Carbohydrate Research, 150 (1986) 23–33
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ROTATIONAL ISOMERISM ABOUT THE C-5–C-6 BOND OF 6-*O*-TRITYL DERIVATIVES OF ALDOHEXOPYRANOSES, AND OF ANALOGS OF D-GALACTOPYRANOSE MODIFIED AT C-4*

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(Received October 28th, 1985; accepted for publication, December 11th, 1985)

ABSTRACT

Differences in rotational isomerism about the C-5–C-6 bond of 4-*O*-acetyl-6-*O*-tritylaldohexopyranose derivatives in the *gluco* and *manno*, as compared with the *galacto*, series are reflected in different contributions towards diamagnetic shielding of the acetoxyl protons, and rotatory characteristics of the compounds. Among 4-deoxy-4-halogeno analogs of methyl β-D-galactopyranoside, rotational isomerism varies little, based on H-5,6,6′ coupling, whereas the 6,6′-protons exhibit enhanced anisochronism as the mass of the halogen atom increases. The identification of resonance signals due to H-6_R and H-6_S, respectively, provides a basis for the consideration of these findings.

INTRODUCTION

The fact that the 4-acetoxyl protons of methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**1**) resonate 0.2–0.3 p.p.m. upfield of the 2- and 3-acetoxyl protons has been attributed[1] to regioselective, diamagnetic shielding by the triphenylmethoxy group. Judging from the spectra of several related compounds, the pronounced shielding found for **1** is orientation-dependent. This feature is dealt with here, as also are associated observations on rotational isomerism about the C-5–C-6 bonds of aldohexopyranose derivatives, particularly some in the *galacto* series.

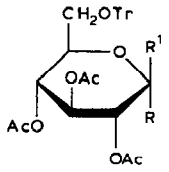
RESULTS AND DISCUSSION

Data analogous to those cited for **1** are found (Table I) in the p.m.r. spectrum of each of several other 6-*O*-trityl derivatives (**2–8**) of D-glucopyranose, as well as of D-mannopyranose (**9** and **10**), in that one of the acetoxyl signals is shifted upfield of the others by at least 0.2 p.p.m. Moreover, as the only *O*-acetyl group in

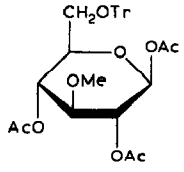
*Dedicated to Professor N. K. Kochetkov.

0008-6215/86/$ 03.50

common is that at O-4, it is most likely that this substituent, in each instance, exhibits enhanced shielding due to the neighboring *O*-trityl group. This has been confirmed for **2** specifically, as already demonstrated[2] for its α anomer (**1**), by a synthesis of the 4-(trideuterioacetyl) analog (**2a**) of **2**. Thus, the n.m.r. spectrum of **2a** differs from that of **2** only in that it contains no OAc signal at δ 1.7.

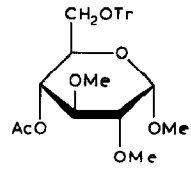


1 R = H, R^1 = OMe
2 R = OMe, R^1 = H
3 R = H, R^1 = OAc



4 R = OAc, R^1 = H
5 R = H, R^1 = Ph
6 R = R^1 = H

7



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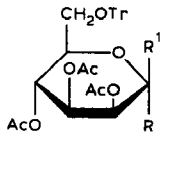
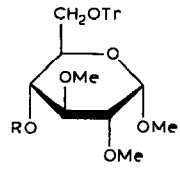
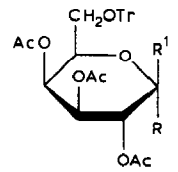


9 R = H, R^1 = OAc
10 R = OAc, R^1 = H



11 R = Me
11a R = Me-d_3



12 R = H, R^1 = OMe
13 R = OMe, R^1 = H

A methoxyl group at C-4 also may experience diamagnetic shielding in similar fashion. Hence, there are four OMe signals in the p.m.r. spectrum of methyl 2,3,4-tri-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside (**11**): at δ 3.70, 3.62, 3.50, and 3.33. However, as there is no signal at δ 3.33 in the spectrum of **11a**, the 4-(trideuteriomethyl) analog of **11**, it is clear that the most strongly shielded methoxyl protons are those at position 4.

D-*galacto* Isomers (**12** and **13**) show less of a spread in OAc chemical shifts (Table I) than do the D-*gluco* and D-*manno* derivatives. Although the former contain both axial and equatorial acetoxyl groups (the resonances of which have not been rigorously identified), the absence of signals in the vicinity of δ 1.7–1.8* suggests that no pronounced shielding influence is contributed to the protons of AcO-4 of **12** and **13** by the 6-*O*-trityl group, in contrast to the situation with **1–10**.

Perhaps related to this difference is a notable departure of the optical rotatory properties of **12** and **13** from those of derivatives **1–10**. A comparison of the molecular rotation ($[M]_D$) of each compound with that of the corresponding

*Data[1,3,4] for a variety of acetylated *gluco*, *manno*, and *galacto* derivatives show that, in the absence of a substituent such as aryl, the acetoxyl protons invariably have chemical shifts greater than δ 1.90.

TABLE I

CHEMICAL SHIFTS FOR ACETOXYL PROTONS AND MOLECULAR ROTATIONS OF 6-*O*-TRITYLALDOHEXOPYRANOSE DERIVATIVES

Derivative	*δ OAc-1 to −4*[a]	$[M]_D$ *OTr*[b] *(degrees)*	$[M]_D$ *OAc*[c]	$\Delta[M]_D$[d]
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**1**)	2.00, 1.93, 1.70	+179[e]	−65	+244
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside (**2**)	2.16, 2.06, 1.78	+950	+473	+577
1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose (**3**)	2.13, 2.06, 2.03, 1.72	+256[e]	+15	+241
1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-α-D-glucopyranose (**4**)	2.10, 2.02, 2.02, 1.73	+564	+397	+167
Phenyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-glucopyranoside (**5**)	2.00, 1.94, 1.70	+120	−14	+134
2,3,4-Tri-*O*-acetyl-1,5-anhydro-6-*O*-trityl-D-glucitol (**6**)	2.05, 2.03, 1.74	+436[e]	+128	+308
1,2,4-Tri-*O*-acetyl-3-*O*-methyl-6-*O*-trityl-β-D-glucopyranose (**7**)	2.13, 2.12, 1.76	—	—	—
Methyl 4-*O*-acetyl-2,3-di-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside (**8**)	1.78	—	—	—
1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-β-D-mannopyranose (**9**)	2.30, 2.20, 2.06, 1.79	−15	−98	+83
1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-α-D-mannopyranose (**10**)	2.38, 2.21, 2.08, 1.80	+436	+128	+308
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-β-D-galactopyranoside (**12**)	2.20, 2.02, 1.90	−292	−50	−242
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-galactopyranoside (**13**)	2.10, 2.05, 1.92	+290	+482	−192

[a]Solvent, $CDCl_3$. [b]Molecular rotation/100 of the 6-*O*-trityl derivative; solvent, $CHCl_3$, unless otherwise indicated. [c]Molecular rotation/100 of the corresponding 6-*O*-acetyl derivative; solvent, $CHCl_3$. [d]$[M]_D$ OTr − $[M]_D$ OAc. [e]Solvent, C_5H_5N.

peracetate shows (Table I) that, whereas a 6-*O*-trityl group makes a substantial *positive* contribution to the rotations of the *gluco* and *manno* isomers, the *galacto* isomers receive a *negative* contribution.

Deviations[5] from Hudson's rules of isorotation[6] caused by aryl aglycon groups* sometimes involve both the A and B rotatory values, That is, the influence of a highly polarizable aryl substituent may extend through a large segment of a molecule. Both the A and B values for 6-*O*-trityl derivatives also are affected, as shown by a comparison with data for the corresponding 6-*O*-acetyl derivatives (Table II); although, as may be expected, the B values constitute the wider range of ratios.

Overall, then, a 6-*O*-trityl substituent appears to exert a different influence in the *gluco* and *manno*, than in the *galacto*, series, both on the shielding of the protons of 4-acetoxyl (or 4-methoxyl) groups, and on rotatory contributions of the chiral centre at C-4 of these molecules. For diamagnetic shielding to occur, the pertinent methyl protons must lie within the shielding zone inherent in the plane of the phenyl ring(s) which, in turn, depends on the orientations of the O-4 and O-6 substituents with respect to each other.

Evidence[3,8–12] based on spin–spin coupling between H-5, H-6_R, and H-6_S in derivatives of D-glucose and D-mannose indicates that rotational isomerism about the C-5–C-6 bonds of these compounds, represented by staggered rotamers **14, 15,** and **16**, involves **14** and, slightly less prominently, **15**. Probably due to the *syn*-1,3 relationship between O-4 and O-6, rotamer **16** is a minor contributor. Despite the great bulk of a trityl group, the rotamer populations of 6-*O*-trityl derivatives are similar to those of the corresponding 6-*O*-acetyl derivatives, judging from the similarity in their coupling parameters (Table III). Hence, conformations of **1–10** that incorporate rotamer **14** are likely to account for the upfield shift for AcO-4 of these *gluco* and *manno* derivatives, because the *O*-trityl group in **15** would be more remote. For compounds of the *galacto* series, wherein rotational isomerism appears to be represented[3,4,10,11,13] by **17** and **18**, substitution of the 6-*O*-acetyl group by *O*-trityl introduces little change in the equilibrium population, judging from the 5,6,6′ couplings observed (Table III). Although the distance between O-4 and O-6 in **17** is comparable to that in **14** (and is much larger in **18**, by analogy with **15**), the absence of a shielding effect on AcO-4 may be taken as evidence that the specific disposition of the phenyl rings with respect to the AcO-4 protons is different in the two series. Perhaps a contributing factor, at present unknown, is a difference in the most favorable orientation of the O-6–C-Tr bond in rotamers representing these 6-*O*-trityl derivatives.

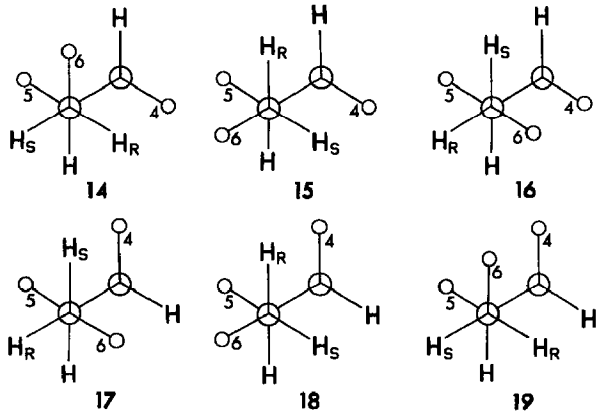
As to the observed differences in molecular rotation, it is noteworthy that the relative orientation of the C-6–O-6 bond with respect to the C-4–O-4 bond in rotamer **14** is opposite to that in **17**: *i.e*, the triphenylmethoxy group in the latter is

*These groups also promote diamagnetic shielding of nearby α-acetyl protons in the aryl glycosides[7], similar to that described here.

TABLE II

OPTICAL PARAMETERS FOR 6-*O*-TRITYL DERIVATIVES AND THE CORRESPONDING 6-ACETATES

		$[M]_D$ (degrees)	A_{OTr}	B_{OTr}			A_{OAc}	B_{OAc}	A/A_{OTr}	B/B_{OTr}
1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-D-glucopyranose	α	564	154	410	1,2,3,4,6-Penta-*O*-acetyl-D-glucopyranose	α	191	206	1.28	0.50
	β	256				β				
Methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-D-glucopyranoside	α	1103	462	641	Methyl 2,3,4,6-tetra-*O*-acetyl-D-glucopyranoside	α	264	203	0.57	0.31
	β	179				β				
1,2,3,4-Tetra-*O*-acetyl-6-*O*-trityl-D-mannopyranose	α	435	225	210	1,2,3,4,6-Penta-*O*-acetyl-D-mannopyranose	α	156	58	0.71	0.20
	β	−15				β				
Methyl 6-*O*-trityl-D-glucopyranoside	α	335	245	90	Methyl D-glucopyranoside	α	216	121	0.85	1.21
	β	−155				β				



to the *right* of the (axial) C-4–O-4 bond, whereas in **14**, it is positioned to the *left* of the (equatorial) C-4–O-4 bond. Perhaps, then, this difference between the two major rotamers helps to account for the fact that the anomalous rotatory contributions of the 6-*O*-trityl substituents in the *galacto* series are opposite in sign to those of the *gluco* and *manno* isomers.

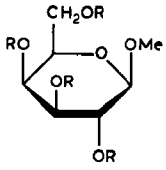
TABLE III

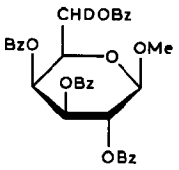
CHEMICAL SHIFTS AND COUPLING DATA[a] FOR H-6_R AND H-6_S OF ALDOHEXOPYRANOSE DERIVATIVES

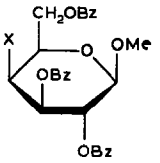
Compound	δ		*J (Hz)*		
	H-6$_R$	*H-6$_S$*	*5,6$_R$*	*5,6$_S$*	*6$_R$,6$_S$*
A. Methyl β-D-glucopyranoside					
2,3,4-tri-*O*-acetyl-6-*O*-trityl	3.10	3.19	5.0	2.1	10.3
2,3,4-tri-*O*-acetyl-6-iodo	3.57	3.64	6.7	2.8	12.0
2,3,4-tri-*O*-acetyl-6-*O*-benzoyl	4.37	4.55	4.6	3.1	12.1
2,3,4,6-tetra-*O*-acetyl	4.29	4.15	4.6	2.5	12.2
β-D-Mannopyranose					
1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl	3.06	3.25	4.5	2.8	11.3
1,2,3,4,6-penta-*O*-acetyl	4.27	4.09	4.7	1.9	12.4
Methyl β-D-galactopyranoside					
2,3,4-tri-*O*-acetyl-6-*O*-trityl	3.32	3.01	5.7	8.0	9.0
2,3,4,6-tetra-*O*-acetyl	4.20	4.14	6.5	7.2	11.5
B. Methyl β-D-galactopyranoside[b]	3.53	3.49	8.0	3.5	11.5
Methyl 4-deoxy-4-iodo-β-D-galactopyranoside[b]	3.34	3.20	7.7	4.8	12.0
C. Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (**29**)	4.29	4.15 (0.14)[c]	4.6	2.5	12.3
Methyl 2,3,6-tri-*O*-acetyl-4-deoxy-β-D-*xylo*-hexopyranoside (**30**)	4.23	4.10 (0.12)[c]	6.0 (6.2)[d]	4.5 (4.2)[d]	11.5 (11.2)[d]
Methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**20**)	4.20	4.14 (0.06)[c]	6.5	7.2	11.5

[a]Solvent, $CDCl_3$, except where otherwise indicated. [b]Solvent, D_2O. [c]δ H-6_R − δ H-6_S. [d]Data for methylene protons of **31**.

Assignment of H-6$_R$ and H-6$_S$ resonances. — As rotational isomerism about the C-5–C-6 bond is reflected in the coupling of H-5 with H-6$_R$ and H-6$_S$, it is necessary to be able to identify the individual H-6 resonances. Stereoselective deuteration at C-6 provides one way[11,13–15], which has been applied for the designation of the H-6$_R$ and H-6$_S$ signals of some *galacto* and *gluco* derivatives. However, there can be uncertainty in transferring those designations to the spectra of analogs in which substituent groups have been altered. As shown[4,16] recently for D-glucopyranose derivatives, for example, the presence of acetyl groups at both O-4 and O-6 (although not at either individually) is accompanied by a reversal in the order of the H-6$_R$ and H-6$_S$ chemical shifts relative to those of the underivatized compound or, indeed, of the 4,6-dibenzoate. It appears that D-mannose derivatives exhibit an analogous effect although, by contrast, it is not observed in the *galacto* series. These distinctions also are evident in the data of Table IIIA. That is, the H-6$_R$ signal is downfield of that of H-6$_S$ for methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside[11] (**20**), as well as for methyl β-D-galactopyranoside (**21**)* and its tetrabenzoate (**22**). This is shown for **22** in Fig. 1, by reference to the corresponding signals of methyl 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranoside-*6-d* (3:1 *S:R*) (**22a**) and, more distinctively, those of the pure 6-*d(S)* diastereomer (**22b**). The latter was prepared by selective removal of the 6-*d(R)* component from the underivatized glycoside mixture[11] with D-galactose oxidase, by taking advantage of the primary deuterium isotope effect on the enzymic pro-*S* dehydrogenation step[17]. It also has recently been found[13], with stereoselectively deuterated compounds, that H-6$_R$ of the α-anomeric counterparts of **20–22** consistently resonates downfield of H-6$_S$.







20 R = Ac
21 R = H
22 R = Bz

22a 6(3*S* : 1*R*)
22b 6(*S*)

23 X = F **25** X = Br
24 X = Cl **26** X = I

Analogs modified at C-4. — Accepting, then, that H-6$_R$ tends to be less strongly shielded than H-6$_S$, nevertheless there are substantial differences among derivatives in the chemical shifts for these two protons ($\delta H_R - \delta H_S$), and in the magnitude of their coupling with H-5. This is evident for the compounds already mentioned. Other compounds examined in this context are analogs[18] of methyl α-D-

*These designations for **21** were inadvertently reversed originally[4]. This error was kindly noted by K. Bock (personal communication), who independently arrived at the correct designations.

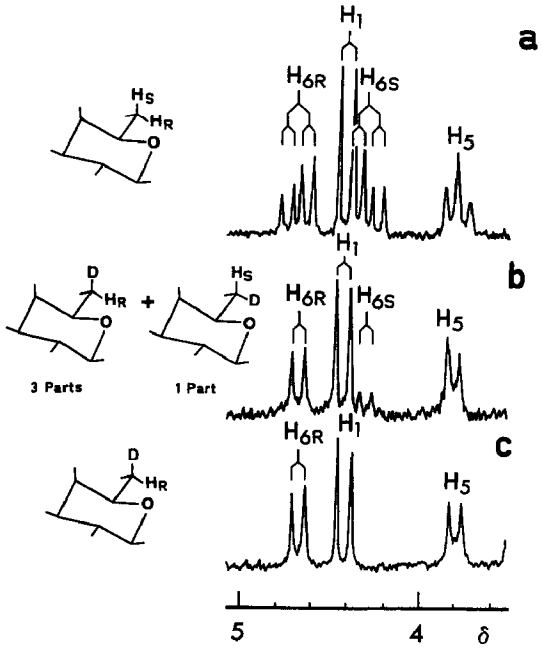


Fig. 1. Partial p.m.r. spectra (100 MHz; solvent, C_6D_6) of (*a*) methyl β-D-galactopyranoside tetrabenzoate (**22**); (*b*) methyl β-D-galactopyranoside-*6-d* (3:1 *S:R*) tetrabenzoate (**22a**); and (*c*) methyl β-D-galactopyranoside-*6-d(S)* tetrabenzoate (**22b**).

galactopyranoside modified at C-4. As seen in Table IV, the 4-deoxy-4-fluoro (**23**), -chloro (**24**), -bromo (**25**), and -iodo (**26**) tribenzoates, in C_6D_6, show a progressive increase in chemical shift difference ($\Delta\delta$) that parallels the increasing size of the halogen atom; upfield displacements of the H-6_S signals appear to account for most of these differences. Similar data were obtained (Table IV) when $CDCl_3$ was the solvent.

In representative structure **27**, which incorporates the elements of rotamer **17**, the halogen atom is *syn* with respect to H-6_S. Although this type of spatial arrangement might be considered a possible contributor to the observed variation in $\Delta\delta$, against this is the absence of a concomitant impact on the chemical shift of H-2 which, with respect to the 4-halogen atom, is positioned similarly to H-6_S. Also, as the values for $J_{5,6R}$ and $J_{5,6S}$ do not differ appreciably (Table IV), the changes in $\Delta\delta$ cannot be attributed to alterations in rotational isomerism about the C-5–C-6 bond in the halides. A more plausible explanation appears to lie in some steric interaction between the 6-benzyloxy group and the halogen atom*—which

*By contrast, polar contributions may be expected to alter the conformational equilibrium about the C-5–C-6 bond. For example[19], rotamer **19** is favored in 6-deoxy-6-fluoro analogs of galactose in which the C-4 substituent is NH_3^+. Other observations[20] on 6-deoxy-6-fluoro analogs of galactose (as well as of glucose), based on coupling between the ^{19}F atom and H-5, point to a preponderant contribution by rotamer **18** (and of rotamer **14**, in the *gluco* series).

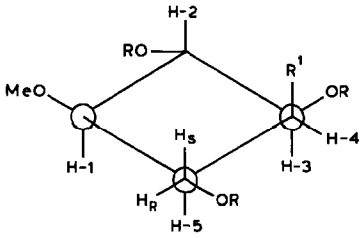
TABLE IV

CHEMICAL SHIFTS AND COUPLING DATA FOR H-6_R AND H-6_S OF ANALOGS OF METHYL 2,3,6-TRI-*O*-BENZOYL-β-D-GALACTOPYRANOSIDE MODIFIED AT C-4

Solvent	R^{1a}	δH_R	δH_S	$\Delta\delta H_R - \Delta\delta H_S$	δH-2	$J_{5,6R}$	$J_{5,6S}$	$J_{6R,6S}$
C_6D_6	F	4.64	4.45	0.19	6.15	7.0	6.0	11.5
	Cl	4.67	4.43	0.24	6.20	6.7	5.4	11.5
	Br	4.62	4.36	0.26	6.18	6.6	5.1	11.4
	I	4.58	4.25	0.33	6.10	7.0	5.0	11.6
	OBz	4.74	4.36	0.38	6.27	6.4	6.2	11.2
$CDCl_3$	Cl	4.76	4.58	0.17	5.83	6.0	5.9	11.8
	Br	4.75	4.55	0.20	5.83	6.6	5.8	11.7
	I	4.73	4.46	0.27	5.83	6.6	5.9	11.6
	OBz	4.68	4.45	0.23	5.85	5.2	6.1	9.8

[a]Substituent on C-4 of **27**.

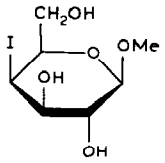
increases with the size of the latter, by analogy with[21] the anisochronism of the methylene protons of carbinols of general formula $R^1R^2C(OH)CH_2OR$, whereby the chemical shift difference increases with an increase in the size of R.



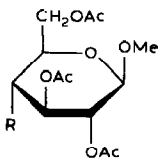
27

Comparing the influence on $\Delta\delta_{R\text{-}S}$ of an OH group on C-4 with that of a halogen atom of greater mass, *i.e.*, methyl β-D-galactopyranoside (**21**) *vs.* methyl 4-deoxy-4-iodo-β-D-galactopyranoside (**28**), it is found (Table IIIB) that the difference increases from 0.04 p.p.m. [δ H-6_R (3.53) − δ H-6_S (3.49)] to 0.14 p.p.m. [δ H-6_R (3.34) − δ H-6_S (3.20)]. Once again, couplings between H-5 and H-6,6′ are similar. It also is noteworthy that, in both instances, the coupling between H-5 and H-6_R exceeds that between H-5 and H-6_S by much more than observed with the corresponding ester derivatives. Perhaps this apparent increase in the prominence of rotamer **18** is a reflection of the change to an aqueous medium. For methyl α-D-galactopyranoside in D_2O also[13], rotamer **18** is favored over **17** and **19**, as well as in the solid state of the monohydrate of this glycoside[22], although an anomalous melting pattern of the latter is considered[22] to involve participation by rotamer **17** as well.

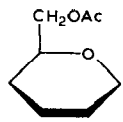
A point of convergence between methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (**20**) and its C-4 *(gluco)* epimer (**29**) is methyl 2,3,6-tri-*O*-acetyl-4-deoxy-β-D-*xylo*-hexopyranoside (**30**), inasmuch as any influence on rotational isomerism attributable to the axial or equatorial acetoxyl groups of **20** or **29**, respectively, is absent. Nor surprisingly, then, coupling between the 5- and 6,6'-protons of **30** is intermediate in size between those of **20** and **29** (Table IIIC), as well as being similar to data[23] for the simple model compound **31**, which exhibits values of $J_{5,6} = 6.2$ Hz, $J_{5,6'} = 4.2$ Hz, and $J_{6,6'} = 11.2$ Hz.



28



29 R = OAc
30 R = H



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EXPERIMENTAL

Proton magnetic resonance spectra were recorded with a Varian HA-100 or XL-300 spectrometer, or a Bruker XL-400 spectrometer. Chemical shifts (δ) are reported with reference to tetramethylsilane. Evaporations were performed under diminished pressure at, or below, 45°. Compounds **1–13** were crystalline and had m.p. and $[\alpha]_D$ values close to those reported in the literature.

*Methyl 2,3-di-*O*-acetyl-4-*O*-trideuterioacetyl-6-*O*-trityl-α-*D*-glucopyranoside* (**2a**). — Methyl 2,3-di-*O*-acetyl-α-D-glucopyranoside (0.5 g), prepared from methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-glucopyranoside as described[1] for the β anomer, was dissolved in cold pyridine (20 mL), and chlorotriphenylmethane (0.5 g) was then added, followed after 6 h by 0.3 mL (3 mmol) of acetic anhydride-d_6. After 2 h, the solution was poured into ice–water (150 mL), and the precipitated material was collected by filtration, dried, and recrystallized from ethanol, to give **2a**, m.p. 134–136°, $[\alpha]_D$ +196° (*c* 4, pyridine). When, in an attempted preparation of **2a**, the tritylation reaction was carried out for 2 h at 95°, prior to trideuterioacetylation at room temperature, the product (m.p. 133–136°) gave a p.m.r. spectrum in which the intensity of each of the three acetoxyl signals accounted for only ~2 protons, indicative of uniform scrambling of the *O*-trideuterioacetyl groups introduced.

*Methyl 2,3-di-*O*-methyl-4-*O*-trideuteriomethyl-6-*O*-trityl-α-*D*-glucopyranoside* (**11**). — To a solution of methyl 2,3-di-*O*-methyl-6-*O*-trityl-α-D-glucopyranoside[24] (0.15 g) in methyl iodide-d_3[25] (1.0 mL) was added silver oxide (0.4 g), the suspension was shaken for 48 h and filtered with the aid of acetone, and the filtrate was evaporated. The residue was recrystallized from light petroleum, to give **11** (0.09

g), m.p. 162–164°, $[\alpha]_D$ +88.0° (*c* 3, acetone) (lit.[26], for the non-deuterated analog, m.p. 164–166°, $[\alpha]_D$ +88.9°).

Methyl 2,3,4,6-tetra-O-benzoyl-β-D-galactopyranoside-6-d(S) (**22b**). — Methyl β-D-galactopyranoside-*6-d* (3:1 *S:R*) (40 mg) in 0.2M phosphate buffer (pH 7.0, 4.0 mL) was incubated at 37° for 3 h with D-galactose oxidase (5 mg, 125 units; Worthington Biochemicals) and catalase (5 mg). A mixture of Amberlite IR-120 (H^+) and Dowex-1 (HCO_3^-) ion-exchange resins was added to the stirred digest, the suspension was filtered, the filtrate was evaporated, and the residue was subjected to benzoylation in pyridine with benzoyl chloride. Recrystallization of the product from methanol afforded **22b**, m.p. 133–134°, $[\alpha]_D$ +106° (*c* 2, chloroform).

ACKNOWLEDGMENTS

The authors thank the Pulp and Paper Research Institute of Canada and the Natural Sciences and Engineering Research Council of Canada for generous support.

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