Carbohydrate Research, 47 (1976) 158–163

Note

^{1}H-N.m.r. study of L-rhamnose, methyl α-L-rhamnopyranoside, and 4-*O*-β-D-galactopyranosyl-L-rhamnose in deuterium oxide

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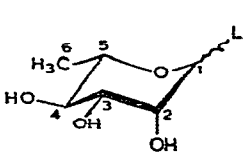
(Received August 20th, 1975; accepted for publication, October 6th, 1975)

Complete analyses of the ^{1}H-n.m.r. spectra of α-L-rhamnose (**1**), β-L-rhamnose (**2**), methyl α-L-rhamnopyranoside (**3**), and 4-*O*-β-D-galactopyranosyl-L-rhamnose (**4**) have been achieved at 300 MHz. The relative shifts for these monosaccharides (relative to those of β-D-glucopyranose), when compared with the general increment rules for aldohexopyranoses[1], reveal an appreciable deviation for H-4. The shifts for **4** are compared with the results for glucose disaccharides[2]. The conformations are *1C*(L) for the rhamnose moieties.

In a previous paper[1], we refined and extended the increment rules[3] which followed from parameters obtained in the 300-MHz ^{1}H-n.m.r. spectra of D-glucose, D-mannose, D-galactose, and their methyl glycosides. We have now obtained the ^{1}H-n.m.r. data of L-rhamnose (**1**,**2**) and methyl α-L-rhamnopyranoside (**3**) and propose increment rules for 6-deoxy derivatives. Previously, we have also modified the rules for the glucose disaccharides[2]. It now seems possible to extend these rules to 4-*O*-β-D-galactopyranosyl-L-rhamnose[4].



1 L = OH–ax (α)
2 L = OH–eq (β)
3 L = OCH_3–ax (α)

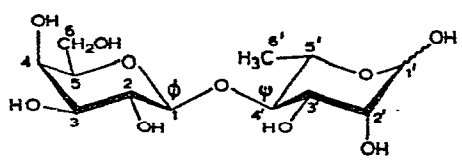


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TABLE I

CHEMICAL SHIFTS FOR COMPOUNDS 1–4, α- AND β-D-MANNOPYRANOSE, AND METHYL α-D-MANNOPYRANOSIDE[a,b]

	H-1	*H-2*	*H-3*	*H-4*	*H-5*	*Me-6*	*OMe*	*H-6A*	*H-6B*
α-L-Rhamnopyranose (1)	5.11	3.92	3.80	3.44	3.87	1.28	—	—	—
	+0.46	+0.65	+0.35	+0.09	+0.45				
α-D-Mannopyranose	5.18	3.92	3.85	3.66	3.82	—	—	3.88	3.76
	+0.53	+0.65	+0.40	+0.31	+0.40				
β-L-Rhamnopyranose (2)	4.86	3.94	3.60	3.36	3.40	1.29	—	—	—
	+0.21	+0.67	+0.15	+0.01	−0.02				
β-D-Mannopyranose	4.90	3.94	3.66	3.58	3.37	—	—	3.91	3.73
	+0.25	+0.67	+0.21	+0.23	−0.05				
Methyl α-L-rhamnopyranoside (3)	4.70	3.93	3.71	3.44	3.64	1.30	3.40	—	—
	+0.05	+0.66	+0.66	+0.09	+0.22				
Methyl α-D-mannopyranoside	4.77	3.94	3.77	3.67	3.62	—	3.42	3.91	3.76
	+0.12	+0.67	+0.32	+0.32	+0.20				
O-β-D-Galactopyranosyl-(1→4)-L-rhamnopyranose (4)									
α-isomer									
β-D-galactopyranosyl unit	4.66	3.55	3.67	3.93	3.69	—	—	3.79	3.75
	+0.01	+0.28	+0.22	+0.57	+0.27			—	—
α-L-rhamnopyranose unit	5.11	3.93	4.02	3.70	3.95	1.35			
	+0.46	+0.66	+0.57	+0.35	+0.53				
	(—)	(+0.01)	(+0.22)	(+0.26)	(+0.08)				
β-isomer									
β-D-galactopyranosyl unit	4.66	3.54	3.67	3.93	3.69	—	—	3.79	3.75
	+0.01	+0.27	+0.22	+0.57	+0.27				
β-L-rhamnopyranose unit	4.88	3.91	3.84	3.64	3.50	1.37	—	—	—
	+0.23	+0.64	+0.39	+0.29	+0.08				
	(+0.02)	(−0.03)	(+0.24)	(+0.28)	(+0.10)				

[a]Values in the second row are the increments obtained by comparison with β-D-glucopyranose. [b]Values in brackets are increments relative to corresponding monosaccharide.

TABLE II

COUPLING CONSTANTS OF THE TITLE COMPOUNDS (IN Hz)

	$^3J(1,2)$	$^3J(2,3)$	$^3J(3,4$	$^3J(4,5)$	$^3J(5,6A)$	$^3J(5,6B)$	$^2J(6A,6B)$	$^3J(5,CH_3\text{-}6)$
α-L-Rhamnopyranose	1.8	3.5	9.6	9.6	—	—	—	6.3
β-L-Rhamnopyranose	1.1	3.5	9.5	9.6	—	—	—	6.2
Methyl α-L-rhamnopyranoside	1.7	3.5	9.6	9.6	—	—	—	6.2
4-*O*-β-D-Galactosyl-L-rhamnopyranose								
β-D-galactopyranosyl unit	7.8	10.0	3.6	0.8	8.7[a]	3.3[a]	−11.6	—
α-L-rhamnopyranose unit	1.9	3.5	9.4	9.5	—	—	—	6.2
β-D-galactopyranosyl unit	7.8	10.0	3.6	0.8	8.7[a]	3.3[a]	−11.6	—
β-L-rhamnopyranose unit	1.1	3.5	9.5	9.5	—	—	—	6.0

[a]The apparent coupling constants are $^3J(5,6A) = 8$ Hz and $^3J(5,6B) = 4$ Hz.

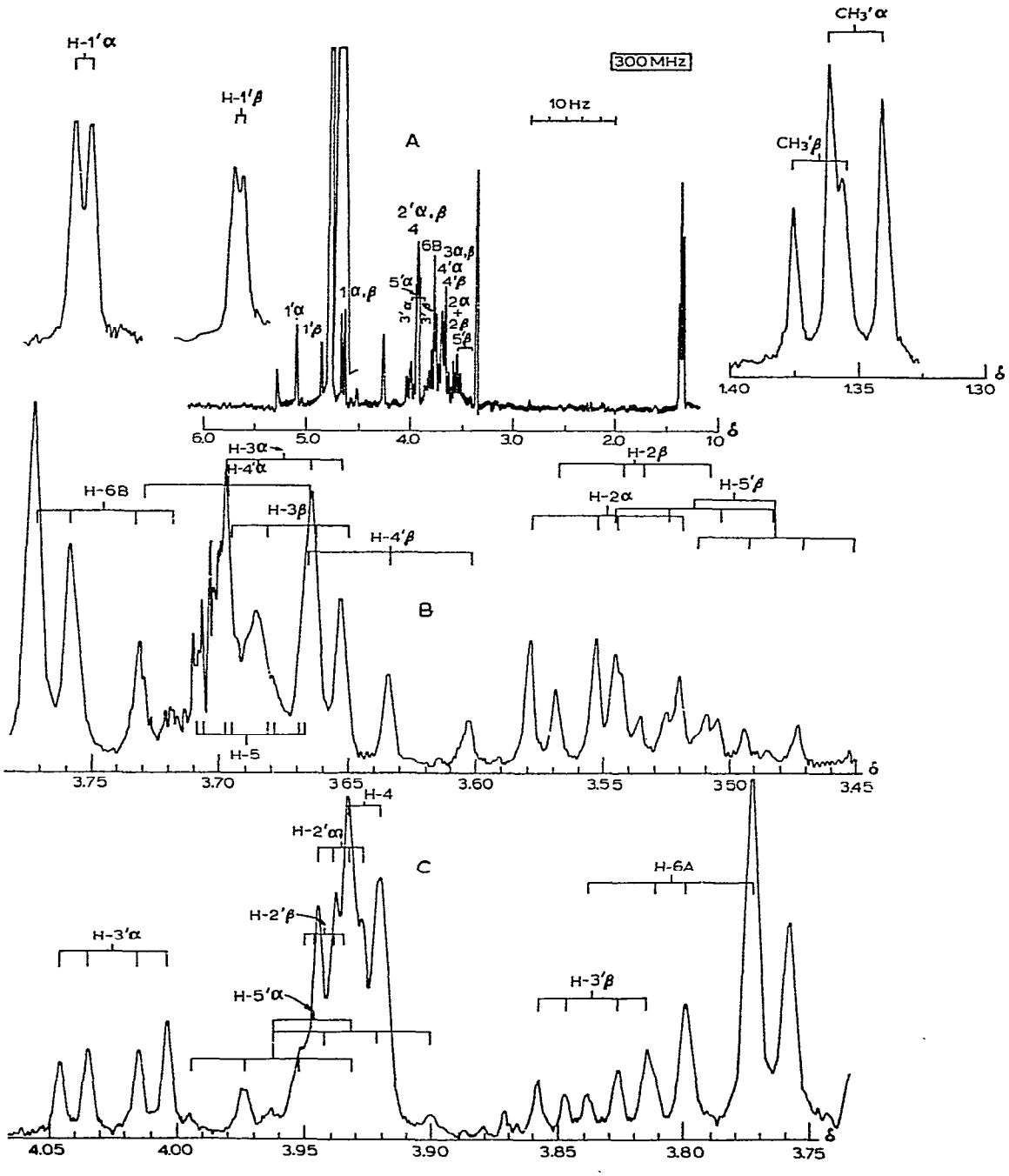

Fig. 1. ^{1}H-N.m.r. spectrum at 300 MHz of *O*-β-D-galactopyranosyl-(1→4)-L-rhamnose in D_2O: *A*, spectrum at 2500-Hz sweepwidth, and details at 100-Hz sweepwidth of Me-6′ and both anomeric protons; *B*, detail at 100-Hz sweepwidth of the region δ 3.45–3.75; *C*, detail at 100-Hz sweepwidth of the region δ 3.75–4.05.

The ^{1}H-n.m.r. parameters of the title compounds are given in Tables I and II. For purposes of comparison, we have included the chemical shifts of the D-mannopyranoses and methyl α-D-mannopyranoside[1]. The coupling constants were extracted from the homo-INDOR spectra and refined by computer-aided simulation procedures with a SIMEQ 16/II programme. The ^{1}H-n.m.r. spectrum of **4** is shown in Fig. 1. The coupling constants show that all the L-rhamnopyranose moieties adopt the *1C*(L) conformation [the β-D-galactopyranosyl rings having the *C1*(D) conformation].

The resonances of the ring protons have been verified by successive homo-INDOR experiments starting from H-1 for the β-D-galactopyranosyl moiety and from the Me-6 doublet for the rhamnopyranoses and the rhamnopyranosyl moieties. Considering α-L-rhamnopyranose (**1**), β-L-rhamnopyranose (**2**), and methyl α-L-rhamnopyranoside (**3**), the shift increments for H-1, H-2, H-3, and H-5 (the chemical shifts of the ring protons of β-D-glucopyranose are the reference values) obey the increment rules as derived for aldohexopyranoses[1] within a range of 0.05 p.p.m. This can also be concluded by comparing the chemical shifts for **1**, **2**, and **3** with those for α- and β-D-mannopyranose and methyl α-D-mannopyranoside (see Table I). It must be noted that the signals for H-1 and H-3 are found at −0.04/−0.07 p.p.m. to higher field (we have introduced[1] a + sign for a downfield shift, in accordance with shift studies on other compounds in our laboratory[5]) than for the D-mannopyranoses and methyl α-D-mannopyranoside, but H-5 is shifted +0.02/+0.05 p.p.m. towards lower field. This must reflect the small change in the nature of the C-6 substituent. It is noteworthy that H-5 in the methyl glycoside **3** is found at −0.23 p.p.m. (higher field) than for the corresponding free sugar (**1**). This trend is generally found in methyl α-D-glycosides[1]. The signals for H-4 in the rhamnoses are observed at −0.22/−0.23 p.p.m. higher field than in the mannoses. This implicates a diagnostic deviation from the aldohexopyranoses and their methyl glycosides. The findings agree with those observed in the permethylated compounds[10].

All the corresponding protons of the non-reducing β-D-galactopyranosyl moieties, except H-2, have the same shift values in both the α- and β-isomers of 4-*O*-β-D-galactopyranosyl-L-rhamnose. The H-5 and H-6 protons of the β-D-galactopyranosyl moiety form an ABMX spin-system (X is H-4) with the same patterns as found in methyl β-D-galactopyranoside[1], lactose[6], lactulose[7], and 2′-deoxylactose[8]. As found in other (1→4)-linked disaccharides[2,6–8], the non-reducing ring has little influence on the chemical shifts of the anomeric protons (of the reducing moieties), but H-3′,4′,5′ (the ring protons on, and vicinal to, the link) suffer a downfield shift of +0.08/+0.3 p.p.m., a behaviour also found in the glucose disaccharides[2]. The effect is relatively small for H-5′. This may be related to the conformational behaviour around the glycosidic link, defined[9] by ϕ and ψ. The signal for H-1′ (the glycosidic proton of the non-reducing ring) is found at δ 4.66, *i.e.*, at +0.24 p.p.m. to lower field than the corresponding value in lactose[6], where the shifts of the other protons in this ring agree very well with those of lactose.

EXPERIMENTAL

The spectra were recorded on a Varian HR 300-MHz instrument, for 10% solutions in D_2O with TSP [sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propionate] as internal standard. L-Rhamnose and methyl α-L-rhamnopyranoside were supplied by Professor C. K. De Bruyne, and 4-*O*-β-D-galactopyranosyl-L-rhamnose by Dr. G. M. Bebault.

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