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N.M.R. SPECTRAL STUDY OF α- AND β-L-ARABINOFURANOSIDES*

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ABSTRACT

Anomeric pairs of L-arabinofuranosides of various aliphatic alcohols were synthesized and then investigated by n.m.r. spectroscopy. The ^{13}C-n.m.r. glycosylation shift of these L-arabinofuranosides is very similar to that of L-arabinopyranosides and other glycopyranosides reported previously. The $^{3}J_{H\text{-}1,H\text{-}2}$ value of these α-L-arabinofuranosides is significantly different from that of the β anomers and can be used for the determination of the anomeric configuration. However, in contrast to the case of glycopyranosides, the $^{1}J_{C\text{-}1,H\text{-}1}$ values of each anomeric series of L-arabinofuranosides are very similar to each other. Some disaccharides containing an L-arabinofuranoside unit were also investigated by n.m.r. spectroscopy.

INTRODUCTION

The α- and β-anomeric pairs of D-glucopyranosides[1,2], D-mannopyranosides[2], L-rhamnopyranosides[2], and L-arabinopyranosides[3] of various aliphatic alcohols were synthesized, and the displacements of ^{13}C resonances of both the sugar and the aglycon residues on glycoside formation were investigated. These resonance displacements (^{13}C-n.m.r. glycosylation shifts) were utilized to elucidate the structures of various biologically active natural glycosides. Furthermore, we also reported the unexpected glycosylation shifts of L-arabinopyranosides on 2-*O*-glycosylation[4,5]. As arabinofuranosyl groups occasionally occur in carbohydrates, as a continuation of these studies, we report herein n.m.r. studies of L-arabinofuranosides.

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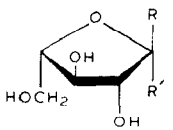
RESULTS AND DISCUSSION

Synthesis of α- and β-L-arabinofuranosides. — Methyl α- (**1**) and β-L-arabinofuranoside (**2**) were prepared by the method of Guthrie and Smith[6]. Propyl α- (**3**) and β- (**4**), 2-propyl α- (**5**) and β- (**6**), *trans*-4-*tert*-butylcyclohexanyl α- (**7**) and β- (**8**), 5α-cholestan-3β-yl α- (**9**) and β- (**10**), *tert*-butyl α- (**11**) and β- (**12**), *d*-menthyl α- (**13**) and β- (**14**), and l-menthyl α- (**15**) and β-L-arabinofuranoside (**16**) were synthesized by condensation of 1,2,3,5-tetra-*O*-acetyl-L-arabinofuranose with the respective alcohol in dichloromethane in the presence of tin tetrachloride[7], followed by deacetylation. The resulting anomeric mixtures were separated into the α and β anomer. Methyl 2-*O*-β-D-glucopyranosyl-α- (**17**) and -β-L-arabinofuranoside (**19**) were synthesized from 2-*O*-β-D-glucopyranosyl-L-arabinose[5] by the method of Guthrie and Smith[6]. Methyl 5-*O*-β-D-glucopyranosyl-α- (**18**) and -β-L-arabinofuranoside (**20**) were prepared by condensation of methyl 2,3-di-*O*-acetyl-α- or -β-L-arabinofuranoside with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide in the presence of mercuric cyanide in toluene[4], followed by deacetylation. Methyl 3-*O*-α-L-arabinofuranosyl-β-D-glucopyranoside (**21**) was synthesized by condensation of methyl 2-*O*-acetyl-4,6-*O*-benzylidene-β-D-glucopyranoside[8] and 2,3,5-tri-*O*-benzyl-L-arabinofuranosyl chloride[9] in the presence of mercuric cyanide in toluene, followed by removal of the protecting groups. The elemental analyses and the physical constants are listed in Table I.



1 R = OH, R′ = OMe
2 R = OMe, R′ = OH
3 R = OH, R′ = $O(CH_2)_2Me$
4 R = $O(CH_2)_2Me$, R′ = OH
5 R = OH, R′ = $OCHMe_2$
6 R = $OCHMe_2$, R′ = OH
7 R = OH, R′ = *trans*-4-*tert*-butylcyclohexyl
8 R = *trans*-4-*tert*-butylcyclohexyl, R′ = OH
9 R = OH, R′ = 5α-cholestan-3β-yl
10 R = 5α-cholestan-3β-yl, R′ = OH
11 R = OH, R′ = CMe_3
12 R = CMe_3, R′ = OH
13 R = OH, R′ = *d*-menthyl
14 R = *d*-menthyl, R′ = OH
15 R = OH, R′ = *l*-menthyl
16 R = *l*-menthyl, R′ = OH

TABLE I

PHYSICAL CONSTANTS OF L-ARABINOFURANOSIDES **3–21**

Compound	*State*	*M.p. (degrees)*	$[\alpha]_D$ *(degrees)*	*Conc.*[a]	*Temp. (degrees)*	*Formula*	*Anal.*			
							Calc.		*Found*	
							C	*H*	*C*	*H*
3	syrup		−192.3	0.44	21	$C_8H_{16}O_5$	49.99	8.39	49.94	8.48
4	syrup		+93.8	0.69	18	$C_8H_{16}O_5$	49.99	8.39	49.96	8.45
5	syrup		−140.2	0.67	21	$C_8H_{16}O_5$	49.99	8.39	49.63	8.59
6	syrup		+91.6	1.13	18	$C_8H_{16}O_5$	49.99	8.39	49.90	8.47
7	powder[b]		−104.2	0.79	18	$C_{15}H_{28}O_5$	62.47	9.79	62.47	10.05
8	powder[c]		+71.6	0.65	18	$C_{15}H_{28}O_5$	62.47	9.79	62.00	9.67
9	powder[b]		−48.9	0.66	19	$C_{32}H_{56}O_5$	73.80	10.84	73.64	11.13
10	powder[b]		+58.8	0.65	19	$C_{32}H_{56}O_5$	73.80	10.84	73.85	10.97
11	syrup		−103.6	0.70	18	$C_9H_{18}O_5$	52.41	8.80	52.32	8.94
12	needles[d]	83.0–85.0	+69.0	1.83	19	$C_9H_{18}O_5$	52.41	8.80	52.40	8.94
13	needles[b]	113.5–115.0	−41.9	0.67	18	$C_{15}H_{28}O_5$	62.47	9.79	62.18	9.90
14	needles[b]	101.0–104.0	+142.3	0.75	18	$C_{15}H_{28}O_5$	62.47	9.79	62.09	9.82
15	needles[b]	143.0–144.5	−197.7	0.64	18	$C_{15}H_{28}O_5$	62.47	9.79	62.61	9.99
16	needles[b]	117.0–119.0	−16.2	0.57	18	$C_{15}H_{28}O_5$	62.47	9.79	62.36	9.94
17	syrup		−92.6	1.24	21	$C_{12}H_{22}O_{10}$	44.17	6.80	43.96	7.20
18	syrup		−54.5	2.80	21	$C_{12}H_{22}O_{10}$	44.17	6.80	43.85	7.12
19	syrup		+16.3	1.01	21	$C_{12}H_{22}O_{10}$	44.17	6.80	43.80	7.01
20	powder[e]		+239.7	0.34	21	$C_{12}H_{22}O_{10}$	44.17	6.80	44.03	6.82
21	syrup		−87.0	0.86	21	$C_{12}H_{22}O_{10}$	44.17	6.80	43.92	7.11

[a]In pyridine. [b]From acetone–hexane. [c]From chloroform–hexane. [d]From ether–hexane. [e]From methanol–ethyl acetate.

Confirmation of chemical shifts of alkyl L-*arabinofuranosides.* — The identification of carbon resonances of **1** and **2** in ($^2H_5$) pyridine was confirmed by a two-dimensional correlation procedure (2D n.m.r.); first, the proton signals of **1** and **2** were assigned by H–H 2D n.m.r., and then the carbon signals were identified by C–H 2D n.m.r. as shown in Table II. Based on these results, the assignments of carbon signals of all other arabinofuranosides were obtained. In the case of **11**, the close-vicinity signals of C-2 (δ 84.4) and C-4 (δ 84.6) were also assigned by 2D n.m.r.

Glycosylation shifts of the sugar carbon signals. — As in the case of D-glucopyranosides[1,2], D-mannopyranosides[2], L-rhamnopyranosides[2], and L-arabinopyranosides[3], the anomeric carbon atom (C-1) of the L-arabinofuranosyl residue was found to be generally deshielded on glycosylation in the decreasing order of methyl, primary, and secondary (unhindered) alcohols (see Table III). It is noteworthy that, in the case of the β-L-anomer series, the glycosylation shift of C-1

TABLE II

^{1}H-CHEMICAL SHIFTS AND COUPLING CONSTANTS, AND ^{13}C CHEMICAL SHIFTS OF METHYL α- (**1**) AND β-L-ARABINOFURANOSIDE[a] (**2**)

Atom number	**1**				**2**			
	δ_H	*Mul.*[b]	J *(Hz)*	δ_C	δ_H	*Mul.*[b]	J *(Hz)*	δ_C
1	5.38	t[c]	1.2	110.5	5.14	d	4.3	103.9
2	4.84	br.s	($^1/_2$W 9)	83.4	4.67	dd	4.3, 6.4	79.6
3	4.84	br.s	($^1/_2$W 9)	78.5	4.81	t	6.4	76.7
4	4.68	ddd	7.0, 4.7, 3.2	85.5	4.55	dt	6.4, 4.0	84.9
5	4.36	dd	3.2, 11.6	62.6	4.26	dd	4.0, 11.5	65.2
5′	4.23	dd	4.7, 11.6		4.17	dd	6.5, 11.5	
OCH_3	3.46	s		54.9	3.48	s		55.1

[a]For solutions in ($^2H_5$) pyridine. [b]Multiplicity. [c]Virtual coupling.

TABLE III

^{13}C-CHEMICAL SHIFTS OF ANOMERIC CARBON ATOMS[a] AND COMPARISON OF SHIFTS OF ANOMERIC CARBON ATOMS, ON L-ARABINOFURANOSYLATION *vs.* L-ARABINOPYRANOSYLATION[b]

Glycoside	*α-L-Arabinofuranoside (α-L-Arabinopyranoside)*		*β-L-Arabinofuranoside (β-L-Arabinopyranoside)*	
	$\delta_{C\text{-}1}$	*Difference*[c]	$\delta_{C\text{-}1}$	*Difference*[c]
Methyl (**1,2**)	110.5	+6.5 (+6.6)	103.9	+6.4 (+7.5)
Propyl (**3,4**)	109.6	+5.6 (+5.5)	102.9	+5.4 (+6.3)
2-Propyl (**5,6**)	107.6	+3.6 (+3.8)	100.9	+3.4 (+4.4)
trans-4-*tert*-Butylcyclohexanyl (**7,8**)	107.3	+3.3 (+3.8)	100.9	+3.4 (+4.4)
tert-Butyl (**11,12**)	107.2	+3.2 (+3.4)	101.0	+3.5 (+4.6)
5-α-Cholestan-3β-yl (**9,10**)	104.2	+0.2 (−0.1)	97.2	−0.3 (+0.5)

[a]For solutions in ($^2H_5$) pyridine. [b]In parentheses. [c]$\delta_{C\text{-}1}$ of glycoside − $\delta_{C\text{-}1}$ of corresponding free sugar.

of L-arabinopyranosides is somewhat greater than that of the corresponding L-arabinofuranoside. On glycosylation with a tertiary alcohol, such as 2-propanol, the C-1 signal remained almost unshifted. It was reported[3] that a slight upfield shift was observed for C-2 of the arabinopyranosyl residue on glycosylation. However, in the case of the L-arabinofuranosyl residue, not only the C-3, -4 and -5 signals, but also the C-2 signal were not displaced by glycosylation. As for the L-arabinofuranosides in the present study, signals due to sugar carbon atoms other than C-1 were found to be only slightly affected by a change in structure of the aglycon; this indicated that these L-arabinofuranosides have a similar conformation of the glycosyl residue in each anomeric series, regardless of the structure of the aglycon.

Glycosylation shifts of the carbon signals of the aglycons. — The methyl carbon atom of the aglycon residue (designated a-C) is generally deshielded on glycoside formation and, in the glycopyranoside series, the shift values for axial anomeric configuration are somewhat less than those for the corresponding equatorial anomers. As shown in Table IV, on β-L-arabinofuranosylation, a-C signals of primary, secondary (unhindered), and tertiary alcohols were shifted downfield with a magnitude similar to that for β-L-arabinopyranosylation, whereas the shift values for α-L-arabinofuranosylation were slightly smaller than those for α-L-arabinopyranosylation.

It has already been found[1-3] that signals due to the carbon atoms vicinal to a-C (designated b-C) are displaced upfield on glycosylation, and the magnitudes of the shifts of two equivalent methyl or methylene carbon atoms of secondary alcohol aglycons are significantly different from each other, depending upon the stereochemical combination between the chirality of C-1 and a-C. It was found that analogous glycosylation shifts of b-C were also observed for both α- and β-L-arabinofuranosylation in a manner similar to that of the corresponding α- and β-L-arabinopyranosylation (see Table V).

Glycosylation shifts for relatively hindered secondary alcohols. — As already observed for D-glucopyranosides[1,2], D-mannopyranosides[2], L-rhamnopyranosides[2],

TABLE IV

COMPARISON OF SHIFTS[a] OF AGLYCON α CARBON ATOM (a-C), ON ARABINOFURANOSYLATION *vs.* L-ARABINOPYRANOSYLATION[b]

Glycoside	α-L-*Arabinofuranoside* (α-L-*Arabinopyranoside*) $\Delta\delta_{a\text{-}C}$[c]	β-L-*Arabinofuranoside* (β-L-*Arabinopyranoside*) $\Delta\delta_{a\text{-}C}$[c]
Methyl (**1,2**)	+5.5 (+6.7)	+5.7 (+5.9)
Propyl (**3,4**)	+5.7 (+7.0)	+6.0 (+6.2)
2-Propyl (**5,6**)	+6.0 (+7.3)	+6.6 (+6.3)
trans-4-*tert*-Butylcyclohexanyl (**7,8**)	+5.8 (+7.2)	+6.5 (+6.7)
tert-Butyl (**11,12**)	+5.6 (+6.5)	+6.5 (+6.5)
5-α-Cholestan-3β-yl (**9,10**)	+6.5 (+7.1)	+7.0 (+6.5)

[a]For solutions in ($^2H_5$)pyridine. [b]In parentheses. [c]$\delta_{a\text{-}C}$ of glycoside − $\delta_{a\text{-}C}$ of aglycon alcohol.

and L-arabinopyranosides[3], the glycosylation shifts of L-arabinofuranosides of the relatively hindered secondary alcohols, *d*- and *l*-menthol, which are substituted at a b-C atom by an alkyl group, are evidently different from those of the aforementioned less hindered secondary alcohols. The degree of this "anomalous shift" was found to depend upon the combination of the chirality of C-1 and a-C. Combination of an α-L-arabinofuranosyl (C-1; *R* chirality) with a *d*-menthyl residue (a-C; *S* chirality), as well as that of a β-L-arabinofuranosyl (C-1; *S* chirality) with a *l*-menthyl (a-C; *R* chirality) residue, resulted in downfield displacements for both the C-1 and a-C signals greater than those for the corresponding L-arabinofuranosyl residues with less hindered secondary alcohol residues, such as the *trans*-4-*tert*-butylcyclohexyl residue. In contrast, both the C-1 and a-C signals of **15** (combination of a C-1 *R* sugar with an *R* aglycon residue) and **14** (combination of a C-1 *S* sugar with an *S* aglycon residue) led to less deshielding than those of **7** and **8**, respectively.

The magnitude of b-C shielding on L-arabinofuranosylation also depended upon the stereochemical combination of C-1 and a-C in the same manner as was observed on D-glucopyranosylation[1,2], D-mannopyranosylation[2], L-rhamnopyranosylation[2], and L-arabinopyranosylation[3] (see Table VI).

Correlation of anomeric configuration with anomeric carbon and proton signals. — Bock and Pedersen[10] reported that in the ^{13}C–^{1}H coupling between C-1 and H-1 of hexopyranose, pentopyranose, and their derivatives, the coupling constant ($^{1}J_{C\text{-}1,H\text{-}1}$) is smaller by about 10 Hz when the anomeric proton is axial than when it is equatorial. A similar result, which is of value for the elucidation of the anomeric configuration, was obtained for D-glucopyranosides[2], D-manno-

TABLE V

COMPARISON OF SHIFTS[a] OF AGLYCON β CARBON ATOMS (b-C AND b′-C) ON L-ARABINOFURANOSYLATION *vs.* L-ARABINOPYRANOSYLATION[b]

Glycoside	*α-L-Arabinofuranoside (α-L-Arabinopyranoside)*			*β-L-Arabinofuranoside (β-L-Arabinopyranoside)*		
		$\Delta_{\delta b\text{-}C}$	$\Delta_{\delta b'\text{-}C}$[c]		$\Delta_{\delta b\text{-}C}$	$\Delta_{\delta b'\text{-}C}$[c]
Propyl (**3,4**)	*R*[d]	−3.3		*S*[d]	−3.4	
	(*R*)	(−3.3)		(*S*)	(−3.4)	
2-Propyl (**5,6**)	*R*	−1.6	−3.8	*S*	−3.8	−1.9
	(*R*)	(−1.8)	(−3.7)	(*S*)	(−3.9)	(−2.1)
trans-4-*tert*-Butylcyclohexanyl (**7,8**)	*R*	−2.1	−4.1	*S*	−4.1	−2.2
	(*R*)	(−2.1)	(−3.9)	(*S*)	(−4.2)	(−2.3)
tert-Butyl (**11,12**)	*R*	−2.3	−4.5	*S*	−4.2	−2.1
	(*R*)	(−2.4)	(−4.5)	(*S*)	(−3.8)	(−2.0)
5-α-Cholestan-3β-yl (**9,10**)	*R*		−2.5	*S*		−2.7
	(*R*)		(−2.6)	(*S*)		(−2.8)

[a]For solutions in ($^{2}H_5$)pyridine. [b]In parentheses. [c]$\delta_{b\text{-}C \text{ or } b'\text{-}C}$ of glycoside − $\delta_{b\text{-}C \text{ or } b'\text{-}C}$ of aglycon. [d]Chirality of anomeric carbon atom as free form.

pyranosides[2], L-rhamnopyranosides[2], and L-arabinopyranosides[3] of various aglycons. It is significant that, in contrast to the case of glycopyranosides, the $^1J_{C\text{-}1,H\text{-}1}$ values of L-arabinofuranosides were found in the range of 168–171 Hz regardless of the anomeric configurations (see Table VII). Thus, the $^3J_{C\text{-}1,H\text{-}1}$ values cannot be used for the determination of the anomeric configuration of L-arabinofuranosides.

Coupling constants between H-1 and H-2 ($^3J_{H\text{-}1,H\text{-}2}$) of 1.2–2.9 and 4.3–4.8 Hz, respectively, were observed for the α- and β-L-arabinofuranosides presently

TABLE VI

^{13}C-CHEMICAL SHIFTS[a] OF ANOMERIC CARBON ATOMS AND COMPARISON OF L-ARABINOFURANOSYLATION SHIFTS OF ANOMERIC CARBON AND AGLYCON a-C, b-C AND b'C ATOMS OF GLYCOSIDES OF *d*- AND *l*-MENTHOL, WITH CORRESPONDING L-ARABINOFURANOSYLATION SHIFTS[b]

Compound	L-*Arabinofuranoside* (L-*Arabinopyranoside*)					
	δC-1	*Chirality*[c]	*Δδ C-1*[d]	*Δδ a-C*[e]	*Δδ b-C*[d]	*Δδ b'-C*[d]
13	110.9	*R,S*	+6.9	+9.0	−2.2	−1.5
		(*R,S*)	(+7.1)	(+10.1)	(−1.8)	(−1.3)
14	99.0	*S,S*	+1.5	+5.4	−5.4	−2.3
		(*S,S*)	(+2.2)	(+5.0)	(−5.7)	(−2.1)
15	105.5	*R,R*	+1.5	+3.9	−2.3	−5.9
		(*R,R*)	(+2.2)	(+5.9)	(−2.3)	(−5.3)
16	104.5	*S,R*	+7.5	+10.3	−1.4	−2.1
		(*S,R*)	(+8.2)	(+10.2)	(−1.2)	(−2.4)

[a]For solutions in ($^2H_5$)pyridine. [b]In parentheses. [c]Chirality combination of C-1 atom as free form, with aglycon a-C atom. [d]δC-1 of glycoside − δC-1 of corresponding free sugar. [e]δa-C, b-C, or b'-C of glycoside − δa-C, b-C, or b'-C of aglycon alcohol.

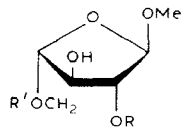
TABLE VII

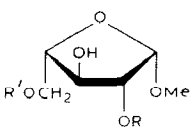
C–H COUPLING CONSTANTS OF ANOMERIC CARBON ATOM AND H,H COUPLING CONSTANTS OF ANOMERIC PROTON OF L-ARABINOFURANOSIDES[a]

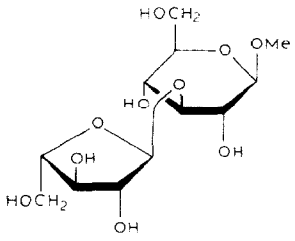
Compound	*α*-L-*Arabinofuranoside*			*Compound*	*β*-L-*Arabinofuranoside*		
	$^1J_{C\text{-}1,H\text{-}1}$ *(Hz)*	$^3J_{H\text{-}1,H\text{-}2}$ *(Hz)*	*δH-1*		$^1J_{C\text{-}1,H\text{-}1}$ *(Hz)*	$^3J_{H\text{-}1,H\text{-}2}$ *(Hz)*	*δH-1*
1	168	1.2[b]	5.38	**2**	170	4.3	5.14
3	169	1.2[b]	5.48	**4**	170	4.8	5.26
5	171	br.s	5.56	**6**	171	4.4	5.37
7	169	br.s	5.69	**8**	169	4.4	5.49
9	170	br.s	5.64	**10**	169	4.8	5.49
11	168	2.9	5.70	**12**	168	4.8	5.54
13	169	1.8	5.57	**14**	171	4.8	5.52
15	171	br.s	5.62	**16**	169	4.4	5.42

[a]For solutions in ($^2H_5$)pyridine. [b]Triplet-like signal by virtual coupling.

studied. It is noteworthy that the anomeric proton signals of α-L-arabinofuranosides exhibited a virtual coupling and were observed as triplet-like or singlet signals, except for **11** and **12**. Thus, the $^3J_{H\text{-}1,H\text{-}2}$ values of L-arabinofuranosides should be useful for the determination of the anomeric configurations of L-arabinofuranosides.







17 R = β-D-Glc*p*, R′ = H **19** R = β-D-Glc*p*, R′ = H **21**

18 R = H, R′ = β-D-Glc*p* **20** R = H, R′ = β-D-Glc*p*

N.m.r. of methyl 2-O-β-D-glucopyranosyl-α- (**17**) *and -β-* (**19**), *and 5-O-β-D-glucopyranosyl-α-* (**18**) *and β-L-arabinofuranoside* (**20**). — As already reported[4], 2-*O*-β-D-glycopyranosylation of α-L-arabinopyranosides of aliphatic alcohols and carboxylic acids sometimes led to a change of the L-arabinopyranosyl ring conformation, resulting in unexpected upfield shifts of the C-3, -4, and -5 signals, and an anomalous variation of $^1J_{C\text{-}1,H\text{-}1}$ and $^3J_{H\text{-}1,H\text{-}2}$ values of the L-arabinopyranosyl

TABLE VIII

^{13}C-CHEMICAL SHIFTS OF INNER SUGAR RESIDUES OF COMPOUNDS **17–21**, β-D GLUCOPYRANOSYLATION SHIFTS[a], AND L-ARABINOFURANOSYLATION SHIFTS[b,c]

Compound	*Sugar residue*[d]					
	δC-1	*δC-2*	*δC-3*	*δC-4*	*δC-5*	*δC-6*
17	108.7	90.8	77.3	85.3	62.6	
	(−1.8)	(+7.4)	(−1.2)	(−0.2)	(0)	
18	110.5	83.4	79.0	83.7	70.2	
	(0)	(0)	(+0.5)	(−1.8)	(+7.6)	
19	103.5	84.5	75.1	84.9	65.2	
	(−0.4)	(+4.9)	(−1.6)	(0)	(0)	
20	103.8	79.0	77.0	82.1	72.9	
	(−0.1)	(−0.6)	+0.3)	(−2.8)	(+7.7)	
21[e]	105.6	74.8	81.8	70.0	78.1	62.4
	[+0.1]	[−0.1]	[+3.5]	[−1.6]	[−0.2]	[−0.3]

[a]In parentheses, δC of glycoside − δC of corresponding methyl arabinofuranoside. [b]In brackets, δC of glycoside − δC of corresponding methyl glycoside. [c]For solutions in ($^2H_5$)pyridine. [d]Potentially reducing residue. [e]^{13}C-Chemical shifts of terminal α-L-arabinofuranosyl residue; 109.8 [−0.7], 82.3 [−1.1], 78.9 [+0.4], 87.6 [+2.1], and 62.9 [+0.3]. For ^{13}C-chemical shifts of terminal sugar residues of other compounds, see previous paper[4].

TABLE IX

C–H COUPLING CONSTANTS OF ANOMERIC CARBON ATOM AND H,H COUPLING CONSTANTS OF ANOMERIC PROTON OF **17–21**[a]

Compound	L-*Arabinofuranosyl residue*			*β*-D-*Glucopyranosyl group*		
	$^1J_{C\text{-}1,H\text{-}1}$ *(Hz)*	$^3J_{H\text{-}1,H\text{-}2}$ *(Hz)*	*δH-1*	$^1J_{C\text{-}1,H\text{-}1}$ *(Hz)*	$^3J_{H\text{-}1,H\text{-}2}$ *(Hz)*	*δH-1*
17	172	s[b]	5.47	158	7.0	5.25
18	170	s[b]	5.34	155	7.4	5.00
19	172	4.2	5.23	159	6.8	5.40
20	170	4.3	5.09	158	7.3	4.91
21	177	s[b]	6.36	156	7.6	4.65

[a]For solutions in ($^2H_5$)pyridine. [b]Singlet.

residue. In contrast to the L-arabinopyranosides, 2-*O*-glucopyranosylation of **1** and **2** (to give **17** and **19**) showed no significant shielding of C-3, -4, and -5, and no change in the values of $^1J_{C\text{-}1,H\text{-}1}$ and $^3J_{H\text{-}1,H\text{-}2}$ for the L-arabinofuranosyl residues. In the case of **19**, it is notable that the downfield-shift values of the signals due to glucosyloxylated carbon atom (C-2) were evidently smaller than those for **17**.

5-*O*-*β*-D-Glucopyranosylation of **1** and **2** (to give **18** and **20**) led to a slight shift for the C-3 (for **18**) or C-2 (for **20**) signals of the L-arabinosyl residues, but no unusual change in the $^1J_{C\text{-}1,H\text{-}1}$ and $^3J_{H\text{-}1,H\text{-}2}$ values were observed (see Tables VIII and IX).

*N.m.r. of methyl 3-*O*-α-*L*-arabinofuranosyl-β-*D*-glucopyranoside* (**21**). — In the spectrum of methyl 3-*O*-α-L-arabinofuranosyl-β-D-glucopyranoside, unexpected displacements of the carbon resonances of the arabinofuranosyl residue were observed. Therefore, the assignments of the carbon signals of **21** were obtained by 2D-n.m.r. spectroscopy, as shown in Table VIII. Comparison of the spectra of **1** and **21** showed a displacement upfield by 1.1 p.p.m. of the signal for C-2′ of the α-L-arabinofuranosyl residue, whereas that for C-4′ was shifted downfield by 2.1 p.p.m. Further, the coupling constants of the proton signals of the L-arabinofuranosyl residue of **21** were changed slightly from the values of **1** (Table II) as follows: $J_{H\text{-}1,H\text{-}2}$ (Table IX), $J_{H\text{-}2,H\text{-}3}$ 4.3; $J_{H\text{-}3,H\text{-}4}$ 4.3; $J_{H\text{-}4,H\text{-}5}$ 4.0, 4.6; and $J_{H\text{-}5,H\text{-}5}$ 11.6 Hz. These results indicated a change of the L-arabinofuranosyl ring conformation.

It was observed that the difference of chemical shifts of disaccharides in D_2O and C_5D_5N solution was always ~−1.0–−1.5 p.p.m. away from that of the methyl glycoside (~+1.0 p.p.m.). The present results should prove useful for the structural elucidation of the structure of natural glycosides and of oligosaccharides carbohydrates containing L-arabinofuranosyl residue.

EXPERIMENTAL

General. — Melting points were determined with a micro hot-stage and are uncorrected. Optical rotations were measured with a Union automatic digital polarimeter for solutions in C_5H_5N.

^{1}H-N.m.r. spectra were recorded with a JEOL GX-270 spectrometer in the F.t. mode at 270 MHz for solutions in C_5D_5N and Me_4Si as an internal standard. Two-dimensional correlation n.m.r. spectra were recorded with a JEOL GX-270 spectrometer for solutions in C_5D_5N, and the data size of the time-domain for COSYP and CHSHF spectra was a 1024 × 256 and 2048 × 128 matrix, respectively.

^{13}C-N.m.r. spectra were recorded at 25.00 MHz with a JEOL FX-100 spectrometer at 22.5° for solutions in C_5D_5N and D_2O; Me_4Si and 1,4-dioxane (δ 67.4) were the internal standards, respectively. Proton-decoupled F.t. n.m.r. and $^1J_{C\text{-}1,H\text{-}1}$ (spectral width, 4 kHz) values were determined with a pulse-flipping angle of 90°, an acquisition time of 1.024 s, a number of data point of 8192, and a pulse-delay time of 0.2–1.0 s.

For column chromatography, silica gel (Kieselgel 60, 70–230 mesh, Merck) was used. High pressure liquid chromatography (l.c.) was carried out with an HLC 803D (Toyo Soda) instrument equipped with a differential refractometer RI-8 (Toyo Soda) as a detector.

*Alkyl α- and β-*L*-arabinofuranosides.* — A solution of L-arabinose (3.2 g) and H_2SO_4 (0.25 mL) in dry methanol[6] (50 mL) was stirred for 24 h at room temperature. The mixture was made neutral with pyridine and concentrated to dryness to give a mixture of **1** and **2**. A solution of this mixture in 13:10:2 acetic anhydride–acetic acid–H_2SO_4 (25 mL) was stirred for 1 h at 0°. Further H_2SO_4 (2 mL) was added at 0°, and the mixture was stirred for 12 h at room temperature. The resulting solution was poured into ice–water and extracted with chloroform. The organic layer was washed with a saturated aqueous solution of $NaHCO_3$ repeatedly, and then with water. After being dried (Na_2SO_4), the solution was concentrated to dryness to give syrupy 1,2,3,5-tetra-*O*-acetyl-L-arabinofuranose in a yield of 70% from L-arabinose.

To a solution of this compound (6.3 mmol) was added an aglycon alcohol (6.3 mmol) in dry dichloromethane (60 mL) and $SnCl_4$ (0.7 mL)[7]. The mixture was kept for 4 h at room temperature, and then poured into a saturated aqueous solution of $NaHCO_3$. The resulting mixture was extracted with chloroform, and the extract was washed with H_2O and concentrated to dryness. The residue was de-acetylated with 5% KOH in methanol (30 mL) for 30 min at room temperature, and the solution was de-ionized with Amberlite MB-3 resin and concentrated to dryness. The crude product, which consisted of the α and β anomers, was separated by chromatography on silica gel and elution with the following solvent systems: 2:3 acetone–benzene for propyl α- (**3**) and β- (**4**), 2-propyl α- (**5**) and β- (**6**), and *tert*-butyl α- (**11**) and β-L-arabinofuranoside (**12**); 1:3 acetone–benzene for *trans*-4-*tert*-butylcyclohexanyl α- (**7**) and β- (**8**), 5α-cholestan-3β-yl α- (**9**) and β- (**10**), and

d-menthyl α- (**13**) and β-L-arabinofuranoside (**14**); and 15:1 chloroform–methanol for *l*-menthyl α- (**15**) and β-L-arabinofuranoside (**16**). The yield of α- and β-L-arabinofuranosides was 15–20 and 10–15%, respectively, from 1,2,3,5-tetra-*O*-acetyl-L-arabinose. Compounds **1** and **2** were separated by chromatography on silica gel by eluting with 3:2 acetone–benzene from the anomeric mixture of methyl L-arabinofuranoside, in a yield of 62 and 16%, respectively, from L-arabinose.

Methyl 2-O-β-D-glucopyranosyl-α- (**17**) *and -β-L-arabinofuranoside* (**19**). — A solution of 2-*O*-β-D-glucopyranosyl-L-arabinose[5] (120 mg) and H_2SO_4 (0.3 mL) in dry methanol (60 mL) was stirred for 3 days at room temperature. The resulting solution was made neutral with Amberlite MB-3 resin, and concentrated to dryness. The residue was chromatographed on silica gel by eluting with 7:2:1 ethyl acetate–ethanol–water (homogeneous) to give **17** (80 mg) and a mixture of **19** and methyl 2-*O*-β-D-glucopyranosyl-β-L-arabinopyranoside[4] (**22**). The mixture was separated by l.c. on silica gel [LiChrosorb Si 60 5 μm, Merck, 7.8 (i.d.) × 300 mm; detection by refraction index; solvent; 7:2:1 ethyl acetate–ethanol–water (homogeneous)] to give **19** (20 mg) and **22** (20 mg).

Methyl 5-O-β-D-glucopyranosyl-α- (**18**) *and -β-L-arabinofuranoside* (**10**). — A mixture of **1** or **2** (2.8 g) and chlorotriphenylmethane (5 g) in pyridine[11] (15 mL) was boiled under reflux for 1 h. To the mixture was added acetic anhydride (10 mL), and the solution was stirred for 1 h at room temperature. Then, it was poured into ice–water and extracted with chloroform. The organic layer was concentrated to dryness, and the residue was dissolved in acetic acid (20 mL) and anhydrous 25% HBr–acetic acid (5 mL) was added with stirring. The resulting precipitate was removed by filtration, and the filtrate was poured into ice–water and extracted with chloroform. The organic layer was washed with a saturated aqueous solution of $NaHCO_3$, and then with water. After being dried (Na_2SO_4), the solution was evaporated to dryness and the residue was purified by chromatography on silica gel by eluting with 1:10 acetone–benzene to give methyl 2,3-di-*O*-acetyl-α- or -β-L-arabinofuranoside in a yield of 20% from the corresponding methyl L-arabinofuranoside.

A mixture of the 2,3-di-*O*-acetyl derivative (α or β anomer) (0.5 g), $Hg(CN)_2$ (1 g), and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (1.5 g) in dry toluene (40 mL) was boiled under reflux for 5 h. After cooling, the insoluble $Hg(CN)_2$ was removed by filtration and the filtrate was concentrated to dryness. The residue was deacetylated with 5% KOH in methanol (30 mL) for 30 min at room temperature, and the resulting precipitate was removed by filtration. The filtrate was de-ionized with Amberlite MB-3 resin and concentrated to dryness. The residue was purified by chromatography on silica gel by eluting with 30:13:1 chloroform–methanol–water (homogeneous) to give **18** or **20** in a yield of 20% from the corresponding methyl 2,3-di-*O*-acetyl-L-arabinofuranoside.

Methyl 3-O-α-L-arabinofuranosyl-β-D-glucopyranoside (**21**). — A mixture of methyl 2-*O*-acetyl-4,6-benzylidene-β-D-glucopyranoside (0.15 g) (prepared by the method of Horton *et al.*[8]), $Hg(CN)_2$ (0.4 g), and 2,3,5-tri-*O*-benzyl-α-L-arabino-

furanosyl chloride[9] (0.7 g) in dry toluene (20 mL) was refluxed for 5 h. The insoluble $Hg(CN)_2$ was removed by filtration, and the filtrate was concentrated to dryness. The residue was deacetylated by boiling for 30 min with 5% KOH in methanol (20 mL), and the solution was diluted with water and extracted with chloroform. The organic layer was dried (Na_2SO_4) and concentrated, and the residue was hydrogenated in the presence of Pd black (20 mg) in ethanol (30 mL) for 15 h. The catalyst was filtered off, and the filtrate was concentrated to dryness. The residue was purified by chromatography on silica gel by eluting with 30:13:1 chloroform–methanol–water (homogeneous) to give **21** in an 18% yield.

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