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^{13}C NMR STUDY OF α- AND β-ANOMERIC PAIRS OF D-MANNOPYRANOSIDES AND L-RHAMNOPYRANOSIDES

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Abstract—^{13}C NMR spectra for a variety of α and β-anomeric series of D-mannopyranosides and L-rhamnopyranosides are presented and analyzed in comparison with those of D-glucopyranosides. The results obtained in the present study are valuable for the structure studies of plant-glycosides as well as carbohydrates, especially for determination of anomeric configurations of mannosides and rhamnosides which has been extremely difficult by other classical techniques.

THE application of ^{13}C NMR spectroscopy to plant-glycosides have been investigated recently[1-3] via carbon resonance displacements of both sugar and aglycone moieties on glucoside-formation (glucosylation shift). Nevertheless, there have been few systematic studies on ^{13}C NMR spectra of mannosides (C-2' epimers of corresponding glucosides) and rhamnosides, mainly because of the difficulties encountered during the preparation of β-anomeric series of mannosides and rhamnosides. We prepared some of β-D-mannopyranosides and published a preliminary report of their ^{13}C NMR spectra.[2] In order to obtain more information about the influences of C-2' configuration of sugar residue on this glycosylation shift, we prepared α- and β-anomeric pairs of D-mannopyranosides and L-rhamnopyranosides and the present paper reports the D-mannosylation and L-rhamnosylation shifts in comparison with the D-glucosylation shift.

EXPERIMENTAL

Materials. Glycosides of MeOH (**1**), i.e. methyl α- and β-D-glucosides, methyl α-D-mannoside and methyl α-L-rhamnoside were commercially available. α-D-Mannosides of propyl alcohol (**2**), isopropyl alcohol (**3**), *trans*-4- *t*-butylcyclohexanol (**4**), *l*-menthol ((−)-**5**), *d*-menthol ((+)-**5**), *t*-BuOH (**6**), 5α-cholestan-3β-ol (**7**) and dammar-24-en-3β,20(*R*)-diol (**8**, 3-O-D-mannoside) and β-D-mannosides of **1**–**8** were prepared according to the procedure used for the synthesis of D-mannopyranosyl-oligosaccharide by Bebault *et al.*[4]

α-L-Rhamnosides of **2**–**8** were synthesized by condensation of α-acetobromorhamnose with an aglycone alcohol in MeCN with $Hg(CN)_2$ followed by saponofication of acetyl groups.[5]

General procedure. The synthesis of β-L-rhamnosides is not well documented in the literature. The present authors prepared β-L-rhamnosides of **1**–**7** by condensation of 4-O-carboethoxy-2,3-O-carbonyl-α-L-rhamnosyl bromide (**9**) with an aglycone alcohol in $CHCl_3$ with Ag_2O as the condensing agent followed by decarbonylation and decarboethoxylation. Reaction of excess alcohol with **9** in MeCN in the presence of $Hg(CN)_2$ also yielded mainly β-L-rhamnosides, while condensation of an equivalent amount of an alcohol with **9** under similar condition yielded the α-anomer. The same result was observed in the syntheses of D-mannosides mentioned above.

α- and β-L-Rhamnosides of *p*-nitrophenol (**10**) were prepared by a modification of the procedures used for the syntheses of the corresponding α-[6] and β-D-mannosides.[7]

β-D-Glucosides of **2**–**8** were prepared by the usual Koenigs–Knorr method. α-D-Glucosides of **2**–**6** were synthesized by condensation of an aglycone alcohol with 3,4,6-tri-O-acetyl-β-D-glucosyl chloride with $Hg(CN)_2$ in MeCN followed by deacetylation.[8]

The experimental details of these syntheses will be reported elsewhere.

NMR spectral measurements. Spectra were taken on JEOL JNM-PFT-100 NMR spectrometer at 25° in C_5D_5N with the concentration 0.06–2.0 m at 25.15 MHz for ^{13}C and 100 MHz for ^{1}H. Proton-decoupled FT measurement— Spectral width: 4 KHz, pulse flipping angle: 90°, acquisition time: 0.4 sec, number of data points: 4096, transient time: 1–2 sec, number of transient: 700–6000. Condition of $^1J_{C-H}$ measurement by gated decoupling— Spectral width: 4 KHz, pulse flipping angle: 90°, acquisition time: 0.4 sec, number of data points: 4096, transient time: 1–2 sec, number of transient: 2000–40000, computer limited resolution: 2 Hz.

RESULTS AND DISCUSSION

The glycosylation shifts are discussed in comparison with the results for D-glucosides.[2]

Glycosylation shifts of sugar moieties (Table 1). The assignment of D-mannopyranosyl and L-rhamnopyranosyl carbon resonances were referred to the reported data for α- and β-D-mannoses and -L-rhamnoses, methyl α-D-mannoside and methyl α-L-rhamnoside in D_2O.[9] It has been reported that in spectra of β-D-glucosides other than those of some of the hindered alcohols such as (−)-**5** (*vide infra*), carbon signals of C-1' (anomeric carbon), −2', −3' and −5' appear at remarkably lower field than those of the corresponding α-anomers.[9] In contrast, only slight differences in the carbon chemical shifts of C-1' and −2' were found between α- and β-anomers of D-mannosides and L-rhamnosides except for those of (+)- and (−)-**5** (*vide infra*), while significant downfield shifts of C-3' and −5' signals from the β-anomers to the corresponding α-anomers were still observed.

With regard to the influence of structures of aglycone alcohols on the glycosylation shifts, C-1' signals of each anomeric series are generally deshielded in the decreasing order of methyl, primary, secondary (unhindered) and tertiary alcoholic D-mannosides and L-rhamnosides as already found in the series of D-glucosides,[2,3] while C-1' signals of α- and β-L-rhamnosides of **10** appear at similar positions to those of the unhindered secondary alcohols. Sugar carbon signals other than C-1' were found to be only slightly affected by the structure change of algycones, indicating that the glycosides of each

Table 1. ^{13}C chemical shifts and anomeric ^{1}H chemical shifts of sugar moieties

	D-gluco-pyranose		D-glucopyranoside of													
			1		2		3		4		(-)-5		(+)-5		6	7
	α	β	α	β	α	β	α	β	α	β	α	β	α	β	β	β
H-1'			5.10	4.64	5.26	4.74	5.31	4.74	5.42	4.92	5.28	4.46	5.53	4.44	5.46	4.74	5.02
C-1'	94.1	98.8	101.3	105.5	100.2	104.4	98.4	102.4	98.5	102.4	102.1	101.5	96.1	105.9	94.7	98.9	102.0
2'	74.4	76.8	74.0*	74.9	74.2*	75.0	74.0*	74.9	74.2*	74.9	74.0	75.2	74.2*	75.6	73.7	75.3	75.2
3'	75.3	78.4*	75.3	78.3	75.4	78.2	75.3	78.0*	75.3	78.0	75.0	78.0*	75.3	78.0*	75.4	78.7	78.3*
4'	72.5	72.0	72.1	71.6	72.3	71.5	72.3	71.5	72.5	71.4	72.4	72.2	72.3	71.8	72.5	71.8	71.7
5'	73.5	78.6*	73.8*	78.3	73.9*	78.2	73.6*	78.2*	73.8*	78.0	74.0	78.7*	73.6*	78.5*	73.7	78.7	78.4*
6'	63.2	63.0	62.8	62.7	62.9	62.7	62.9	62.7	63.1	62.6	62.9	63.3	63.0	62.9	63.1	62.9	62.8

	D-manno-pyranose		D-mannopyranoside of																	
			1		2		3		4		(-)-5		(+)-5		6		7		8	
	α	β	α	β	α	β	α	β	α	β	α	β	α	β	α	β	α	β	α	β
H-1'			5.12	4.60	5.28	4.72	5.40	4.88	5.52	5.02	5.36	4.92	5.62	4.88	5.56	5.00	5.52	5.00	5.52	4.88
C-1'	95.7	95.7	102.6	102.7	101.2	101.8	99.2	99.2	99.5	99.4	103.7	98.4	97.1	103.6	96.1	96.2	99.5	99.2	97.5	104.2
2'	73.0*	73.0	72.0*	71.9	71.9*	72.2	72.4*	72.5	72.6*	72.8	72.3*	73.0	72.8*	72.5	72.8*	73.7	72.8*	73.0	72.8*	72.3
3'	72.5*	75.6	73.0*	75.5	72.8*	75.7	72.8*	75.5	72.9*	75.8	72.9*	75.9	72.9*	75.9	73.4*	76.0	73.0*	76.0	73.0*	75.9
4'	69.2	68.6	69.0	68.8	68.9	69.1	69.0	68.7	69.3	69.1	69.2	69.5	68.9	69.1	69.3	69.0	69.5	69.2	69.0	69.3
5'	74.2	78.3	75.1	78.7	74.8	78.8	74.9	78.4	75.2	78.9	75.2	78.4	75.3	78.7	74.5	78.4	75.3	78.9	75.5	78.8
6'	63.1	63.1	63.1	62.8	62.9	63.0	62.9	62.7	63.4	63.1	63.2	63.4	63.1	63.1	63.1	63.0	63.4	63.1	63.1	63.2

	L-rhamno-pyranose		L-rhamnopyranoside of																		
			1		2		3		4		(-)-5		(+)-5		6		7		8	10	
	α	β[a]	α	β	α	β	α	β	α	β	α	β	α	β	α	β	α	β	α	α	β
H-1'			5.04	4.55	5.02	4.60	5.20	4.72	5.18	4.93	5.30	4.90	5.23	4.83	5.92	4.87	5.44	4.94	5.20	6.08	5.58
C-1'	95.8	(94.6)	102.6	102.6	101.1	101.3	99.2	99.5	99.1	99.3	97.2	103.1	103.0	98.0	95.7	95.6	99.3	99.2	102.4	99.9	98.6
2'	73.3*	(72.4)	72.7*	72.1	72.6*	72.1	72.5	72.8	72.3	72.8	72.6*	72.3	72.3*	73.1	73.2*	72.6	72.8	72.8	72.7*	71.3*	71.7
3'	72.5*	(73.8)	72.1*	75.3	72.0*	75.1	72.5	75.6	72.3	75.5	72.3*	75.5	71.9*	75.6	72.4*	75.3	72.8	75.4	72.1*	72.2*	74.8
4'	74.2	(72.9)	73.8	73.7*	73.7	73.5*	73.9	73.9*	73.6	73.8*	73.2	73.6*	73.3	73.8*	73.9	73.4	74.1	73.6*	73.9	73.3	73.8*
5'	69.0	(73.1)	69.5	73.4*	69.3	73.2*	69.5	73.3*	69.3	73.2*	69.8	73.2*	69.3	73.1*	68.9	73.4	69.7	73.1*	69.5	71.3	73.2*
6'	18.8	(18.0)	18.6	18.5	18.4	18.3	18.4	18.6	18.2	18.6	18.2	18.6	17.9	18.3	18.2	18.6	18.6	18.6	18.3	18.3	18.4

*These assignments may be reversed in each vertical column.
[a]Measured in D_2O (in parentheses), see reference 9.

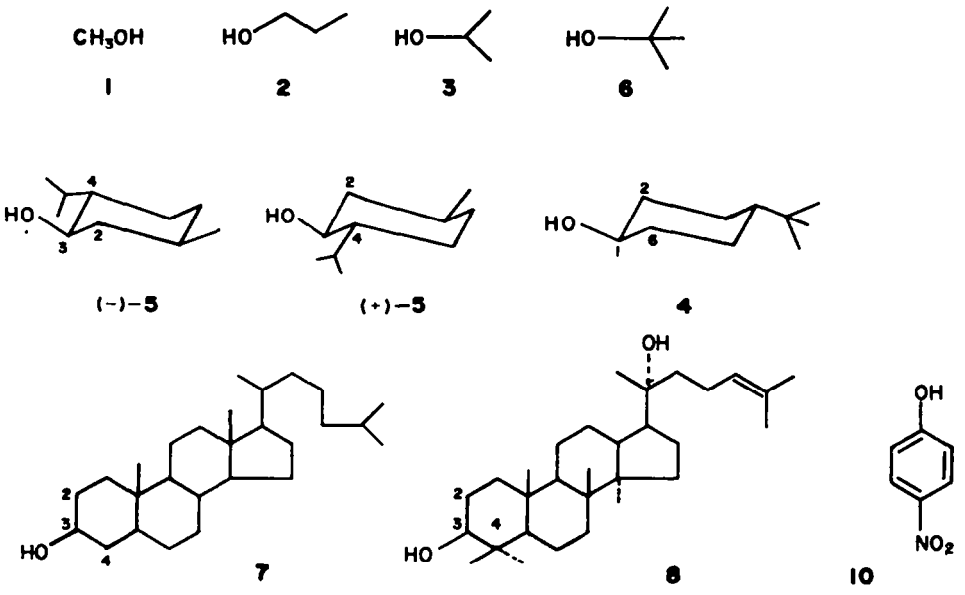


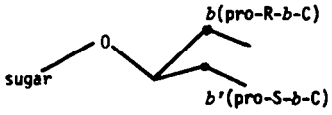
Table 2. ^{13}C chemical shifts and glycosylation shifts ($\Delta\delta$ in ppm, in parentheses)[b] of aglycone moieties (1).

	α-D-glc[c]	β-D-glc[c]	α-D-man[c]	β-D-man[c]	α-L-rha[c]	β-L-rha[c]
	$\delta_{a\text{-}C}$ ($\Delta\delta_{a\text{-}C}$)	$\delta_{a\text{-}C}$ ($\Delta\delta_{a\text{-}C}$)	$\delta_{a\text{-}C}$ ($\Delta\delta_{a\text{-}C}$)	$\delta_{a\text{-}C}$ ($\Delta\delta_{a\text{-}C}$)	$\delta_{a\text{-}C}$ ($\Delta\delta_{a\text{-}C}$)	$\delta_{a\text{-}C}$ ($\Delta\delta_{a\text{-}C}$)
1	54.9 (+5.5)	56.7 (+7.3)	54.4 (+5.0)	56.5 (+7.1)	54.4 (+5.0)	56.4 (+7.0)
2	69.6 (+5.7)	71.2 (+7.3)	68.9 (+5.0)	71.0 (+7.1)	69.0 (+5.1)	70.9 (+7.0)
3	69.7 (+6.3)	71.0 (+7.6)	68.5 (+5.1)	70.2 (+6.8)	68.6 (+5.2)	70.3 (+6.9)
4	76.9 (+6.6)	77.7 (+7.4)	75.7 (+5.4)	77.1 (+6.8)	75.6 (+5.3)	77.2 (+6.9)
6	74.7 (+6.9)	75.3 (+7.5)	74.5 (+6.7)	75.3 (+7.5)	74.2 (+6.4)	75.0 (+7.2)
7		77.2 (+6.7)	75.9 (+5.4)	76.9 (+6.4)	75.7 (+5.2)	77.3 (+6.8)
10					162.0 (-3.4)	162.9 (-2.5)

[b] $\Delta\delta$: δ (glycoside) − δ (aglycone).
[c] D-glc, D-man and L-rha stand for D-glucopyranoside, D-mannopyranoside and L-rhamnopyranoside, respectively.

Table 3. ^{13}C chemical shifts and glycosylation shifts of aglycone moieties (2)

			$\delta_{b\text{-}C}$ ($\Delta\delta_{b\text{-}C}$)	$\delta_{b'\text{-}C}$($\Delta\delta_{b'\text{-}C}$)			$\delta_{b\text{-}C}$ ($\Delta\delta_{b\text{-}C}$)	$\delta_{b'\text{-}C}$($\Delta\delta_{b'\text{-}C}$)
	α-D-glc	S[d]	23.1 (-3.5)		β-D-glc	R[d]	23.3 (-3.3)	
2	α-D-man	S	23.0 (-3.6)		β-D-man	R	23.3 (-3.3)	
	β-L-rha	S	23.2 (-3.4)		α-L-rha	R	23.1 (-3.5)	
	α-D-glc	S	21.7 (-3.9)	23.6 (-2.0)	β-D-glc	R	23.8 (-1.8)	22.0 (-3.6)
3	α-D-man	S	22.4 (-3.2)	23.5 (-2.1)	β-D-man	R	23.7 (-1.9)	21.3 (-4.3)
	β-L-rha	S	22.0 (-3.6)	23.9 (-1.7)	α-L-rha	R	23.5 (-2.1)	21.5 (-4.1)
	α-D-glc	S	32.5 (-4.2)	34.3 (-2.4)	β-D-glc	R	34.5 (-2.2)	32.8 (-3.9)
4	α-D-man	S	32.4 (-4.3)	34.2 (-2.5)	β-D-man	R	34.5 (-2.2)	32.7 (-4.0)
	β-L-rha	S	32.8 (-3.9)	34.6 (-2.1)	α-L-rha	R	34.1 (-2.6)	32.2 (-4.5)
	α-D-glc	S			β-D-glc	R	29.9 (-2.5)	34.8 (-4.4)
7	α-D-man	S	28.3 (-4.1)	36.5 (-2.7)	β-D-man	R	29.9 (-2.5)	34.8 (-4.4)
	β-L-rha	S	28.3 (-4.1)	36.5 (-2.7)	α-L-rha	R	29.7 (-2.7)	34.6 (-4.6)
	α-D-glc	S	28.8 (-2.8)		β-D-glc	R	29.0 (-2.6)	
6	α-D-man	S	28.7 (-2.9)		β-D-man	R	28.8 (-2.8)	
	β-L-rha	S	28.7 (-2.9)		α-L-rha	R	28.6 (-3.0)	



[d] Chirality of anomeric carbon as a free form.

anomeric series have a similar ring-conformation of the sugar residue regardless of the structures of algycone alcohols.

Glycosylation shifts of aglycone carbon signals (Tables 2 and 3). Signals due to a carbinol carbon (tentatively abbreviated as *a*-C) are generally deshielded by *ca.* +7.0 ppm on β-D-mannosylation or β-L-rhamnosylation as in the case of β-D-glucosylation,[2,3] whereas it is significant that the magnitude of the downfield shift of *a*-C resonances on α-glycosylation is somewhat smaller than that on β-glycoslylation, especially on α-D-mannosylation and α-L-rhamnosylation; i.e. by *ca.* +5.2 ppm for methyl, primary and secondary (unhindered) alcohols and by +6.7 ~ +6.4 ppm for *t*-BuOH (**6**). In contrast to aliphatic alcohols, the phenolic carbon signal is shielded on glycosylation,[10] i.e. C-1 of **10** is shielded by −3.4 and −2.5 ppm on α- and β-L-rhamnosylation, respectively.

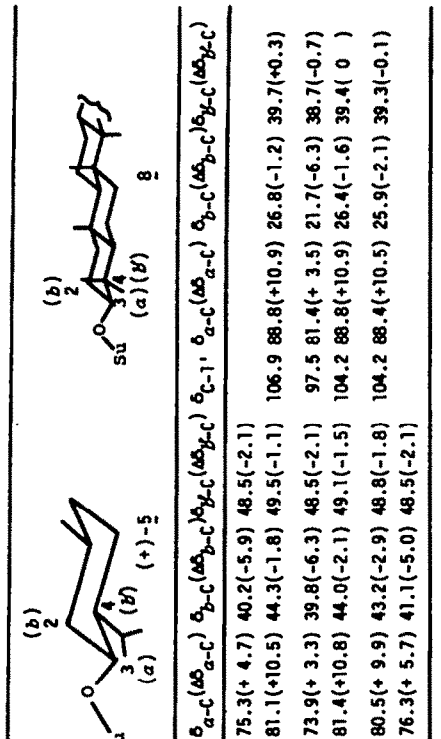
In general, signals due to the vicinal carbons to *a*-C (tentatively abbreviated as *b*-C) are shielded on glucosylation and the absolute values of the upfield shifts of two equivalent methyls or methylenes of secondary alcohols, **3**, **4**, and **7** are very different from each other, depending on the stereochemical relation between *a*-C and C-1'.[1-3] This novel effect was further substantiated in the present study of mannosylation and rhamnosylation shifts of **3**, **4** and **7**, being summarized as follows. On β-D-mannosylation and α-L-rhamnosylation as well as β-D-glucosylation (chirality of each C-1' is R as a free form), pro-S-*b*-C is always more shielded than pro-R-*b*-C, while on α-D-mannosylation and β-L-rhamnosylation as well as α-D-glucosylation (chirality of each C-1' is *S* as a free form), pro-R-*b*-C is more shielded than pro-S-*b*-C.

Glycosylation shifts for relatively hindered alcohols (Table 4). As already reported for D-glucosides, the glucosylation shifts for relatively hindered alcohols such as (−)-**5**, (+)-**5**, and 3β-, 6α- and 12β-hydroxyl groups of dammarane type triterpenes differ from those of the above mentioned less hindered alcohols owing to a change in the conformation of the glycoside-linkage.[1-3] The spectra of D-mannosides and L-rhamnosides of (−)- and (+)-**5** in the present study further revealed that this characteristic glycosylation shift evidently depends upon the stereochemical combination of C-1' and *a*-C but is almost unaffected by the configuration of C-2' of the sugar residue. For β-D-mannoside, α-L-rhamnoside and β-D-glucoside of (+)-**5** (chirality of C-3(*a*-C):S) as well as α-D-mannoside, β-L-rhamnoside and α-D-glucoside of (−)-**5** (chirality of C-3(*a*-C):R), signals due to both C-3 and C-1' are more deshielded than those of the corresponding glycosides of the less hindered alcohols such as **4**. To the contrary, signals of C-3 and C-1' of β-D-mannoside, α-L-rhamnoside and β-D-glucoside of (−)-**5** as well as those of α-D-mannoside, β-L-rhamnoside and α-D-glucoside of (+)-**5** were found to be somewhat less deshielded than those of the corresponding glycoside of **4** etc. It should be noted that this decrease of the downfield shift is more evident in the case of α-glycoside-series than the corresponding β-anomeric series.

The magnitude of *b*-C shielding by D-mannosylation and L-rhamnosylation, depends on the stereochemical combination of *a*-C and C-1' as was also observed in the case of the D-glucosylation reported previously.[2,3]

A similar glycosylation shift was also observed in the spectra of α-D-mannoside and α-L-rhamnoside of the 3β-OH group of the triterpene (**7**). Further studies on the glycosylation shifts for more complex hindered alcohols are under progress.

Table 4. ^{13}C chemical shifts and glycosylation shifts of aglycone moieties (3)



	$\delta_{C-1'}$	$\delta_{a-C}(\Delta\delta_{a-C'})$	$\delta_{b-C}(\Delta\delta_{b-C'})$	$\delta_{b-C}(\Delta\delta_{b-C'})$	$\delta_{C-1'}$	$\delta_{a-C}(\Delta\delta_{a-C'})$	$\delta_{b-C}(\Delta\delta_{b-C'})$	$\delta_{b-C}(\Delta\delta_{b-C'})$	$\delta_{C-1'}$	$\delta_{a-C}(\Delta\delta_{a-C'})$	$\delta_{b-C}(\Delta\delta_{b-C'})$	$\delta_{b-C}(\Delta\delta_{b-C'})$
α-D-glc S	102.1	81.0(+10.4)	49.3(−1.3)	43.5(−2.6)	96.1	75.3(+ 4.7)	40.2(−5.9)	48.5(−2.1)				
β-D-glc R	101.5	77.0(+ 6.4)	48.5(−2.1)	41.2(−4.9)	105.9	81.1(+10.5)	44.3(−1.8)	49.5(−1.1)	106.9	88.8(+10.9)	26.8(−1.2)	39.7(+0.3)
α-D-man S	103.7	80.8(+10.2)	49.1(−1.5)	43.3(−2.8)	97.1	73.9(+ 3.3)	39.8(−6.3)	48.5(−2.1)	97.5	81.4(+ 3.5)	21.7(−6.3)	38.7(−0.7)
β-D-man R	98.4	76.4(+ 5.8)	48.5(−2.1)	41.1(−5.0)	103.6	81.4(+10.8)	44.0(−2.1)	49.1(−1.5)	104.2	88.8(+10.9)	26.4(−1.6)	39.4(0)
α-L-rha R	97.2	74.6(+ 4.0)	48.2(−2.4)	39.9(−6.2)	103.0	80.5(+ 9.9)	43.2(−2.9)	48.8(−1.8)	104.2	88.4(+10.5)	25.9(−2.1)	39.3(−0.1)
β-L-rha S	103.1	81.2(+10.6)	49.2(−1.4)	44.1(−2.0)	98.0	76.3(+ 5.7)	41.1(−5.0)	48.5(−2.1)				

Table 5. Molecular rotation differences (M_D) in MeOH

	α-D-glc			α-D-man			α-L-rha		
	$[M]_D^f$	$[M]_D^g$	M_D	$[M]_D^f$	$[M]_D^g$	M_D	$[M]_D^f$	$[M]_D^g$	M_D
1	+324°			+180°			-147°		
1[e]	+334°			+167°			-148°		
2	+268°	0°	+268°	+137°	0°	+137°	-153°	0°	-153°
3	+253°	0°	+253°	+132°	0°	+132°	-176°	0°	-176°
4	+265°	0°	+265°	+141°	0°	+141°	-223°	0°	-223°
6	+301°	0°	+301°	+161°	0°	+161°	-131°	0°	-131°
7[e]				+375°	+79°	+296°	-205°	+79°	-284°
(-)-5	+194°	-78°	+272°	- 85°	-78°	- 7°	-375°	-78°	-297°
(+)-5	+536°	+78°	+458°	+318°	+78°	+240°	- 10°	+78°	- 88°

	β-D-glc			β-D-man			β-L-rha		
	$[M]_D^f$	$[M]_D^g$	M_D	$[M]_D^f$	$[M]_D^g$	M_D	$[M]_D^f$	$[M]_D^g$	M_D
1	- 68°			-127°			+185°		
1[e]	- 60°			-146°			+182°		
2	- 81°	0°	- 81°	-112°	0°	-112°	+183°	0°	+183°
3	- 71°	0°	- 71°	-151°	0°	-151°	+176°	0°	+176°
4	- 41°	0°	- 41°	-129°	0°	-129°	+173°	0°	+173°
6	- 34°	0°	- 34°	- 79°	0°	- 79°	+131°	0°	+131°
7[e]	- 56°	+79°	-135°	- 65°	+79°	-144°	+381°	+79°	+302°
(-)-5	-227°	-78°	-149°	-332°	-78°	-254°	- 49°	-78°	+ 29°
(+)-5	+111°	+78°	+ 33°	+ 77°	+78°	- 1°	+308°	+78°	+230°

[e]Measured in C_5H_5N.
[f]Molecular rotation of glycoside.
[g]Molecular rotation of aglycone.

Determination of anomeric configuration of mannosides and rhamnosides. In the structure studies of mannosides and rhamnosides both of which have an axial 2'-OH group in their stable conformation, the coupling constant of the anomeric proton signal ($^3J_{H1'-H2'}$), is of no use for determination of their anomeric configuration, since anomeric proton signals of both series generally appear as a slightly broadened singlet. Instead, the configuration has been currently assigned by means of comparison of the molecular rotation difference, $M_D(=[M]_{D(\text{glycoside})}-[M]_{D(\text{aglycone})})$ with that of the corresponding methyl glycoside.[11] Having the anomeric pairs of D-mannosides and L-rhamnosides, the molecular rotation of each glycoside was determined and compared as shown in Table 5. The M_D values of D-mannosides and L-rhamnosides of (-)- and (+)-5, the glycosylation shifts of which are evidently anomalous, were found to be very far from the expected values. It should be noted that M_D of α-D-mannoside of (-)-5 may lead to the erroneous assignment of its anomeric configuration, if the M_D value of its anomeric counterpart is unknown!

It has been reported that the direct bonded C–H coupling constant of C-1' signals ($^1J_{C1'-H1'}$) of hexopyranoses and pentopyranoses are characteristic of the anomeric configuration; $^1J_{C1'-H1'}$ is consistently *ca.* 10 Hz smaller when H-1' is axial than when it is equatorial.[12] In alcoholic and phenolic D-mannosides and L-rhamnosides, $^1J_{C1'-H1'}$ was found to depend mainly upon the anomeric structure regardless of variety of aglycones. This was promising for the determination of the anomeric configuration with the aid of chemical shift differences of C-3' and C-5' as well as the consideration of the glycosylation shifts mentioned above.

Finally, it was demonstrated that the anomeric proton signals of α-D-mannosides and α-L-rhamnosides appear always at lower field (δ 5.02–5.92) than those of the corresponding β-anomers (δ 4.55–4.93). This difference is also helpful in the differentiation of the anomeric structure, though occasional deviation by the change of aglycone-structures or of the condition of the measurement (temperature, concentration and solvent) was observed.

Table 6. Coupling constants: $^1J_{C1-H1}$ (Hz)

	D-man		L-rha	
	α	β	α	β
1	166	156	168	158
2	166	155	166	152
3	166	154	166	154
4	164	155	168	154
(-)-5	166	154	168	152
(+)-5	164	154	166	154
6	165	153	164	152
7	166	156	167	158
8	166	156		
10			168	158

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