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5-THIO-D-RIBOPYRANOSE

PART III[1]. CONFORMATIONAL EQUILIBRIA IN THE METHYL D-RIBOPYRANOSIDES, THEIR 1-THIO, 5-THIO, AND 1,5-DITHIO ANALOGUES, AND THE RELATED TRIACETATES

N. A. HUGHES

Department of Organic Chemistry, The University, Newcastle upon Tyne NE1 7RU (Great Britain)

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ABSTRACT

Conformational equilibria have been estimated by n.m.r. spectroscopy for the methyl 2,3,4-tri-*O*-acetyl-α- and -β-D-ribopyranosides (**1'a** and **1'b**), their 1-thio (**2'a**, **2'b**), their 5-thio (**3'a**, **3'b**), and their 1,5-dithio (**4'a**, **4'b**) analogues. Only **1'b** shows a preference for the *1C* conformation; the others favour the *C1* form to various extents. These results are discussed in terms of polar and steric effects. Similar estimations have been made on the unacetylated D-ribopyranosides (**1–4**) and, where a definite conformational assignment is possible, these follow the same trend as the triacetates (**1'–4'**). These results are compared, where possible, with the results of X-ray crystallographic studies.

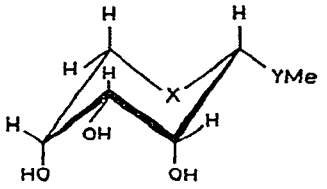
INTRODUCTION

The synthesis of the methyl 1,5-dithio-α- and -β-D-ribopyranosides (**4a** and **4b**) described in Part II[1] completed the series of compounds related to methyl α- and -β-D-ribopyranosides[2,3] (**1a** and **1b**) by substitution of oxygen by sulphur at C-1 and/or C-5. The monothio derivatives, namely the methyl 1-thio-α- and -β-D-ribopyranosides[4] (**2a** and **2b**), and the methyl 5-thio-α- and -β-D-ribopyranosides[2] (**3a** and **3b**) have been described in earlier papers. The availability of this set of compounds made possible a study of the effect of replacement of oxygen by sulphur at C-1 and/or C-5 on the favoured conformations. Replacement at C-1 could result in a change of the anomeric effect, whereas replacement at C-5 would also be expected to markedly affect the geometry of the six-membered ring because of the greater length of the C–S bond. The results in this paper are based upon n.m.r. measurements, but simultaneously Professor G. A. Jeffrey and Dr. R. L. Girling of the University of Pittsburgh have been studying the thio compounds by X-ray crystallographic methods; some of their results have already been published[5] in preliminary form.

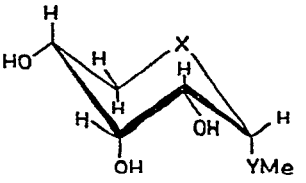
DISCUSSION

The earliest applications of n.m.r. spectroscopy to the study of conformations of D-ribopyranose derivatives were on the free sugar[6–8]. The spectra revealed the

α-anomers (a series)

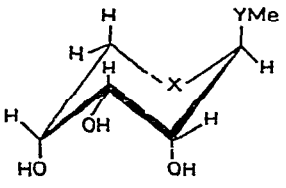


1C

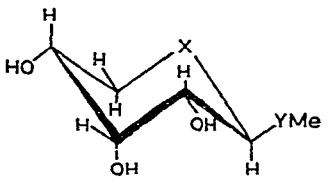


C1

β-anomers (b series)



1C



C1

1 X = Y = O
2 X = O, Y = S
3 X = S, Y = O
4 X = Y = S

(The related 2,3,4-triacetates are indicated by a prime notation, *e.g.* **1'a**).

presence of all four pyranoid and furanoid forms, but the lack of separation of all the signals made quantitative estimations impossible. However, it was concluded that *C1* and *1C* forms were present in significant amount for both α- and β-D-ribopyranose, in agreement with theoretical calculations[8]. A similar conclusion was made[9] for methyl β-D-ribopyranoside (**1b**).

In 1966, Coxon[10] examined a number of 2,3,4-tri-*O*-benzoyl-D-ribopyranosyl derivatives. Use of the tribenzoates simplified interpretation of the spectra, because the ring proton signals were generally well-separated from each other and the spectra could be analysed on a first-order basis. It was found that α-D-ribopyranosyl derivatives preferred the *C1* conformation, but the β-anomers could exist predominantly in either the *C1* or *1C* conformations, depending upon the nature of the C-1 substituent. No thio derivatives were included in this study. More recently, Horton and Durette, in a series of papers now summarised in a review article[11], have made an extensive study of aldopyranose conformations, paying particular attention to pentopyranose derivatives. This study included a thioribose derivative, namely 1-thio-β-D-ribopyranose tetra-acetate[12].

Ribopyranoside triacetates

In view of these earlier results, initial studies were made on the triacetates **1'–4'** of the ribopyranosides **1–4**. Triacetates **2'a** and **2'b** have not been described previously; **1'a** and **3'a** have been reported[2,13] as gums, but they have now been

obtained in crystalline form. With one exception, spectra were obtained for solutions in chloroform-*d* and the signals for coupled protons were sufficiently well-separated for the spectra to be resolved on a first-order basis. Partial overlap sometimes occurred for the signals of H-2 and H-4, but for the only compound (**1'b**) where there was evidence for coupling between these two protons, they were sufficiently well-separated. The H-5 signals of **3'b** in chloroform-*d* solution appeared as a "deceptively simple" doublet and the H-2, H-3, and H-4 signals were not well-separated. A better spectrum was obtained with benzene as solvent when the H-5 signals appeared as part of an ABX system and were treated as such. It has previously been shown[14] that conformational equilibria are generally insensitive to changes of solvent of similar dielectric constant. In the present study, only minor differences in coupling constants were observed for compounds where well-resolved spectra were obtained in both chloroform-*d* and benzene (*e.g.* **4'b**). For most compounds, one of the $J_{4,5}$ values was considerably higher than the other, and this was assigned to $J_{4,5a}$. For **1'a**, **2'b**, **4'a**, and **4'b**, this assignment was confirmed, because H-5e could be identified by the presence of long-range coupling with H-3 (see later). In view of the small differences in the $J_{4,5}$ values for **1'b**, no attempt was made to assign the H-5 signals in the spectrum of this compound. Axial protons generally resonate at higher field than related equatorial protons[15] and, for the seven compounds where identification of the H-5e and H-5a signals was possible, only one (**2'b**) is an exception to this generalisation.

The results are shown in Table I (chemical shifts) and Table II (coupling constants), and will be discussed for each anomeric pair in turn.

TABLE I

FIRST-ORDER CHEMICAL SHIFTS[a] FOR THE METHYL D-RIBOPYRANOSIDE TRIACETATES AND THEIR ANALOGUES

Compound	*Solvent*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5e*	*H-5a*	*OMe*	*SMe* or *COMe*
1'a	$CDCl_3$	5.32	4.93	4.55	4.97	6.42	6.00	6.54	7.96, 7.88[b]
1'b	$CDCl_3$	5.28	4.97	4.62	4.85	6.21[c]	6.00[c]	6.55	7.94, 7.86[b]
2'a	$CDCl_3$	4.98	4.80	4.62	4.97	6.35	5.80	—	7.94, 7.90[b], 7.83
2'b	$CDCl_3$	5.16	4.94	4.52	4.92	5.89	6.24	—	7.92, 7.90, 7.89, 7.84
3'a	$CDCl_3$	5.48	4.78	4.40	4.83	7.62	6.89	6.56	7.98, 7.90, 7.83
3'b	C_6H_6	5.41	4.53	4.38	4.83	7.48	7.34	6.86	8.30, 8.24[b]
4'a	$CDCl_3$	5.91	4.70	4.46	4.88	7.53	6.72	—	7.99, 7.93, 7.83[b]
4'b	$CDCl_3$	5.98	4.84	4.41	4.88	7.42	6.87	—	7.98, 7.92, 7.82[b]
4'b	C_6H_6	5.99	4.75	4.20	4.99	7.76	7.07	—	8.39, 8.28, 8.26, 8.20

[a] τ values measured at 90 MHz. [b] Six-proton singlet. [c] Assignment uncertain.

*Methyl 2,3,4-tri-*O*-acetyl-α- and -β-*D*-ribopyranosides* (**1'a** *and* **1'b**). The coupling constants obtained for these compounds in chloroform-*d* are closely similar to those reported[13] for solutions in acetone-d_6 by Horton and Durette. From the $J_{4,5e}$ and $J_{4,5a}$ values, they concluded that the α-anomer **1'a** was largely (65%) in the

TABLE II

FIRST-ORDER COUPLING CONSTANTS[a] FOR THE METHYL D-RIBOPYRANOSIDE TRIACETATES AND THEIR ANALOGUES

Compound	*Solvent*	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5e}$	$J_{4,5a}$	$J_{5e,5a}$	^4J
1'a	$CDCl_3$	3.3	3.4	3.4	4.4	8.4	11.4	0.8 ($J_{3,5e}$)
1'b	$CDCl_3$	3.4	3.4	3.4	2.9[b]	4.0[b]	12.4	0.8 ($J_{2,4}$)
2'a	$CDCl_3$	4.2	3.1	3.1	4.0	7.4	12.0	
2'b	$CDCl_3$	7.0	3.1	3.1	4.1	7.5	11.7	0.3 ($J_{3,5e}$)
3'a	$CDCl_3$	3.2	3.6	3.0	4.0	11.6	12.8	
3'b	C_6H_6	7.4	3.0	2.6	4.6	7.4	13.6	
4'a	$CDCl_3$	5.0	2.6	2.8	4.0	11.2	13.0	~1 ($J_{3,5e}$)
4'b	$CDCl_3$	10.5	2.5	~2.5	4.5	11.2	13.0	~1 ($J_{3,5e}$)
4'b	C_6H_6	10.4	2.6	2.2	4.4	11.2	12.5	1.0 ($J_{3,5e}$)

[a]In Hz, measured at 90 MHz. [b]Assignment uncertain.

C1 conformation, whereas the β-anomer **1'b** was more in the *1C* conformation (61%). Confirmation of these preferences is obtained in this study by the observation of sizeable, long-range coupling constants between 1,3-diequatorially related protons. In the α-anomer **1'a**, these are H-3 and H-5e in the *C1* conformation, and for the β-anomer **1'b**, H-2 and H-4 in the *1C* conformation. Similar values for $J_{3,5e}$ have been reported[10,16] for other α-D-ribopyranose derivatives.

*Methyl 2,3,4-tri-*O*-acetyl-1-thio-α- and -β-*D*-ribopyranosides* (**2'a** *and* **2'b**). The close similarity of all the coupling constants, except $J_{1,2}$, for these compounds suggests that they both have the same proportion of *C1* and *1C* forms. The larger $J_{1,2}$ value of **2'b** clearly identifies it as the β-anomer. Assuming that the substitution of OMe by SMe has not greatly affected the ring geometry, the fact that $J_{4,5a}$ is only slightly less in these compounds than in **1'a** suggests that they are *both* mainly in the *C1* conformation with, perhaps, a slightly greater contribution from the *1C* form than in **1'a**. The anomeric effect of a methylthio group is less than that of a methoxyl group[17]. This would result in less preference by **2'b** for the *1C* form with its three axial groups, in keeping with the observation that **2'b** has a preference for the *C1* conformation whereas its oxygen analogue **1'b** has a slight preference for the *1C* form. Very similar results were obtained[12] for the related β-D-ribopyranose tetra-acetate (43% *C1*) and its 1-thio analogue (66% *C1*). In the same paper[12], it was suggested that the anomeric effect of an acetylthio group is not markedly different from that of an acetoxy group if it is 1,3-diaxially related to an acetoxy group. If this consideration also applies to a methylthio group, such a situation occurs in **2'a** in the *C1* form, which would explain why the conformational preferences of **2'a** and **1'a** are so similar, in contrast to their β-anomers.

*Methyl 2,3,4-tri-*O*-acetyl-5-thio-α- and -β-*D*-ribopyranosides* (**3'a** *and* **3'b**). The high value for $J_{4,5a}$ (11.6 Hz) suggests that **3'a** is very largely in the *C1* conformation. The lower value of $J_{4,5a}$ (7.4 Hz) for **3'b** indicates an increased *1C* contribution for this anomer but, taken with $J_{1,2}$ (7.5 Hz), suggests that the preponderant conforma-

tion is still *C1*. Inspection of models suggests that substitution of the ring-oxygen atom by a sulphur atom would be expected to destabilise the *1C* conformation relative to the *C1* conformation in these D-ribopyranose compounds, The main difference in the ring sulphur-containing conformation *1C* is the decreased separation of the axial acetoxy groups at C-2 and C-4 owing to a slight convergence of the C–O bonds at C-2 and C-4. In the model of the ring oxygen-containing system, these bonds are divergent. The same models suggest that there is little effect on the separation of the axial methoxyl group at C-1 and the axial acetoxy group at C-3 in the *C1* conformation of the α-anomer **3'a**.

The recently reported[18] "hockey stick" effect arising from orbital repulsion between a sulphur atom in a six-membered ring and a β-axial heteroatom-containing substituent would also destabilise the *1C* conformation relative to the *C1* conformation, for there are two such interactions in the *1C* conformation of the 5-thio-D-ribopyranose derivatives and none in the *C1* conformation. These two effects may be expected to overshadow any alteration of the anomeric effect of the methoxyl group due to substitution of the ring heteroatom. The results obtained agree with these expectations. In the α-anomer **3'a**, all three effects favour the *C1* conformation and the compound is very largely, if not exclusively, in this conformation. In the β-anomer **3'b**, the anomeric effect would oppose the other two effects, and this would account for the small but recognisable contribution from the *1C* form.

*Methyl 2,3,4-tri-*O*-acetyl-1,5-dithio-α- and -β-*D*-ribopyranosides* (**4'a** *and* **4'b**). The $J_{4,5a}$ values for these compounds are identical and high (11.2 Hz), suggesting that both compounds are very largely in the *C1* conformation. The existence of sizeable, long-range coupling constants between H-3 and H-5e is in agreement with this conclusion. As with **2'a** and **3'a**, the higher $J_{1,2}$ value of **4'a** confirms its anomeric structure. The $J_{1,2}$ values for both **4'a** and **4'b** are the highest in the series for both compounds, but this is probably due to the existence of two C–S bonds. Vicinal coupling constants generally show[19] an increase with decreasing electronegativity of substituents. The effect is probably present in the other thio compounds but is particularly marked in these cases where two sulphur atoms are present. The finding that both **4'a** and **4'b** are very largely in the *C1* conformation is not unexpected in view of the earlier results and comments. The anomeric effect of the thiomethyl group in the dithioglycosides **4'** is probably even less than it is in the monothioglycosides **2'** and may well be offset by the steric preference of the thiomethyl group to take up an equatorial configuration. Consequently, the conformations of the dithioglycosides **4'** may be determined mainly by the steric and polar effects already described for the 5-thio-D-ribopyranosides **3'** and favouring the *C1* conformation.

Free ribopyranosides

The spectra of the free glycosides were obtained at 60 MHz in pyridine solution after exchange of hydroxyl hydrogen-atoms for deuterium. Only for one compound (**3a**) was a spectrum obtained in which all the proton signals were clearly discernible. In compounds **1**, **2**, and **3**, the low-field doublets were assumed to arise from H-1. In

the dithioglycosides **4**, the H-1 signals were not discernible, but the H-5 signals at higher field were readily recognised. No overall improvement was obtained for solutions in deuterium oxide. The results are given in Table III. As before, these are discussed for each anomeric pair in turn, together with any information from X-ray crystallographic studies.

TABLE III

FIRST-ORDER CHEMICAL SHIFTS[a] AND COUPLING CONSTANTS[a] FOR THE METHYL D-RIBOPYRANOSIDES AND ANALOGUES

Compound		*H-1*	*H-5e*		*H-5a*	*OMe*	*SMe*	$J_{1,2}$	$J_{4,5e}$	$J_{4,5a}$	$J_{5e,5a}$
1a		5.23				6.54		3			
1b		4.98				6.60		3.5			
2a	(1-thio)	5.09					7.74	3			
2b	(1-thio)	4.69					7.84	6			
3a[b]	(5-thio)	5.34	7.49		6.72	6.67		3	4	11	13
3b	(5-thio)	5.06		6.95[c]		6.55		6			
4a	(1,5-dithio)		7.15		6.58		7.73		3	8	13
4b	(1,5-dithio)		7.24		6.48		7.75		4	11	13

[a] τ values and Hz, measured at 60 MHz in pyridine solutions. [b] Confirmed at 90 MHz. Remaining data: τ 5.84 (H-2 and H-4), 5.49 (H-3) $J_{2,3}$ 3 Hz. [c] Deceptively simple doublet.

*Methyl α- and -β-*D*-ribopyranosides* (**1a** *and* **1b**). Since the dihedral angles of H-1 and H-2 are approximately equal for both conformations of **1a**, little can be deduced from the low $J_{1,2}$ value. The syrupy nature of the compound has precluded X-ray crystallographic studies. However, the low value of $J_{1,2}$ (3.5 Hz) for the β-anomer **1b** clearly indicates a preponderance of the *1C* conformation. This is also the conformation in the crystal[20], where it is stabilised by a hydrogen bond between OH-2 and O-4.

*Methyl 1-thio-α- and -β-*D*-ribopyranosides* (**2a** *and* **2b**). As with the previous compounds, the low $J_{1,2}$ value of **2a** does not allow any conformational assignment to be made. The X-ray crystallographic study[5] indicated the *1C* conformation, stabilised as in **1b** by a hydrogen bond between OH-2 and O-4. The triacetate **2'a**, lacking the hydrogen bond, prefers the *C1* conformation in solution. The β-anomer **2b** appears to show a preference for the *C1* conformation ($J_{1,2}$ 6 Hz). Unfortunately, it was not possible to produce crystals of adequate quality for X-ray analysis.

*Methyl 5-thio-α- and -β-*D*-ribopyranosides* (**3a** *and* **3b**). The α-anomer **3a** gave a spectrum which could be completely analysed, and the high $J_{4,5a}$ value (11 Hz) clearly indicates a high proportion of the *C1* conformation. The crystal also exists[21] in the *C1* conformation even though hydrogen bonding between OH-2 and OH-4 should be possible in the alternative *1C* conformation (see **4a**). The H-5 signals for the β-anomer **3b** appeared as a deceptively simple doublet, and no information about $J_{4,5a}$ could be derived. However, $J_{1,2}$ (6 Hz) suggests a preference for the *C1* form, and this conformation is found[21] in the crystal.

Methyl 1,5-dithio-α- and -β-D-ribopyranosides (**4a** *and* **4b**). The lower $J_{4,5a}$ value (8 Hz) for **4a** suggests that, although the *C1* conformation is preferred for both compounds, a higher *1C* content is present in **4a** than in its β-anomer **4b** ($J_{4,5a}$ 11 Hz). No such difference was observed for the triacetates **4'**. Interestingly, **4a** and **4b** adopt different conformations in the crystalline state, so that the methylthio group is equatorial for both compounds[5,21]. The β-anomer **4b** is in the *C1* conformation[21], but the α-anomer **4a** is especially interesting in that two types of molecule are present, both in the *1C* conformation, but with hydrogen bonding from OH-2 to O-4 in one and from OH-4 to O-2 in the other[5]. The preference, presumably for steric reasons, of the methylthio group for an equatorial configuration apparently still persists to a small extent in pyridine solution, where little support from hydrogen bonding can be expected, and must account for the small *1C* contribution observed for **4a**.

SUMMARY

The results described in this paper and by others are summarised in Table IV. Where n.m.r. spectral data are available both for the free glycosides and their triacetates, they show the same trends. For all the compounds but one, the *C1* conformation is preferred, although the extent of this preference may vary. The exception is methyl β-D-ribopyranoside (**1b**) and its triacetate **1'b**, each of which has a preference for the *1C* form. The anomeric effect of the methoxyl group is apparently the dominant effect in these compounds. The substitution of sulphur for oxygen at C-1 and/or C-5 favours the *C1* conformation for all the other compounds. As has already been discussed, this can be rationalised in terms of a reduced anomeric effect and, in the case of substitution at C-5, the change in ring geometry and the polar "hockey stick" effect. The conformations of the free glycosides in the crystalline state agree with the findings for solutions in pyridine where comparisons are possible, with one exception, namely methyl 1,5-dithio-α-D-ribopyranoside (**4a**) which exists in the

TABLE IV

CONFORMATIONAL PREFERENCES OF METHYL D-RIBOPYRANOSIDES AND ANALOGUES

D-*Ribopyranoside*		*Glycoside triacetate* (*n.m.r.*)	*Free glycoside*	
			(*n.m.r.*)	(*X-ray*)
	α-	*C1*>*1C*	?	—
	β-	*1C*>*C1*	*1C*>*C1*	*1C*[a]
1-thio	α-	*C1*>*1C*	?	*1C*[b]
1-thio	β-	*C1*>*1C*	*C1*>*1C*	—
5-thio	α-	*C1*⩾*1C*	*C1*>*1C*	*C1*[c]
5-thio	β-	*C1*>*1C*	*C1*>*1C*	*C1*[c]
1,5-dithio	α-	*C1*⩾*1C*	*C1*>*1C*	*1C*[b]
1,5-dithio	β-	*C1*⩾*1C*	*C1*⩾*1C*	*C1*[c]

[a]Ref. 20. [b]Ref. 5. [c]Ref. 21.

crystal in the *1C* conformation. Methyl 1-thio-α-D-ribopyranoside (**2a**), which also exists in the *1C* form in the crystal, may also be an exception; the conformation of the free glycoside **2a** in pyridine is uncertain, but the corresponding triacetate **2'a** prefers the *C1* conformation in solution. In the three crystalline compounds, **2a**, **4a**, and **4b**, containing a methylthio group, this group is found in an equatorial configuration, suggesting that, at least in the crystal, steric factors are important. The existence of intramolecular hydrogen bonds in **2a** and **4a** would stabilise the *1C* conformation necessary to enable the methylthio group to adopt an equatorial configuration. In solution, the hydrogen bonding is less effective and the *C1* form is favoured, although the equatorial preference of the methylthio group is still detectable in **4a** which has a higher *1C* content than its anomer **4b**.

EXPERIMENTAL

N.m.r. spectra were determined either at 60 MHz on a Perkin–Elmer R10 spectrometer or at 90 MHz on a Brucker Spectrospin spectrometer. Tetramethylsilane was used as an internal reference.

Acetylations were performed in the usual way, using acetic anhydride in pyridine.

Materials. — The compounds used have been described previously[1–4], with the exception of the following.

Methyl 2,3,4-tri-O-acetyl-α-D-ribopyranoside (**1'a**). This was prepared from methyl α-D-ribopyranoside obtained by chromatography[2] of a mixture of methyl D-ribosides on a basic ion-exchange resin, and had m.p. 85–87° (from light petroleum), $[\alpha]_D$ +85° (*c* 1.0, chloroform); lit.[13], $[\alpha]_D$ +86.6° (*c* 1.6, chloroform) (Found: C, 49.6; H, 6.4. $C_{12}H_{18}O_8$ calc.: C, 49.6; H, 6.2%).

Methyl 2,3,4-tri-O-acetyl-β-D-ribopyranoside (**1'b**). This was a syrup, $[\alpha]_D$ −87° (*c* 0.7, chloroform); lit.[13], $[\alpha]_D$ −88.1° (*c* 0.99, chloroform) (Found: C, 50.0; H, 5.7%).

Methyl 2,3,4-tri-O-acetyl-1-thio-α-D-ribopyranoside (**2'a**). This had m.p. 87–89° (from light petroleum), $[\alpha]_D$ +139° (*c* 1.0, chloroform) (Found: C, 47.1; H, 5.8; S, 10.5. $C_{12}H_{18}O_7S$ calc.: C, 47.1; H, 5.9; S, 10.45%).

Methyl 2,3,4-tri-O-acetyl-1-thio-β-D-ribopyranoside (**2'b**). This had m.p. 58–60° (from light petroleum), $[\alpha]_D$ −72° (*c* 1.0, chloroform) (Found: C, 47.1; H, 6.0; S, 10.6%).

Methyl 2,3,4-tri-O-acetyl-5-thio-β-D-ribopyranoside (**3'b**). This had m.p. 57–59° (from light petroleum), $[\alpha]_D$ −107° (*c* 0.8, dichloromethane) (Found: C, 47.3; H, 5.9; S, 10.3%).

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