			
C-2	68.8	76.9	+8.1	68.3	-0.5	69.6	+0.8	76.9	+8.1	77.2	+8.4	68.2	-0.6
C-3	68.8	68.6	-0.2	78.0	+9.2	69.6	+0.8	75.6	+6.8	68.5	-0.3	74.3	+5.5
C-4	68.3	68.9	+0.6	66.5	-1.8	77.2	+8.9	66.2	-2.1	77.3	+9.0	77.4	+9.1
C-5	63.3	63.3	0	63.7	+0.4	60.7	-2.6	63.4	+0.1	60.4	-2.9	60.4	-2.9
Ph-$\underline{C}H_2$-1	69.2	69.1		69.2		69.2		68.7		69.0		69.0	
Ph-$\underline{C}H_2$-2		72.1						72.1		72.1			
Ph-$\underline{C}H_2$-3				71.3				70.7				71.1	
Ph-$\underline{C}H_2$-4						71.6				71.5		71.3	
Solvent	DMSO-$-d_6$	$CDCl_3$											

A= Benzyl β-L-arabinopyranoside

Table 3. ^{13}C-NMR data for oligosaccharides containing L-arabinose at the reducing end (δ)

	Compounds	6	20	21	22				23				A		18		19			
	Anomers				αp	βp	αf	βf	αp	βp	αf	βf	αp	βp	αp	βp	αp	βp	αf	βf
	Carbons																			
	C-1	97.9	99.1	98.1	96.0	93.1	101.0	95.9	96.1	92.9	100.2	95.3	97.4	93.2	96.1	92.8	96.2	92.9	99.7	95.0
	$^1J_{C-1,H-1}$			167.4																
	C-2	78.6	76.6	75.8	81.0	78.8	90.3	84.5	79.4	77.8	87.9	81.6	73.0	69.7	79.3	80.0	77.9	76.7		
	C-3	76.5	67.7	67.9	72.7	68.5			69.5	68.3			73.2	69.4	72.9	68.4	69.9			
Arabinose	C-4	74.7	68.8	68.6	68.7	69.3	83.5	82.1	69.1	69.8	83.6		79.1	79.3	79.2	77.7	77.2			
	C-5	58.5	63.2	63.0	66.1	63.2	62.0	63.4	66.4	63.0	61.9	63.6	66.2	62.5	65.5	62.1	66.0	62.5	62.3	63.0
	PhCH	103.7																		
	C-1			102.2					101.8	103.1	100.7	101.9			101.8	103.0	101.7	102.9	103.0	100.8
	$^1J_{C-1,H-1}$			171.2																
	C-2			70.8					71.0						71.0		71.0			
	C-3			70.3					70.9						70.9		70.8			
Rhamnose	C-4			72.0					73.3	72.6					73.0	72.8	73.7	72.7		
	C-5			68.6					69.8						69.6	69.8	69.5	69.8		
	C-6			17.79					17.45						17.36	17.46	17.29	17.44		
	C-1	100.8	105.0		103.6	104.4	102.6	103.0					104.6	104.4	104.5	104.6	102.8	104.4		
	$^1J_{C-1,H-1}$																			
	C-2	71.8	74.0		74.2								74.3		73.1	74.3	73.9			
	C-3	71.6	78.6		76.7	76.8							76.7		76.6		76.5			
Glucose	C-4	70.3	70.6		70.6	70.5							70.4		70.5	70.3	70.4			
	C-5	73.0	77.0		76.9	76.7							76.5		76.4		76.5			
	C-6	61.8	61.6		61.8	61.7							61.6		61.6		62.3	61.4		
	Solvent	$CDCl_3$	$DMSO-d_6$		D_2O															

A= 4-O-β-D-Glucopyranosyl-L-arabinose

tive having a fixed anomeric configuration at the reducing end. An other possibility to overcome the complexity of the spectra may be the investigation of the corresponding alditol, prepared by the reduction of the oligosaccharide.

EXPERIMENTAL

General. M.ps were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured with a Perkin–Elmer 241 polarimeter; equilibrium values are given for compounds **18**, **19**, **22** and **23**. ^{1}H- and ^{13}C-NMR spectra were taken at room temp and at the frequency of 100.1 or 25.16 NHz with Jeol MH-100 and Varian XL-100-FT-15 spectrometers, using TMS or dioxan as internal reference.

TLC was performed on DC Alurolle Kieselgel 60 F 254 (Merck); detection was effected by charring with sulfuric acid. Both, Kieselgel G and Kieselgel H (Reanal) were used for column chromatography. GLC was carried out on a Hewlett-Packard 5840 A instrument fitted with a helical stainless-steel column (4 ft × 0.2 mm i.d.) packed with 10% of UCW-982 on Gas chrom Q (80–100 mesh). The temperature programme was started from 275° at 2.5°/min (a); isotherm (b). The carrier gas was nitrogen at 20 ml/min.

Reaction of benzyl exo - 3,4 - O - benzylidene - β - L - arabinopyranoside with α - acetobrome - D - glucose

Benzyl *exo* - 3,4 - O - benzylidene - β - L - arabinopyranoiside (**1**, 6.57 g) was dissolved in abs benzene (200 ml) and nitromethane (200 ml) and the soln was evaporated at atmospheric pressure to half its volume. It was cooled to 60° and treated with $Hg(CN)_2$ (5.56 g) and α-acetobrome-D-glucose (**3**, 9.05 g), and then stirred for 20 h under anhydrous conditions. The mixture was diluted with CH_2Cl_2 (100 ml), filtered, and concentrated. The residue was dissolved in CH_2Cl_2 (300 ml), the mixture was filtered, and the filtrate was washed with 5% Klaq (2 × 50 ml) and water (2 × 50 ml). After drying over Na_2SO_4 the organic layer was concentrated to a syrupy residue which crystallised on standing.

The crude product contained benzyl *exo*-3,4-O-benzylidene- (**5**, R_T 8.53 min), and benzyl *endo* - 3,4 - O - benzylidene - 2 - O - (2,3,4,6 - tetra - O - acetyl - β - D - glucopyranosyl) - β - L - arabinopyranoside (**6**, R_T 7.34 min) in a ratio of 47:53 (GLC). Recrystallization from EtOH (700 ml) gave 4.20 g (31.9%) of pure **6**, m.p. 179–181°, $[\alpha]_D$ +103° (c 1.03, $CHCl_3$), R_f 0.65 (benzene-MeOH, 95:5), R_T 7.34 min (a column). ^{1}H NMR data (δ, ppm): 7.50–7.20 (m, 10H, aromatic protons); 5.92 (s, 1H, PhCH); 5.20–4.89 (m, 3H, H-2', 3', 4'); 4.96 (d, 1H, H-1'); 3.34 (m, 1H, H-2); 1.96 (s, 12H, 40Ac). (Found: C, 59.72; H, 5.90. Calc. for $C_{33}H_{38}O_{14}$: C, 60.18; H, 5.82%.)

A small amount of the mother liquor was concentrated. Its ^{1}H-NMR spectrum showed two signs of PhCH belonging to **5** (6.19 ppm) and to **6** (5.92 ppm), respectively. Compound **5** was unseparable from traces of **6** by TLC.

Benzyl exo - 3,4 - O - *benzylidene* - 2 - O - (2,3,4 - *tri* - O - *acetyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside* **7**

Compound **1** (4.68 g) was dissolved in abs benzene (300 ml) and nitromethane (300 ml) and the soln was evaporated at atmospheric pressure to half its volume. It was cooled to 45° and treated with $Hg(CN)_2$ (4.32 g) and α-acetobromo-L-rhamnose (**4**, 6.04 g), and then stirred. After 15 min, more. $Hg(CN)_2$ (2.16 g) and **4** (3.02 g) were added, and stirring was continued for 30 min. The usual work-up gave a syrupy residue, which was crystallized from EtOH (48 ml) to yield 3.28 g of **7**. The mother liquor was evaporated and applied to a Kieselgel G column (eluant: CH_2Cl_2–EtOAc 95:5) to obtain second crops of pure **7** (2.80 g).

The overall yield of **7**: 6.08 g (71.0%), m.p. 138–140°, $[\alpha]_D$ + 39° (c 0.90, $CHCl_3$), R_f 0.71 (light pefroleum-EtOAc, 2:1), R_T 3.58 min (b column). ^{1}H-NMR data (δ, ppm): 7.50–7.20 (m, 10H, aromatic protons); 6.16 (s, 1H, PhCH); 5.42–5.02 (m, 4H, H-1',2',3',4'); 4.94 (d, 1H, H-1); 4.86–4.47 (m, 3H, $PhCH_2$ and H-3); 4.22-3.64 (m, 5H, H-2,4,5_a,5_e and H-5'); 2.10, 2.02 and 1.99 (3s, 9H, 30Ac); 1.06 (d, 3H, C_5-CH_3). (Found: C, 62.41; H, 5.99. Calc. for $C_{31}H_{36}O_{12}$: C, 61.99; H, 6.04%.)

Benzyl endo - 3,4 - O - *benzylidene* - 2 - O - (2,3,4 - *tri* - O - *acetyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside* **8**

Compound **2** (0.80 g) was treated with **4** for 1 h in 1:1 abs benzene–nitromethane in the presence of $Hg(CN)_2$ as described for **7**. The syrupy product was chromatographed on a Kieselgel G column, using 2:1 light petroleum–EtOAc as the eluant. Yield: 0.68 g (46.5%), $[\alpha]_D$ + 74° (c 1.97, $CHCl_3$), R_f 0.63 (light petroleum–EtOAc, 2:1), R_T 3.28 min (b column). ^{1}H-NMR data (δ, ppm): 7.60–7.20 (m, 10H, aromatic protons); 5.90 (s, 1H, PhCH); 5.45–5.27 (m, 2H, H-3',4'); 4.99 (m, 2H, H-1', 2'); 4.90 (d, 1H, H-1); 4.67 (q, 2H, $PhCH_2$); 4.54 (dd, 1H, H-3); 4.26 (m, 1H, H-4); 4.05 (m, 2H, H-5_a,5_e) 3.89-3.60 (m, 2H, H-2,5'); 2.09, 2.02 and 1.98 (3s, 9H, 30Ac); 1.03 (d, 3H, C_5-CH_3); $J_{1,2}$ = 3.5 Hz; $J_{2,3}$ = 7.6 Hz; $J_{3,4}$ = 6.1 Hz; $J_{5,6'}$ = 6.2 Hz. (Found: C, 61.79; H, 6.10. Calc. for $C_{31}H_{36}O_{12}$: C, 61.99; H, 6.04%.)

Benzyl endo - 3,4 - O - *benzylidene* - 2 - O - (2,3,4,6 - tetra - O - benzyl - β - D - *glucopyranosyl*) - β - L - *arabinopyranoside* **9**

A soln of **6** (0.90 g) in abs MeOH (50 ml) was treated with 1N methanolic NaOMe (0.3 ml). After standing at room temp for 16 h the mixture was neutralised with Amberlite IR-120 (H^+) resin and concentrated. The residue (0.66 g) without isolation was benzylated with benzyl chloride (25 ml) in the presence of KOH (2.5 g) at 100° for 4 h. The organic layer was then removed by decantation and the residue was washed with CH_2Cl_2 and filtered. After addition of a small amount of $NaHCO_3$, the filtrate was steam distilled and the syrupy product was crystallised from EtOH (27 ml) to give 642 mg (55.2%) of **9**, m.p. 94–96°, $[\alpha]_D$ +93° (c 0.71, $CHCl_3$), R_f 0.73 (benzene–MeOH, 199:1). ^{1}H-NMR data (δ, ppm): 7.50–7.05 (m, 30H, aromatic protons); 5.84 (s, 1H, PhCH); 5.11 (d, 1H, H-1); 4.98 (d, 1H, H-1'). (Found: C, 74.35; H, 6.35. Calc. for $C_{53}H_{54}O_{10}$: C, 74.80; H, 6.40%.)

Benzyl exo - 3,4 - O - *benzylidene* - 2 - O - (2,3,4 - *tri* - O - *benzyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside* **10**

Compound **7** (3.87 g) was saponified and the product (2.91 g), without isolation, was benzylated as described for the preparation of **9**, to obtain 3.72 g (77.5%) of crystalline **10**. Recrystallisation from EtOH (84 ml) gave 2.58 g (53.8%), m.p. 99–101°, $[\alpha]_D$ +69° (c 0.71, $CHCl_3$), R_f 0.59 (light petroleum-EtOAc, 2:1). ^{1}H-NMR (δ, ppm): 7.50–7.10 (m, 25H, aromatic protons); 6.10 (s, 1H, PhCH); 1.24 (d, 3H, C_5-CH_3). (Found: C, 73.98; H, 6.47. Calc. for $C_{46}H_{48}O_9$: C, 74.17; H, 6.50%.)

Benzyl endo - 3,4 - O - *benzylidene* - 2 - O - (2,3,4 - *tri* - O - *benzyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside* **11**

Compound **8** (0.67 g) was saponified and benzylated as described for the preparation of **9**. The syrupy product (0.57 g; 68.6%) was chromatographed on a Kieselgel G column with 2:1 light petroleum-EtOAc mixture to obtain pure crystalline **11** (0.48 g; 57.8%). After recrystallisation from EtOH had m.p. 90–92°, $[\alpha]_D$ +110° (c 0.60, $CHCl_3$), R_f 0.53 (light petroleum-EtOAc, 2:1). ^{1}H-NMR data (δ, ppm): 7.60–7.00 (m, 25H, aromatic protons); 5.96 (s, 1H, PhCH); 1.18 (d, 3H, C_5-CH_3). (Found: 74.28; H, 6.62. Calc. for $C_{46}H_{48}O_9$: C, 74.17; H, 6.50%.)

Benzyl 4 - O - *benzyl* - 2 - O - (2,3,4,6 - *tetra* - O - *benzyl* - β - D - *glucopyranosyl*) - β - L - *arabinopyranoside* **13**

To a soln of **9** (0.45 g) in a mixture of CH_2Cl_2 (8 ml) and ether (3 ml) were added $LiAlH_4$ (0.30 g) and a soln of $AlCl_3$ (0.90 g) in ether (5 ml), and the mixture was heated under reflux for 15 min. It was then cooled and the excess reagent was decomposed with EtOAc (5 ml) and water (10 ml). The mixture was diluted with ether (30 ml) and decanted from $Al(OH)_3$. The residue was washed with ether (2 × 30 ml). The combined organic layers were washed with water (2 × 15 ml), dried (Na_2SO_4) and concentrated. The crystalline residue (0.44 g; 97.5%) was recrystallised from a mixture of ether (4 ml) and light petroleum (20 ml) to yield pure **13** (0.33 g; 73.2%). m.p. 70–74°, $[\alpha]_D$ +84° (c 0.69, $CHCl_3$). (Found: C, 74.73; H, 6.57. Calc. for $C_{53}H_{56}O_{10}$: C, 74.63; H, 6.62%.)

100 mg of **13** was conventionally acetylated for ^{1}H-NMR study: (δ, ppm): 7.40–7.05 (m, 30H, aromatic protons); 5.32 (dd,

1H, H-3); 5.25 (d, 1H, H-1); 1.73 (s, 3H, OAc); $J_{1,2}$ = 3.2 Hz; $J_{2,3}$ = 9.1 Hz; $J_{3,4}$ = 3.6 Hz.

Reductive ring cleavage of benzyl exo - 3,4 - O - *benzylidene* - 2 - O - (2,3,4 - *tri* - O - *benzyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside with* $LiAlH_4$ - $AlCl_3$ reagent

Compound **10** (2.00 g) was hydrogenolysed with $LiAlH_4$ (408 mg) and $AlCl_3$ (714 mg) as described for the reaction of **9**. The syrupy product (1.95 g; 97.2%) containing benzyl 3-O-benzyl-(**14**) and benzyl 4 - O - benzyl - 2 - O - (2,3,4 - tri - O - benzyl - α - L - rhamnopyranosyl) - β - L - arabinopyranoside **15** in a ratio of 1:3 (TLC) was column chromatographed to give 460 mg (22.4%) of **14** and 1.18 g (58.8%) of **15**.

Compound **14** was syrup, had $[\alpha]_D$ +61° (c 0.48, $CHCl_3$), R_f 0.14 (light petroleum-EtOAc, 2:1). (Found: C, 74.23; H, 6.80. Calc. for $C_{46}H_{50}O_9$: C, 73.97; H, 6.75%.)

100 mg of **14** was conventionally acetylated for ^{1}H-NMR study: (δ, ppm): 7.50–7.10 (m, 25H, aromatic protons); 5.38 (m, 1H, H-4); 2.04 (s, 3H, OAc); 1.12 (d, 3H, C_5-CH_3).

Compound **15** was syrup, had $[\alpha]_D$ +77.5° (c 0.62, $CHCl_3$), R_f 0.33 (light petroleum–EtOAc, 2:1). (Found: C, 74.18; H, 6.70. Calc. for $C_{46}H_{50}O_9$: C, 73.97; H, 6.75%.)

100 mg of **15** was conventionally acetylated for ^{1}H-NMR study: (δ, ppm): 7.50–7.10 (m, 25H, aromatic protons); 5.14 (dd, 1H, H-3); 1.80 (s, 3H, OAc); 1.18 (d, 3H, C_5-CH_3); $J_{2,3}$ = 10.5 Hz; $J_{3,4}$ = 3.2 Hz.

Benzyl 4 - O - *benzyl* - 2 - O - (2,3,4 - *tri* - O - *benzyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside* **15**

Compound **11** (0.45 g) was hydrogenolysed as described for the reaction of **9**, to give 0.44 g (97.5%) of pure **15**.

Benzyl 3 - O - *benzyl* - 4 - O - (2,3,4,6 - *tetra* - O - *acetyl* - β - D - *glucopyranosyl*) - 2 - O - (2,3,4 - *tri* - O - *benzyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside* **16**

Compound **14** (300 mg) was treated with **3** (198 mg) in 1:1 abs benzene–nitromethane (60 ml) in the presence of $Hg(CN)_2$ (122 mg) at 60°. After 10 and 20 h more $Hg(CN)_2$ (122 mg) and **3** (198 mg) were added and the mixture was stirred for 30 h. The usual manner gave a syrupy product which after twice purification by column chromatography–using CH_2Cl_2–acetone 95:5 and light petroleum–EtOAc 1:3, as the eluant–gave pure syrupy **16** (230 mg; 53.2%), $[\alpha]_D$ +42° (c 0.79, $CHCl_3$). (Found: C, 66.78; H, 6.40. Calc. for $C_{60}H_{68}O_{18}$: C, 66.90; H, 6.36%.)

Benzyl 4 - O - *benzyl* - 3 - O - (2,3,4,6 - *tetra* - O - *acetyl* - β - D - *glucopyranosyl*) - 2 - O - (2,3,4 - *tri* - O - *benzyl* - α - L - *rhamnopyranosyl*) - β - L - *arabinopyranoside* **17**

Compound **15** (460 mg) was treated with **3** as described for the preparation of **16**, to give a syrupy product, which after purification by column chromatography gave 490 mg (73.9%) of pure syrupy **17**; $[\alpha]_D$ +45° (c 0.36, $CHCl_3$), R_f 0.71 (CH_2Cl_2–acetone, 95:5). (Found: C, 67.02; H, 6.30. Calc. for $C_{60}H_{68}O_{18}$: C, 66.90; H, 6.36%.)

4 - O - β - D - *glucopyranosyl* - 2 - O - α - L - *rhamnopyranosyl* - L - *arabinose* **18**

Compound **16** (210 mg) was deacetylated with NaOMe (5 mg) in abs MeOH (30 ml) for 12 h. The soln was neutralised with Amberlite IR-120 (H^+) resin, filtered and concentrated. The residue without isolation was hydrogenated in the presence of PdC (100 mg) in a mixture of EtOH (15 ml) and AcOH (5 ml) for 48 h. The catalyst was filtered off, the filtrate was concentrated and the traces of acetic acid are removed from the residue by additional distillation with benzene (3 × 5 ml). Yield: 75 mg (83.9%); amorphous; $[\alpha]_D$ +19° (c 0.48, water), R_f 0.43 (1-butanol–MeOH–H_2O, 2:1:1). (Found: C, 44.66; H, 6.55. Calc. for $C_{17}H_{30}O_{14}$: C, 44.54; H, 6.60%.)

3 - O - β - D - *glucopyranosyl* - 2 - O - α - L - *rhamnopyranosyl* - L - *arabinose* **19**

Compound **17** (420 mg) was saponified and then hydrogenated in the presence of PdC, as described for the preparation of **18**. The product (148 mg; 82.8%) was purified by column chromatography on Kiesselgel H, with 1-butanol–MeOH–H_2O 2:1:1 as the eluant, to give amorphous **19** (110 mg; 61.5%), $[\alpha]_D$ 0° (c 0.74, water), R_f 0.44 (1-butanol–MeOH–H_2O, 2:1:1). (Found: C, 44.70; H, 6.52. Calc. For $C_{17}H_{30}O_{14}$: C, 44.54; H, 6.60%.)

Benzyl 2 - O - β - D - *glucopyranosyl* - β - L - *arabinopyranoside* **20**

Compound **6** (1.80 g) was saponified with NaOMe (10 mg) in abs MeOH (60 ml) for 12 h. After work-up the product was dissolved in EtOH (40 ml) and 0.1 *N* H_2SO_4 (40 ml) and boiled for 5 h. The hot soln was neutralised with $BaCO_3$, filtered and concentrated. The residue (1.00 g; 90.9%) was crystallised from EtOAc to yield 420 mg (38.2%) of **20**; m.p. 199–200°, $[\alpha]_D$ +119° (c 0.70, water), R_f 0.61 (1-BuOH–MeOH–H_2O, 2:1:1). (Found: C, 53.59; H, 6.52. Calc. for $C_{18}H_{26}O_{10}$: C, 53.73; H, 6.51%.)

Benzyl 2 - O - α - L - *rhamnopyranosyl* - β - L - *arabinopyranoside* **21**

Compound **7** (1.20 g) was saponified and then hydrolysed as described for the preparation of **20**. The crystalline product (730 mg; 94.6%) was recrystallised from a mixture of EtOAc (40 ml) and EtOH (4 ml) to give 260 mg (33.7%) of **21**; m.p. 216–220°, $[\alpha]_D$ +100° (c 0.65, water), R_f 0.62 (1-butanol-MeOH-H_2O, 2:1:1). (Found: C, 56.09; H, 6.69. Calc. for $C_{18}H_{26}O_9$: C, 55.95; H, 6.78%.)

2 - O - β - D - *glucopyranosyl* - L - *arabinose* **22**

Compound **20** (330 mg) was hydrogenated in the presence of PdC (100 mg) in EtOH (15 ml) and acetic acid (5.ml) for 72 h. The product was purified by column chromatography on Kieselgel H with 1-butanol–MeOH–H_2O 2:1:1 as the eluant, to give syrupy **22** (210 mg; 82.0%). Crystallisation from abs MeOH gave 103 mg (40.2%) of pure **22**; m.p. 120–123°, $[\alpha]_D$ +35° (c 0.65, water), R_f 0.44 (1-BuOH–MeOH–H_2O, 2:1:1). (Found: C, 42.53; H, 6.50. Calc. for $C_{11}H_{20}O_{10}$:C, 42.31; H, 6.46%.)

2 - O - α - L *rhamnopyranosyl* - L - *arabinose* **23**

Compound **21** (280 mg) was hydrogenated in the presence of PdC, as described for the preparation of **22**. The product (200 mg; 93.2%) was purified by column chromatography on Kieselgel H with 1-BuOH–MeOH–H_2O 2:1:1, as the eluant, to yield syrupy **23** (120 mg; 55.9%). After crystallisation from abs MeOH had m.p. 141–145°, $[\alpha]_D$ + 12° (c 0.51, water), R_f 0.51 (1-butanol–MeOH–H_2O, 2:1:1). (Found: C, 44.71; H, 6.71. Calc. for $C_{11}H_{20}O_9$: C, 44.59; H, 6.80%.)

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