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N.M.R.-SPECTRAL STUDIES OF 2-LINKED GLYCOSIDES: 2-*O*-GLYCOSYLATION SHIFTS OF 2-*O*-GLYCOSYLATED α- AND β-L-ARABINOPYRANOSIDES

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ABSTRACT

Anomalous glycosylation shift values of the signals for C-1 (the anomeric carbon atom) and C-2 (the glycosyloxylated carbon atom) were sometimes observed for 2-*O*-β-D-glycopyranosyl (or -β-D-xylopyranosyl)-β-D-glucopyranosides, whereas no remarkable displacements of the other sugar-carbon signals were observed in these cases. This can be explained in terms of change of the orientation of the glycosyl linkages, owing to strong, steric interaction between the 2-*O*-glycosyl group and the 1-*O*-aglycon (or -sugar) group. Various 2-*O*-glycosylated α- and β-L-arabinopyranosides were synthesized. In the case of α-L-arabinopyranosides, the processes of 2-*O*-β-D-glucosylation, -β-D-xylosylation, and -α-L-arabinosylation resulted in unexpected, upfield shifts of the C-3, -4, and -5 signals, together with displacement of the C-1 and -2 resonances. Furthermore, significant alteration of the values of $^3J_{H1,H2}$ and $^1J_{C1,H1}$ was also observed for the 2-*O*-glycosylated α-L-arabinopyranoside moiety, indicating an increase in the contribution of the $^1C_4$ conformation of the glycosylated α-L-arabinopyranoside in these cases. On the other hand, no remarkable variation in the signals of C-3, -4, and -5, or in the $^3J_{H1,H2}$ and $^1J_{C1,H1}$ values, was found for 2-*O*-α-L-rhamnosylation, except for 4-epihederagenin-3-yl 2-*O*-α-L-rhamnopyranosyl-α-L-arabinopyranoside. In the present study, such unusual 2-*O*-glycosylation shifts were not encountered for the 2-*O*-glycosylation of β-L-arabinopyranosides.

INTRODUCTION**

To expand the applicability of ^{13}C-n.m.r. spectroscopy to carbohydrate

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**Throughout the present article, all sugar units are pyranoid, unless specified otherwise.

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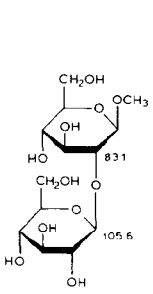
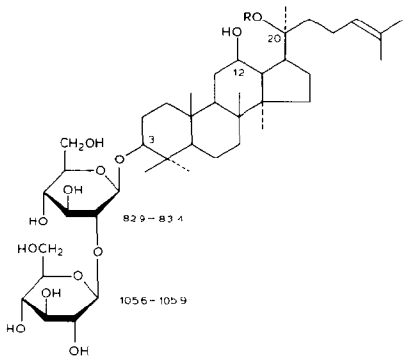
chemistry, we have been engaged in investigation of displacements of the carbon resonances of both the sugar and the aglycon moieties that occur on glycoside formation, the so-called "glycosylation shifts (g.s.)", which have been utilized in structure elucidation of a variety of biologically active, natural glycosides[1–5]. During the course of these studies, the anomalous g.s. of signals due to the anomeric carbon atom of the glycosyl group and the glycosyloxylated carbon atom was sometimes observed for 1,2-linked glycobiosyl moieties.

As already reported, on going from methyl β-D-glucopyranoside to methyl β-sophoroside (**1**), the D-glucosyloxylated carbon atom is deshielded by 8.2 p.p.m., and its signal appears at δ 83.1, whereas that of the anomeric carbon atom associated with the linkage at O-2 is observed[5] at δ 105.6. Similar g.s. values were observed for the β-sophoroside and 2-*O*-β-D-xylopyranosyl-β-D-glucopyranoside moieties at the 3β-hydroxyl group of triterpenes[6,7] (**2–6**) and a diterpene[8] (**7**) in which neither *gem*-dimethyl group on C-4 is oxygenated. However, the g.s. values

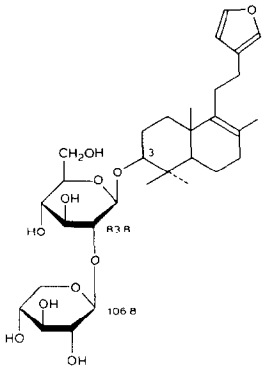


1

Methyl
β-sophoroside



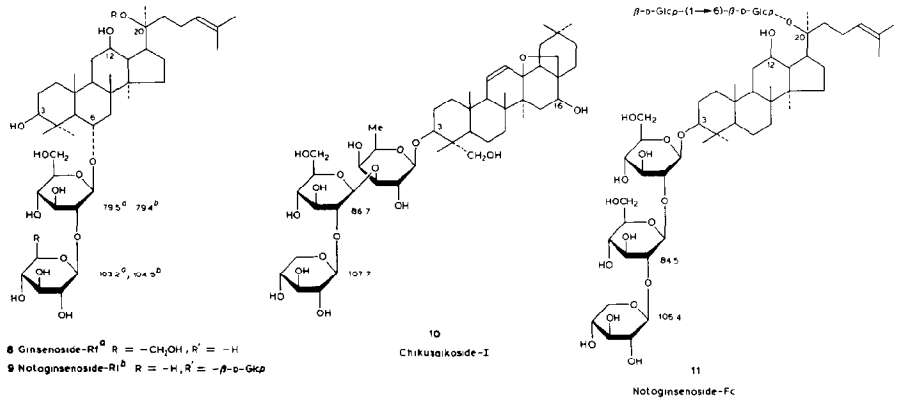
2 Ginsenoside-Rb$_1$ R = β-D-Glcp-(1→6)-β-D-Glcp
3 Ginsenoside-Rb$_2$ R = α-L-Arap-(1→6)-β-D-Glcp
4 Ginsenoside-Rb$_3$ R = β-D-Xylp-(1→6)-β-D-Glcp
5 Ginsenoside-Rc R = α-L-Araf-(1→6)-β-D-Glcp
6 Ginsenoside-Rd R = β-D-Glcp



7
Baiyunoside

of the β-sophoroside and 2-*O*-β-D-xylosyl-β-D-glucopyranoside moieties at the 6α-hydroxyl group of the dammarane type of triterpene[9] [ginsenoside-Rf (**8**) and notoginsenoside-Rl (**9**)] were found to be exceptional; both the glycosyloxylated and the anomeric carbon atom are remarkably less deshielded than in the case of compound **1**. The assignments of these signals were substantiated by the application of selective deuteration[9]. In contrast, the carbon atoms involved in the (1→2) linkage of the 2-*O*-β-D-xylosyl-β-D-glucopyranoside moiety were more deshielded than those in **1**, remarkably for[10] chikusaikoside-I (**10**) and slightly for[11] notoginsenoside-Fc (**11**). Because no significant change was observed in the chemical shifts of the other carbon signals, or in the coupling constants of the anomeric-proton and carbon signals of the glycosylated D-glucose unit, these unusual displacements can be explained in terms of orientational change of the glycosyl linkage, due to the

1,2-*gauche*, steric interaction between the 1-*O*-aglycon group and the 2-*O*-glycosyl residue.

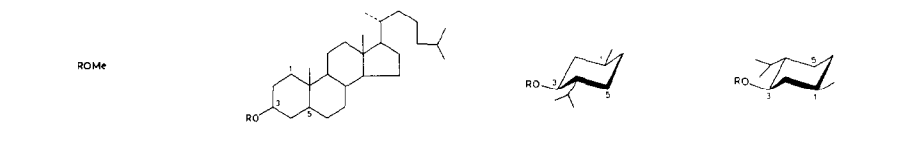


On the other hand, an abnormal g.s. of a different type was reported[12] for the *O*-2-linked arabinosyl unit of the 2-*O*-α-L-rhamnopyranosyl-α-L-arabinopyranosyl ester of platycodin-D (a saponin from *Platycodon grandiflorum*).

Previously, we had investigated the g.s. of α- and β-L-arabinopyranosides formed from a variety of alcohols, and reported[3] that the $^4C_1$ conformation must be predominant, regardless of the structure of the aglycon. In continuation of this study, we now present the results of a systematic study of the n.m.r. spectroscopy of some *O*-2-linked α- and β-L-arabinopyranosides.

RESULTS AND DISCUSSION

Synthesis of 2-O-*glycosyl*-L-*arabinopyranosides*. — 2-*O*-Glycosyl-α- and -β-L-arabinopyranosides were synthesized from the following alcohols: methanol (**12**), 5α-cholestan-3β-ol (**23**), and *d*- and *l*-menthol (**32** and **41**), the last two having been used as representatives of the relatively hindered secondary alcohols in our serial



12 R = H
13 R = α-L-Araf
14 R = β-D-Glcp-(1→2)-α-L-Araf
15 R = β-D-Xylp-(1→2)-α-L-Araf
16 R = α-L-Arap-(1→2)-α-L-Araf
17 R = α-L-Rhap-(1→2)-α-L-Araf
18 R = β-L-Araf
19 R = β-D-Glcp-(1→2)-β-L-Araf
20 R = β-D-Xylp-(1→2)-β-L-Araf
21 R = α-L-Arap-(1→2)-β-L-Araf
22 R = α-L-Rhap-(1→2)-β-L-Araf

23 R = H
24 R = α-L-Araf
25 R = β-D-Glcp-(1→2)-α-L-Araf
26 R = β-D-Xylp-(1→2)-α-L-Araf
27 R = α-L-Arap-(1→2)-α-L-Araf
28 R = α-L-Rhap-(1→2)-α-L-Araf
29 R = β-L-Araf
30 R = β-D-Glcp-(1→2)-β-L-Araf
31 R = α-L-Rhap-(1→2)-β-L-Araf

32 R = H
33 R = α-L-Araf
34 R = β-D-Glcp-(1→2)-α-L-Araf
35 R = β-D-Xylp-(1→2)-α-L-Araf
36 R = α-L-Arap-(1→2)-α-L-Araf
37 R = α-L-Rhap-(1→2)-α-L-Araf
38 R = β-L-Araf
39 R = β-D-Glcp-(1→2)-β-L-Araf
40 R = α-L-Rhap-(1→2)-β-L-Araf

41 R = H
42 R = α-L-Araf
43 R = β-D-Glcp-(1→2)-α-L-Araf
44 R = α-L-Rhap-(1→2)-α-L-Araf
45 R = β-L-Araf
46 R = β-D-Glcp-(1→2)-β-L-Araf
47 R = α-L-Rhap-(1→2)-β-L-Araf

TABLE I

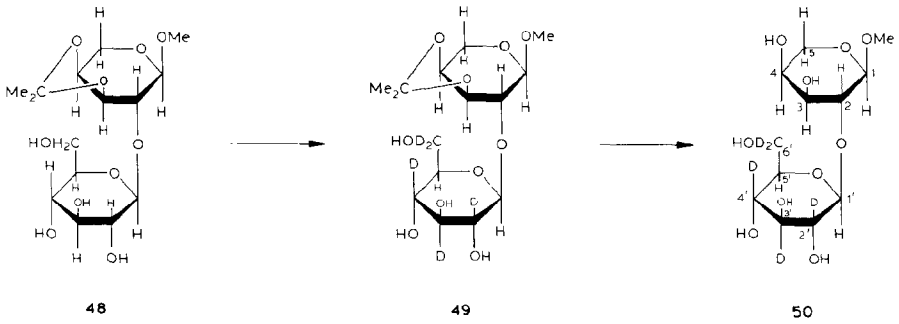
SOME PHYSICAL CONSTANTS OF 2-*O*-GLYCOPYRANOSYL-L-ARABINOPYRANOSIDES

Compound	*State*	*M.p. (degrees)*	*Crystallization solvent*	$[\alpha]_D^{20}$ *(degrees)*[a]	*Conc.*
14	colorless needles	193.0–194.0	methanol–ethyl acetate	−36.8	0.80
15	colorless needles	187.5–189.0	methanol–ethyl acetate	−48.5	0.92
16	white powder		methanol–ethyl acetate	−5.4	0.93
17	colorless syrup			−58.3	2.33
19	white powder		methanol–ethyl acetate	+91.7	0.69
20	colorless needles	182.0–184.0	ethanol–ethyl acetate	+95.3	0.60
21	colorless needles	228.0–230.0	ethanol	+122.1	0.61
22	colorless needles	184.0–186.0	ethanol	+95.7	0.67
24	colorless needles	181.0–184.0	chloroform–hexane	−0.2	0.87
25	colorless needles	246.0–249.0	ethanol–chloroform	−15.0	0.73
26	colorless needles	207.0–208.0	methanol–chloroform	−24.1	0.87
27	colorless needles	187.0–190.0	methanol–chloroform	−9.0	0.81
28	colorless needles	203.0–205.0	methanol–chloroform	−35.3	0.94
29	colorless needles	215.5–216.5	chloroform	+98.6	0.67
30	white powder		methanol	+80.2	0.62
31	colorless needles	188.0–189.0	methanol	+48.6	0.67
34	colorless syrup			+8.0	3.66
35	white powder		acetone	+1.9	0.53
36	colorless syrup			+32.5	1.36
37	colorless needles	99.0–100.0	acetone–hexane	+30.5	0.63
39	colorless needles	208.0–209.0	methanol–ethyl acetate	+131.9	1.00
40	colorless syrup			+106.4	1.43
43	colorless needles	172.0–173.0	acetone	−79.8	0.82
44	white powder		ethyl acetate–hexane	−102.6	0.68
46	white powder		methanol–ethyl acetate	+61.5	0.66
47	colorless syrup			+12.1	2.55

[a]In pyridine.

studies[1–3] on g.s. The α-and β-L-arabinopyranosides were prepared from these alcohols by the following procedures: α anomers by the Koenigs–Knorr method, and β anomers by the Fischer or the Banoub–Bundle method[13]. These glycosides were respectively converted into the 3,4-isopropylidene acetals[14]. Glycosylation of these acetals with a per-*O*-acetylglycosyl bromide and $Hg(CN)_2$, followed by removal of the protecting groups, yielded[15] the respective 2-*O*-glycosyl-α- and -β-L-arabinopyranosides listed in Table I.

Assignments of proton and carbon signals of methyl 2-O-β-D-glucopyranosyl-α-L-arabinopyranoside (**14**). — The unambiguous characterization of carbon signals due to the α-L-arabinopyranoside moiety of **14** was very difficult, because of the unexpected displacement of *all* of the carbon resonances; not only those of C-1, -2, and -3, but also, those of C-4 and -5. Therefore, assignments of the proton signals were first made by selective deuteration[5,9,16] of the D-glucosyl group. On refluxing compound **48** with deuterated Raney nickel in D_2O to give **49**, followed by removal of the isopropylidene group[15], compound **50** was obtained; in compound



48 49 50

Scheme 1. Selective deuteration of methyl 2-*O*-β-D-glucopyranosyl-α-L-arabinopyranoside.

TABLE II

^{1}H-CHEMICAL SHIFTS, COUPLING CONSTANTS, AND ^{13}C-CHEMICAL SHIFTS OF METHYL 2-*O*-β-D-GLUCOPYRANOSYL($^2H_5$)-α-L-ARABINOPYRANOSIDE

Group	*Proton*	δ_H	*Multiplicity*	J *(Hz)*	*Carbon atom*	δ_C
Arabinosyl	H-1	4.83	d	4.8	C-1	102.9
	H-2	4.61	dd	4.8, 6.6	C-2	80.0
	H-3	4.46	—[a]	—	C-3	72.5
	H-4	4.42	—	—	C-4	67.6
	H-5	4.27	dd	10.9, 5.3	C-5	64.4
		3.71	dd	10.9, 1.7		
Glucosyl	H-1′	5.20	s		C-1′	105.2
	H-5′	3.82	s		C-5′	78.2
Methoxyl	OCH_3	3.45	s		OCH_3	55.8

[a]Not observed, owing to overlapping.

50, C-2′, -3′, -4′, and -6′,6′ of the β-D-glucopyranosyl group were selectively deuterated (see Scheme 1). This resulted in the disappearance of signals due to H- and C-2′, -3′, -4′, and -6′,6′ of the β-D-glucopyranosyl group, and the alteration of its H-1′ and -5′ signals to a singlet, facilitating assignment of the signals due to the α-L-arabinopyranoside unit. This technique, coupled with a decoupling experiment, led to definite assignments of the proton signals, shown in Table II.

Furthermore, by means of the proton, selective-decoupling technique, accurate identification of the carbon signals due to the α-L-arabinopyranoside unit was furnished, and then, comparison with this result led to assignment of the carbon signals of all of the other, 2-linked α-L-arabinopyranosides, as shown in Table III.

Glycosylation shifts of 2-O-glycosylated α-L-arabinopyranosides. — The n.m.r. spectrum of each 2-*O*-glycosyl-α-L-arabinopyranoside was compared with that of the corresponding α-L-arabinopyranoside. As already mentioned, on going from methyl β-D-glucopyranoside to methyl β-sophoroside (**1**), glycosylation of the 2-hydroxyl group led to a remarkable displacement of the signals due to anomeric

TABLE III

^{13}C-CHEMICAL SHIFTS OF SUGAR MOIETIES OF 2-*O*-GLYCOPYRANOSYL-α-L-ARABINOPYRANOSIDES, AND GLYCOSYLATION SHIFTS (IN PARENTHESES)

Compound	$\delta_{C\text{-}1}$ ($\Delta\delta$)[a]	$\delta_{C\text{-}2}$ ($\Delta\delta$)	$\delta_{C\text{-}3}$ ($\Delta\delta$)	$\delta_{C\text{-}4}$ ($\Delta\delta$)	$\delta_{C\text{-}5}$ ($\Delta\delta$)	$\delta_{C\text{-}1'}$	$\delta_{C\text{-}2'}$	$\delta_{C\text{-}3'}$	$\delta_{C\text{-}4'}$	$\delta_{C\text{-}5'}$	$\delta_{C\text{-}6'}$
13	105.8	72.1	74.2	69.0	66.5						
14	102.7	79.9	72.4	67.5	64.2	105.1	75.5	78.2	71.3	78.2	62.4
	(−3.1)	(+7.8)	(−1.8)	(−1.5)	(−2.3)						
15	103.1	80.1	73.0	67.8	64.7	105.9	75.3	78.0	70.9	67.1	
	(−2.7)	(+8.0)	(−1.2)	(−1.2)	(−1.8)						
16	103.1	79.6	73.1	67.9	64.8	105.5	72.7	74.3	69.0	66.6	
	(−2.7)	(+7.5)	(−1.1)	(−1.1)	(−1.7)						
17	103.6	76.6	73.9	69.0	65.7	102.3	72.7[b]	72.3[b]	73.9	69.7	18.3
	(−2.2)	(+4.5)	(−0.3)	(0)	(−0.8)						
24	102.6	72.4	74.5	69.3	66.6						
25	100.4	81.2	72.8	67.8	64.7	105.7	76.0	78.0[b]	71.4	78.4[b]	62.5
	(−2.2)	(+8.8)	(−1.7)	(−1.5)	(−1.9)						
26	100.2	80.4	72.9	67.9	64.8	105.8	75.1	77.7	70.9	67.1	
	(−2.4)	(+8.0)	(−1.6)	(−1.4)	(−1.8)						
27	100.2	79.5	72.9	67.9	64.7	105.2	72.4	74.1	68.7	66.4	
	(−2.4)	(+7.1)	(−1.6)	(−1.4)	(−1.9)						
28	100.2	76.5	74.8	69.5	66.1	102.1	72.8[b]	72.4[b]	74.0	69.5	18.5
	(−2.4)	(+4.1)	(+0.3)	(+ 0.2)	(−0.5)						
33	106.3	72.6	74.3	69.1	66.4						
34	103.4	79.5	72.8	67.6	64.1	105.0	75.3	77.9[b]	71.8	78.1[b]	62.9
	(−2.9)	(+6.9)	(−1.5)	(−1.5)	(−2.3)						
35	103.7	80.1	73.0	67.9	64.4	105.9	75.4	78.0	71.0	67.3	
	(−2.6)	(+7.5)	(−1.3)	(−1.2)	(−2.0)						
36	103.6	79.8	72.7	67.6	64.1	105.7	72.7	74.2	69.0	66.9	
	(−2.7)	(+7.2)	(−1.6)	(−1.5)	(−2.3)						
37	103.3	75.9	73.5[b]	68.7	64.8	101.7	72.5[c]	72.2[c]	73.7[b]	69.6	18.3
	(−3.0)	(+3.3)	(−0.8)	(−0.4)	(−1.6)						
42	101.4	72.2	74.4	69.2	66.6						
43	98.4	80.9	72.5	67.5	64.1	105.6	75.7	78.0[b]	71.4	78.3[b]	62.6
	(−3.0)	(+8.7)	(−1.9)	(−1.7)	(−2.5)						
44	98.7	75.9	74.9	69.4[b]	66.2	101.9	72.7[c]	72.3[c]	73.9	69.5[b]	18.3
	(−2.7)	(+3.7)	(+0.5)	(+ 0.2)	(−0.4)						

[a] $\Delta\delta$ = δ_C of 2-*O*-glycosyl-α-L-arabinoside − δ_C of corresponding α-L-arabinoside. [b,c] These assignments may have to be reversed in each row.

and to glycosyloxylated carbon atoms, whereas other carbon signals and the coupling constant of the anomeric-proton signal of the glycosylated β-D-glucoside unit were almost unaffected. In contrast, on going from methyl α-L-arabinoside (**13**) to methyl 2-*O*-β-D-glucosyl-α-L-arabinoside (**14**), besides the displacement of the anomeric and glucosyloxylated carbon signals, signals due to C-3, -4, and -5 of α-L-arabinoside were unexpectedly displaced upfield by 1.5–2.3 p.p.m. Furthermore, the coupling constant of the anomeric-proton signal, $^3J_{H1,H2}$ (decreasing from 6.9 to 4.3–5.6 Hz) and $^1J_{C1,H1}$ (increasing from 156–158 to 160–164 Hz) of the α-L-arabinoside moiety were also significantly changed (see Table IV), indicating in-

TABLE IV

C–H COUPLING CONSTANTS OF ANOMERIC CARBON SIGNALS AND H,H COUPLING CONSTANTS BETWEEN THE ANOMERIC PROTON AND H-2 OF 2-*O*-GLYCOPYRANOSYL-α-L-ARABINOPYRANOSIDES

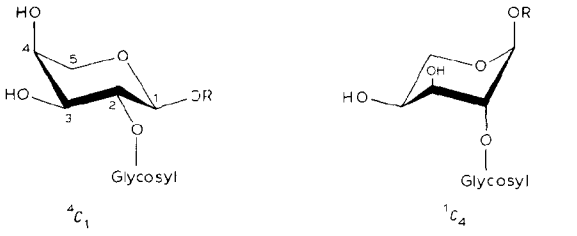
Compound	α-L-*Arabinopyranosyl*			2-O-*Glycopyranosyl*		
	$^1J_{C\text{-}1,H\text{-}1}$ *(Hz)*	$^3J_{H\text{-}1,H\text{-}2}$ *(Hz)*	$\delta_{H\text{-}1}$[a]	$^1J_{C\text{-}1',H\text{-}1'}$ *(Hz)*	$^3J_{H\text{-}1',H\text{-}2'}$ *(Hz)*	$\delta_{H\text{-}1'}$[a]
13	158	6.9	4.56			
14	160	4.9	4.82	158	7.6	5.18
15	163	5.3	4.77	160	6.9	5.08
16	162	5.6	4.76	158	6.9	5.11
17	156	[b]	[b]	170	s[c]	6.03
24	158	6.9	4.86			
25	164	5.6	5.12	158	7.6	5.16
26	160	5.6	5.09	158	6.6	5.12
27	160	5.6	5.09	158	6.6	5.14
28	156	6.3	4.94	168	s[c]	6.14
33	156	6.9	4.76			
34	162	4.7	5.19	160	7.6	5.08
35	160	5.3	5.00	160	7.3	5.11
36	164	4.9	5.06	156	6.9	5.03
37	160	5.6	4.91	170	s[c]	6.08
42	158	6.9	4.77			
43	164	4.3	5.17	156	7.6	5.11
44	158	6.6	4.89	170	s[c]	6.15

[a]Chemical shift of anomeric proton. [b]Not observed, owing to overlapping. [c]s = singlet.

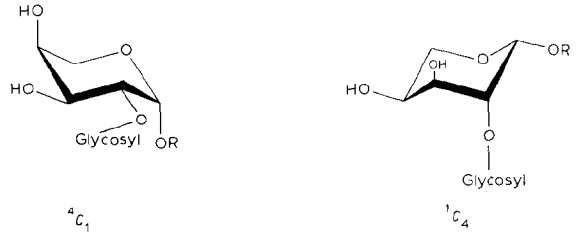
crease in the axial nature of the anomeric C-1–O–aglycon bonding, whereas the carbon resonances due to the β-D-glucosyl unit appeared at positions similar to those of **1**. A similar, unexpected g.s. was also observed for other 2-*O*-β-D-glucosyl-α-L-arabinosides, as well as 2-*O*-β-D-xylosyl- and 2-*O*-α-L-arabinosyl-α-L-arabinosides examined in the present study, although the g.s. values of the glycosyloxylated carbon signal varied somewhat with the structure of the aglycon and the glycosyl group.

As already mentioned, in some cases of β-sophorosides and 2-*O*-β-D-xylosyl-β-D-glucosides, the 1,2-*gauche* interaction between the 2-*O*-glycosyl group and the 1-*O*-aglycon is relieved by change of the orientation of the glycosyl linkage. In contrast to this, the significant influences of 2-*O*-β-glucosylation, -β-xylosylation, and -α-arabinosylation on the C-3, -4, -5 chemical-shifts and $^1J_{C1,H1}$ and $^3J_{H1,H2}$ values suggested that, in these cases, the 1,2-*gauche*, steric interaction was relieved by an increase in the population of the $^1C_4$ form of the 2-*O*-glycosylated α-L-arabinoside in which the relative orientation of the 1- and 2-substituents are *anti* (see Fig. 1).

It is notable that, for α-L-rhamnosyl-α-L-arabinoside, these anomalous g.s. values have not been observed, except for **37** and 4-*epi*-hederagenin (EH)-3-yl 2-*O*-α-L-rhamnosyl-α-L-arabinoside the latter of which showed extremely anomalous g.s., as recently reported by Kizu and Tomimori[17] (assignments for C-3 and -4 of



Alkyl 2-*O*-glycopyranosyl-α-L-arabinopyranoside



Alkyl 2-*O*-glycopyranosyl-β-L-arabinopyranoside

Fig. 1.

the α-L-arabinoside unit reported by them were reversed), although that of hederagenin did not exhibit such an unusual g.s.

Glycosylation shifts of 2-O-glycosylated β-L-arabinopyranosides. — The identification of the proton signals of methyl β-L-arabinoside (**18**) in C_5D_5N was furnished by a decoupling experiment, and its C-2, -3, and -4 signals in C_5D_5N were unambiguously assigned by the proton, selective-decoupling technique as shown in Table V. The carbon chemical shifts of the 2-*O*-β-D-glucosyl- and 2-*O*-α-L-rhamnosyl-α-L-arabinosides of **12, 23, 32,** and **41**, and the 2-*O*-β-D-xylosyl- and 2-*O*-α-L-arabinosyl-α-L-arabinosides of **12** are listed in Table VI.

TABLE V

^{1}H-CHEMICAL SHIFTS, COUPLING CONSTANTS, AND ^{13}C-CHEMICAL SHIFTS OF METHYL β-L-ARABINOPYRANOSIDE

Proton	δ_H	*Multiplicity*	J *(Hz)*	*Carbon atom*	δ_C
H-1	5.16	d	3.3	C-1	102.1
H-2	4.61	dd	3.3, 9.2	C-2	70.5
H-3	4.46	dd	9.2, 3.3	C-3	70.9
H-4	4.37	dd	3.3, 2.6	C-4	70.0
H-5	4.03	d	2.6	C-5	63.9
OCH_3	3.43	s		OCH_3	55.3

TABLE VI

^{13}C-CHEMICAL SHIFTS OF SUGAR MOIETIES OF 2-*O*-GLYCOPYRANOSYL-β-L-ARABINOPYRANOSIDES, AND GLYCOSYLATION SHIFTS (IN PARENTHESES)

Compound	$\delta_{C\text{-}1}$ ($\Delta\delta$)[a]	$\delta_{C\text{-}2}$ ($\Delta\delta$)	$\delta_{C\text{-}3}$ ($\Delta\delta$)	$\delta_{C\text{-}4}$ ($\Delta\delta$)	$\delta_{C\text{-}5}$ ($\Delta\delta$)	$\delta_{C\text{-}1'}$	$\delta_{C\text{-}2'}$	$\delta_{C\text{-}3'}$	$\delta_{C\text{-}4'}$	$\delta_{C\text{-}5'}$	$\delta_{C\text{-}6'}$
18	102.1	70.5	70.9	70.0	63.9						
19	101.2	79.7	70.3	69.7	63.7	106.4	75.5	78.2	71.4	78.2	62.5
	(−0.9)	(+9.2)	(−0.6)	(−0.3)	(−0.2)						
20	101.3	79.4	70.3	69.5	63.7	107.0	75.2	78.0	70.9	67.0	
	(−0.8)	(+8.9)	(−0.6)	(−0.5)	(−0.2)						
21	101.2	79.3	70.2	69.5[b]	63.7	106.8	72.7	74.3	69.2[b]	66.7	
	(−0.9)	(+8.8)	(−0.7)	(−0.5)	(−0.2)						
22	101.1	78.4	70.6	69.8[b]	63.4	104.3	72.5[c]	72.0[c]	73.9	69.0[b]	18.6
	(−1.0)	(+7.9)	(−0.3)	(−0.2)	(−0.5)						
29	99.2	70.7	71.1	70.3	64.3						
30	98.5	80.0	70.5	69.7	64.1	106.5	75.6	78.3	71.7	78.3	62.8
	(−0.7)	(+9.3)	(−0.6)	(−0.6)	(−0.2)						
31	98.9	77.6	71.0	70.0[b]	64.1	103.9	72.7[c]	72.2[c]	73.9	69.7[b]	18.6
	(−0.3)	(+6.9)	(−0.1)	(−0.3)	(−0.2)						
38	96.8	70.6	71.2	70.0	64.6						
39	96.5	79.7	70.4	69.7	64.5	106.5	75.6	78.3	71.8	78.3	62.9
	(−0.3)	(+9.1)	(−0.8)	(−0.3)	(−0.1)						
40	96.0	75.2	70.7	69.9	64.5	103.5	72.6[b]	72.1[b]	73.8	69.9	18.5
	(−0.8)	(+4.6)	(−0.5)	(−0.1)	(−0.1)						
45	102.8	71.0	71.0	70.0	64.4						
46	102.1	79.8	70.4	69.4	64.0	106.2	75.5	78.0	72.2	78.0	63.2
	(−0.7)	(+8.8)	(−0.6)	(−0.6)	(−0.4)						
47	101.7	74.9	71.0	70.4	64.3	103.0	72.6[b]	72.2[b]	73.8	69.6	18.4
	(−1.1)	(+3.9)	(0)	(+0.4)	(−0.1)						

[a] $\Delta\delta$ = δ_C of 2-*O*-glycosyl-β-L-arabinoside − δ_C of corresponding β-L-arabinoside. [b,c] These assignments may have to be reversed in each row.

The g.s. of these 2-linked β-L-arabinosides from the corresponding β-L-arabinoside was compared with that of 2-*O*-glycosyl-α-L-arabinoside. In contrast to the case of 2-*O*-glycosylation of α-L-arabinoside, no significant shielding of C-3, -4, -5, and no change in the value of $J_{C1,H1}$ and $^3J_{H1,H2}$ were observed for the 2-*O*-glycosylated β-L-arabinoside series (see Tables VI and VII), indicating the predominance of the $^4C_1$ conformation of the β-L-arabinoside portion. This can be explained by the fact that even in the $^1C_4$ form, the relative orientation of the 1,2-substituents is still *gauche* in the case of β-L-arabinosides. It was noted that the magnitude of g.s. of the signal of the glycosyloxylated carbon atom was relatively higher, and that of the signal of the anomeric carbon atom was smaller, than those of the corresponding 2-*O*-glycosyl-α-L-arabinoside.

No significant displacement of the signals of aglycon carbon atoms by the 2-*O*-glycosylation was observed either for the α- or the β-L-arabinoside series.

The present results should prove useful for structural elucidation of glycosides and carbohydrates having *O*-substituted arabinopyranoside moieties.

TABLE VII

C–H COUPLING CONSTANTS OF ANOMERIC CARBON SIGNALS AND H,H COUPLING CONSTANTS BETWEEN THE ANOMERIC PROTON AND H-2 OF 2-*O*-GLYCOPYRANOSYL-β-L-ARABINOPYRANOSIDES

Compound	*β-L-Arabinopyranosyl*			*2-O-Glycopyranosyl*		
	$^1J_{C\text{-}1,H\text{-}1}$ *(Hz)*	$^3J_{H\text{-}1,H\text{-}2}$ *(Hz)*	$\delta_{H\text{-}1}$[a]	$^1J_{C\text{-}1',H\text{-}1'}$ *(Hz)*	$^3J_{H\text{-}1',H\text{-}2'}$ *(Hz)*	$\delta_{H\text{-}1'}$[a]
18	168	3.3	5.16			
19	170	3.3	5.32	160	7.6	5.20
20	170	3.3	5.30	158	6.9	5.04
21	168	3.3	5.31	160	7.3	5.00
22	166	2.6	5.36	168	s[b]	5.70
29	165	3.3	5.48			
30	169	3.3	5.68	158	7.3	5.21
31	168	3.6	5.63	168	s[b]	5.89
38	166	3.3	5.51			
39	166	3.6	5.73	158	7.6	5.13
40	167	3.6	5.64	171	s[b]	5.94
45	164	3.3	5.40			
46	170	3.3	5.61	158	7.3	5.05
47	166	3.6	5.47	169	s[b]	6.12

[a]Chemical shift of anomeric proton. [b]s = singlet.

EXPERIMENTAL

General. — Melting points were determined on a micro hot-stage and are uncorrected. Optical rotations were measured with a Union automatic digital polarimeter at 20° for solutions in C_5H_5N. For column chromatography, silica gel (Kieselgel 60, 70–230 mesh; Merck) was used. ^{13}C-N.m.r. spectra were recorded with a JEOL JNM-PFT-100 spectrometer at 25° for 0.15–0.3M solutions in C_5D_5N, at 25.15 MHz, using Me_4Si as internal standard. For proton-decoupled, F.t. measurement: spectral width, 4 kHz; pulse flipping angle, 90°; acquisition time, 0.4 s; number of data points, 4096; transient time, 1.0 s; number of transients, 720–2400. Conditions for measurement of $^1J_{C1,H1}$ by gated decoupling: spectral width, 4 kHz; pulse flipping angle, 90°; acquisition time, 0.4 s; number of data points, 4096; transient time, 1.0 s; number of transients, 1440–4800; computer-limited resolution, 2 Hz. ^{1}H-N.m.r. spectra were recorded in the F.t. mode, with a JEOL-FX-270 spectrometer for 0.05–0.1M solutions in C_5D_5N at 270 MHz, using Me_4Si as the internal standard.

Synthesis of 2-O-glycosyl-α-L-arabinopyranosides. — Methyl α-L-arabinoside (**13**) was prepared as already described[5]. The α-L-arabinosides (**24, 33,** and **42**) of **23, 32,** and **41** were prepared by a modification of the previous procedure[3], as follows. A mixture of the aglycon alcohol (of **23, 32,** or **41**; 5 mmol), $Hg(CN)_2$ (7 mmol), and 2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl bromide (7 mmol) in dry toluene (60 mL) was boiled under reflux for 5 h, and cooled. The insoluble

$Hg(CN)_2$ was removed by filtration, and the filtrate was evaporated to dryness. The residue was deacetylated with 5% KOH in MeOH (50 mL) during 30 min at room temperature, and the precipitate was removed by filtration. The solution was de-ionized with Amberlite MB-3 resin, and evaporated to dryness. The residue was suspended in H_2O, and extracted with $CHCl_3$ for **24**, and with EtOAc for **33** and **42**. The organic layer was evaporated to dryness, and the residue crystallized, to give each α-L-arabinoside. In the case of **33**, the residue was purified by chromatography on silica gel by eluting with 1:1 C_6H_6–acetone; for physical constants, see ref. 3; yield, 60–80% from the aglycon alcohol.

A mixture of each α-L-arabinoside (1 g) and $ZnCl_2$ (0.8 g) in dry acetone (6.6 mL)[14] was stirred for 2–3 days at room temperature. The mixture was made neutral with 5% KOH in H_2O, and the precipitate was removed by filtration. The filtrate was diluted with H_2O, extracted with $CHCl_3$, and the extract evaporated to dryness, to give the respective 3,4-*O*-isopropylidene-α-L-arabinoside of the corresponding aglycon as a colorless syrup or powder in a yield of 70–85%.

A mixture of the isopropylidene acetal (3 mmol), $Hg(CN)_2$ (4.5 mmol), and the respective per-*O*-acetylglycosyl bromide (4.5 mmol) in dry toluene (40 mL) was similarly treated, to give the 2-*O*-glycosylated isopropylidene acetal. A solution of the product in H_2O (50 mL) containing oxalic acid (5 mmol) was boiled under reflux[15] for 30 min in the case of glycosides of **12, 32,** and **41**, and for 5 h in the case of those of **23**. The solution was made neutral with Amberlite MB-3 resin, and then evaporated to dryness. The residue crystallized directly, or after chromatography on silica gel by eluting with the following solvent systems to give each 2-*O*-glycosyl-α-L-arabinoside (yield: 50–77% from the corresponding 3,4-*O*-isopropylidene-α-L-arabinoside); $CHCl_3$–MeOH, 4:1 for **17**, 5:1 for **43** and **44**, and 20:3 for **27**, and C_6H_6–acetone, 1:2 for **35** and **36**, and 1:3 for **34**. The elemental analysis of each glycoside was consistent with the molecular formula expected; physical constants are listed in Table I.

Synthesis of 2-O-glycosyl-β-L-arabinopyranosides. — A solution of L-arabinose (5 g) in 1.5% dry HCl–MeOH was boiled under refluxed for 100 min, cooled, made neutral with Amberlite MB-3 resin, and evaporated to dryness. The residue crystallized from EtOH, to afford methyl β-L-arabinoside (**18**; 1 g).

The β-L-arabinosides (**29, 38,** and **45**) of **23, 32,** and **41** were prepared by the following procedure[13]. To a solution of L-arabinose tetraacetate (6.6 mmol) and an aglycon alcohol (6.6 mmol) in dry CH_2Cl_2 (60 mL) was added $SnCl_4$ (0.9 mL). The mixture was kept for 4 h at room temperature, and poured into a saturated, aqueous solution of $NaHCO_3$. The resulting mixture was extracted with $CHCl_3$, and the extract was washed with H_2O, and evaporated to dryness. The residue was deacetylated with 5% KOH in MeOH (60 mL) for 30 min at room temperature, and the solution de-ionized with Amberlite MB-3 resin, and evaporated to dryness. The crude product, which consisted of the α and β anomers, was separated by chromatography on silica gel by eluting with 15:1 $CHCl_3$–MeOH, to give the respective β-L-arabinoside; yield, 50–60%.

Each 2-*O*-glycosyl-β-L-arabinoside was prepared from the corresponding β-L-arabinoside through each 3,4-isopropylidene acetal by the procedure used for the synthesis of 2-*O*-glycosyl-α-L-arabinosides. The crude product was purified by crystallization directly, or after chromatography on silica gel by eluting with the following solvent systems: $CHCl_3$–MeOH, 5:1 for **46**, and 6:1 for **30, 31, 40,** and **47**. The elemental analysis of each 2-*O*-glycosylated β-L-arabinoside was consistent with the molecular formula expected; physical constants are listed in Table I. The yields from the corresponding 3,4-*O*-isopropylidene-β-L-arabinosides were 50–75%.

Selective deuteration of methyl 2-O-β-D-glucosyl-α-L-arabinoside (**14**). — A solution of **48** (200 mg) in D_2O (3 mL) was evaporated to dryness. To the residue were added D_2O (3 mL) and deuterated Raney nickel W-7 (3 mL, settled volume), prepared by the procedure reported [5], and the mixture was boiled under reflux for 10 h, cooled, the catalyst removed by filtration, and the filtrate made neutral with Amberlite MB-3 resin, and evaporated to dryness. The product was chromatographed on silica gel by eluting with $CHCl_3$–MeOH 7:1 to give methyl 2-*O*-β-D-glucosyl(2,3,4,6,6-$^2H_5$)-3,4-*O*-isopropylidene-α-L-arabinoside (**49**), which was treated with oxalic acid as already described, affording methyl 2-*O*-β-D-glucosyl(2,3,4,6,6-$^2H_5$)-α-L-arabinoside (**50**; 60 mg).

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