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DETERMINATION OF THE CONFIGURATIONS OF TERTIARY ALCOHOLIC CENTERS IN BRANCHED-CHAIN CARBOHYDRATE DERIVATIVES

PMR SPECTROSCOPY WITH A LANTHANIDE SHIFT-REAGENT

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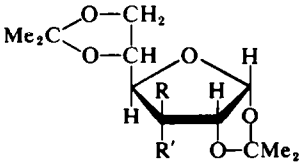
Abstract—Examination of the PMR spectral changes (expressed as shift gradients of individual protons) wrought by graduated addition of the paramagnetic lanthanide complex tris[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato]europium(III) [Eu(fod)$_3$] permitted assignment of the configuration at tertiary alcoholic centers of certain sugar derivatives. The configurations of the tertiary position of 3-*C*-(1,3-dithian-2-yl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**), lethyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-(dithian-2-yl)-α-D-*ribo*-hexopyranoside (**2**) and the corresponding 3-*C*-butyl compound (**2a**), and methyl 2-*C*-(1,3-dithian-2-yl)-3,4-*O*-isopropylidene-β-D-ribopyranoside (**3**) were assigned by comparison with reference spectra. The proton shift-gradients for 5-*C*-benzoyloxymethyl-2,3-*O*-cyclohexylidene-1-*O*-*p*-tolylsulfonyl-1(*R*),2(*S*),3(*S*),5(*R*)-cyclohexanetetrol (**4**), taken in conjunction with the spin–spin coupling values, permit direct assignment of relative stereochemistry in the latter compound.

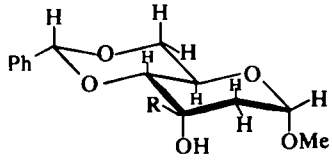
INTRODUCTION

Application of bulky, Lewis acidic complexes of lanthanides as shift reagents[1] for simplifying PMR spectra has proved[2] successful with examples of various molecular types. Simple, qualitative spectral expansion resulting from differentially enhanced chemical shifts has often proved sufficient to permit extraction of the desired NMR-spectral information from a previously complex spectrum, by exposing fine structure that is either concealed or complicated by overlapping resonances in the original spectrum, or by allowing comparison of the gross spectral response of the unknown structure with that of closely related molecules of known geometry. The latter approach was employed[3] in elucidating the structures of the isomeric pair of tertiary alcohols prepared by addition of ethynylmagnesium bromide to methyl 2,3,6-trideoxy-D-*glycero*-hexopyranosid-4-ulose. The configuration at the quaternary center of 2,3:4,5-di-*O*-benzylidene-β-D-fructopyranose was likewise determined by lanthanide-shift NMR spectroscopy, although in this case a correlation was made between the shift gradient [the shift induced by an (arbitrary) unit molar proportion of added complex] and the distance of the europium atom from each of several salient protons.[4]

The quantitative dependence[5] of observed shifts upon the relationship $(3\cos^2\theta - 1)/r^3$ between the effective europium–proton distance and the H—Eu—O angle for the OH group involved in coordination, appears to hold in multifunctional compounds[6] as well as in those having only a single Lewis basic center, as long as the various functional groups having nonbonding electrons are sufficiently separated to preclude multiple coordination. Bidentate coordination has been demonstrated, however, in complexes of α,α′-bipyridyl and 1,10-phenanthroline with tris[β-diketonato] complexes of several lanthanides,[7] and failure of the foregoing algebraic expression to account even qualitatively for the observed chemical shifts indicates that the susceptibility tensor does not approximate to axial symmetry in this circumstance. In the sugar series, simultaneous coordination of the europium center to O-3 and O-5 of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose has been suggested[8] to explain the anomalously large shift-gradient of the H-5 signal of this molecule.

The present report describes the application of PMR spectroscopy with a lanthanide shift-reagent, tris[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato]europium[9] [Eu(fod)$_3$], for determining the sterochemistry of the tertiary alcoholic centers of five synthetic branched-chain sugar derivatives, 3-*C*-(1,3-dithian-2-yl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**), methyl 4,6-*O*-benzylidene-2-deoxy-3-*C*-(1,3-dithian-2-yl)-α-D-*ribo*-hexopyranoside (**2**), the 3-*C*-(1-butyl) analogue (**2a**), methyl 2-*C*-(1,3-dithian-2-yl)-3,4-*O*-isopropylidene-β-D-ribopyranoside (**3**), and 5-*C*-(benzoyloxymethyl)-2,3-*O*-cyclohexylidene-1-*O*-*p*-tolylsulfonyl-1(*R*),2(*S*),3(*S*),5(*R*)-cyclohexanetetrol (**4**). Stereochemical characterization of such tertiary alcohol derivatives

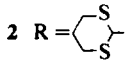




1 R =  , R′ = OH

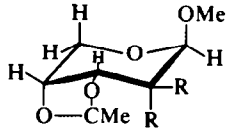
1a R = H, R′ = OH

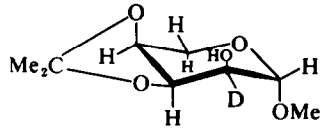
1b R = OH, R′ = H

2 R = 

2a R = Bu

2b R = H

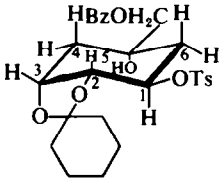




3a

3 R =  , R′ = OH

3b R = OH, R′ = H



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is notoriously difficult because of the inapplicability of conventional PMR spectroscopy employing spin-coupling data, and the lack of suitable reference compounds. In the discussion that follows, it has been assumed throughout that the favored site for coordination is the free OH group,[10] although direct correlation of shift gradients with structure by the Robertson–McConnell relationship[5] proved unsuccessful, as in the case of the aromatic diamines[7]; consideration of bidentate interactions, however, permitted interpretation of the data in a manner consistent with the molecular structures.

RESULTS AND DISCUSSION

PMR spectra for the five compounds were recorded at 100 MHz in carbon tetrachloride (**1**, **3**, **3a**, **3b**, and **4**) or chloroform-*d* (**2**, **2a**, and **2b**), and the shift gradient for the signal of each identifiable proton was determined by addition of $Eu(fod)_3$ at various concentrations. Table 1 records chemical shifts for protons in each compound before addition of the shift reagent, and gives the shift gradient for each signal in ppm per equivalent of added lanthanide complex.

3-C-(1,3-*Dithian*-2-*yl*)-1,2:5,6-*di*-O-*isopropylidene*-α-D-*allofuranose* (**1**). The PMR spectrum (Fig 1) of compound **1**, which was prepared by nucleophilic addition[11] of the 1,3-dithian-2-yl anion to the carbonyl group of 1,2:5,6-di-*O*-isopropylidene-α-D-*ribo*-hexofuranos-3-ulose, exhibited $J_{1,2}$ and $J_{4,5}$ couplings (4·1 and 9·0 Hz, respectively) similar in magnitude to those of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1a**, $J_{1,2}$ 4·0 Hz) and its D-*gluco* 3-epimer (**1b**, $J_{1,2} \sim 3{\cdot}5$, $J_{4,5} \sim 8{\cdot}5$ Hz).[8] Substantial conformational uniformity throughout the series of three compounds may thus be inferred.[12] It is observed (Table 1) that H-4 and H-2 exhibit a larger shift-gradient than H-5; this indicates clearly that complexation occurs at the "lower" side of the molecule, requiring that the 3-OH group reside in the "down" or (*R*) configuration, remote from H-5. Armitage and Hall[8] have noted that, whereas in the D-*allo* alcohol **1a** the shift gradient of H-5 is relatively small (as expected from monodentate coordination at O-3), the most strongly shifted resonance of the 3-epimeric D-*gluco* alcohol **1b** is that of H-5. Accordingly, the *allo* configuration can be securely assigned to compound **1** from this evidence. Additional support is afforded by the observation that only one *C*-methyl resonance is shifted strongly in compound **1**, whereas three of te four *C*-methyl signals of the D-*gluco* alcohol[8] **1b** are moved downfield to a similar extent.

This assignment is entirely in accord with chemical evidence of numerous examples[13] in which nucleophiles have been observed to add stereo-

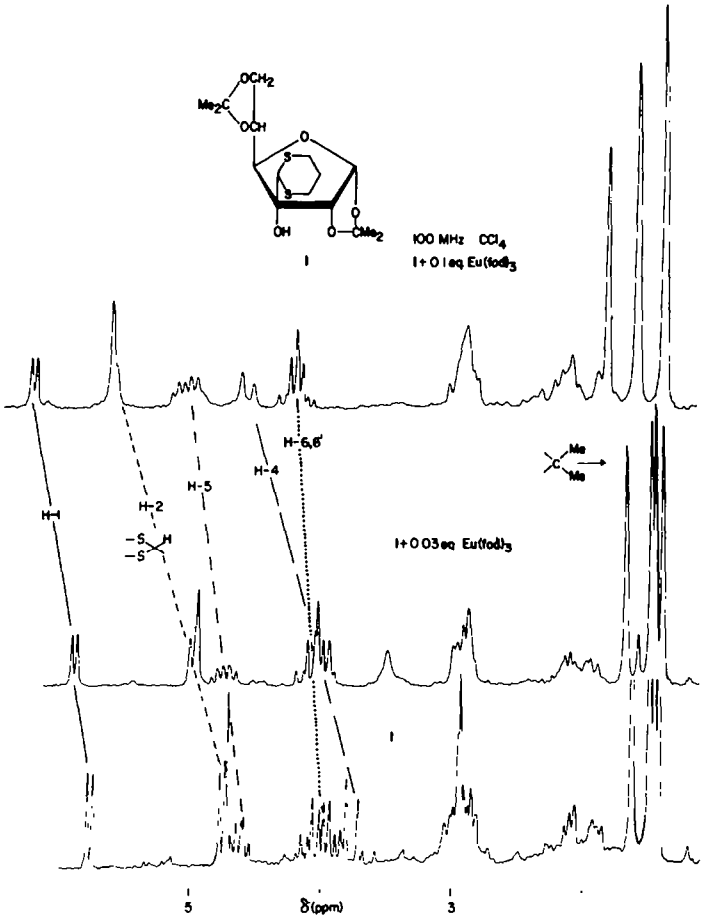

Fig 1. Unperturbed (lower) and progressively europium-shifted 100-MHz PMR spectra of 3-*C*-(1,3-dithian-2-yl)-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (**1**) in carbon tetrachloride.

specifically to the original ketone to give products having the D-*allo* configuration.

Methyl 4,6-O-*benzylidene*-2-*deoxy*-3-C-(1,3-*dithian*-2-*yl*)-α-D-ribo-*hexopyranoside* (**2**) *and its* 3-C-*butyl analogue* (**2a**). These two compounds, which were prepared from a 3-ulose precursor[14] by by nucleophilic addition,[15] gave NMR spectra (Fig 2) that were only partly interpretable. In each spectrum it was possible to identify the OMe, H-1, and benzylic-proton resonances, and the H-5 resonance was discernible in the spectrum of **2**. In contrast, the corresponding analogue lacking the chain branch, namely methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside (**2b**), gave an NMR spectrum (Fig 3) in which complete assignment of all signals was possible. From data in Table 1 it is immediately apparent that the shift gradients of the signals identifiable (H-1, OMe, PhCH) in the NMR spectra of **2** and **2a** are virtually identical with those of the corresponding resonances observed in the spectrum of the reference compound **2b**, suggesting that complexing of the reagent "below" the ring exerts essentially the same effect on H-1 and the protons of the anomeric methyl group in **2**, **2a**, and **2b**. As the *trans*-decalin type of ring fusion in these compounds constrains the pyranoid ring to the *Cl*(D) form as the only possible chair conformation, and as the chemical shifts of the resonances in question are essentially constant in the three examples, the D-*ribo* stereochemistry may be assigned with confidence to **2** and **2a**; this conclusion accords with the previously observed[16] steric course of addition of non-carbon nucleophiles to the same 3-ulose precursor.

Methyl 2-C-(1,3-*dithian*-2-*yl*)-3,4-O-*isopropylidene*-β-D-*ribopyranoside*[11] (**3**). As expected from the foregoing considerations, the PMR spectrum (Fig 4) of the chain-branched glycoside **3** provides no directly interpretable information concerning the configuration at the tertiary alcoholic center; however, it is possible to extract a complete set of chemical shifts and shift gradients (Table 1) for the protons attached to the pyranoid ring. The PMR spectrum (Fig 5) of methyl 3,4-*O*-isopropy-

Table 1. Shift gradients and unperturbed chemical shifts of signals in the 100-MHz PMR spectra of compounds **1**, **1b**, **2**, **2a**, **2b**, **3**, **3a**, **3b**, and **4**

Signal	Shift gradient[a] (Chemical shift[b])								
	1[c,d]	**1b**[c,e]	**2**[f,g]	**2a**[d,f]	**2b**[f,g]	**3**[c,g]	**3a**[c,g]	**3b**[c,g]	**4**[c,g]
H-1	8·0(5·77)	5·2(5·78)	10·5(4·81)	9·0[h](4·70)	8·0(4·77)	12·0(4·69)	9·5(4·48)	13·2(4·68)	3·3(4·84)
H-2	16·0(4·74)	7·0(4·38)			11·0(2·18)	—	—	13·2(3·74)	3·5(4·10)
H-2′	—	—			7·0(1·96)	—	—	—	—
H-3	—	17·0(~ 4·15)			22·5(2·64)	6·0(~ 4·06)	8·5(4·36)	12·4(4·14)	3·5(4·45)
H-4	15·0(3·75)	14·5(3·87)			9·0(4·15)	3·5(~ 4·06)	4·5(4·15)	4·6(4·19)	8·5(~ 2·6)
H-4′	—	—			—	—	—	—	5·5(1·90)
H-5	7·0(4·64)	26·0(~ 4·20)	4·0(~ 4·3)		2·5(4·28)	3·5(3·74)	4·5(3·61)	8·0(3·90)	16·0(4·14)
H-5′	—	—			—	3·0(3·74)	3·5(3·59)	5·0(3·90)	12·0(4·14)
H-6	3·0(4·08)	9·5(~ 3·93)			3·0(3·78)	—	—	—	6·0(~ 2·06)
H-6′	4·0(3·90)	9·0(~ 3·93)			5·5(3·57)	—	—	—	4·5(1·70)
OMe	—		5·5(3·36)	6·3[h](3·34)	5·0(3·36)	2·5(3·28)	2·5(3·28)	7·5(3·42)	—
PhC<u>H</u>	—		3·0(5·57)	2·7[h](5·47)	2·5(5·60)	—	—	—	—
$C(Me)_2$	≤ 0(1·41)			—	—	—	1·5(1·26)	2·5(1·31)	2·2(1·35)
	≤ 1·0(1·44)			—	—	—	~ 0(1·46)	4·5(1·47)	3·3(1·52)
	~ 0·5(1·48)			—	—	—	—	—	—
	1·5(1·62)			—	—	—	—	—	—

[a]In ppm per equivalent of $Eu(fod)_3$ added. [b]In ppm. [c]Dissolved in CCl_4. [d]Recorded with a JEOL MH-100 spectrometer. [e]Data from ref. 8; $Eu(dpm)_3$ was used as the shift reagent. [f]Dissolved in $CDCl_3$. [g]Recorded with a Varian HA-100 spectrometer. [h]These values are in the correct relative proportions; there is, however, substantial uncertainty (± ~ 25%) in absolute magnitudes.

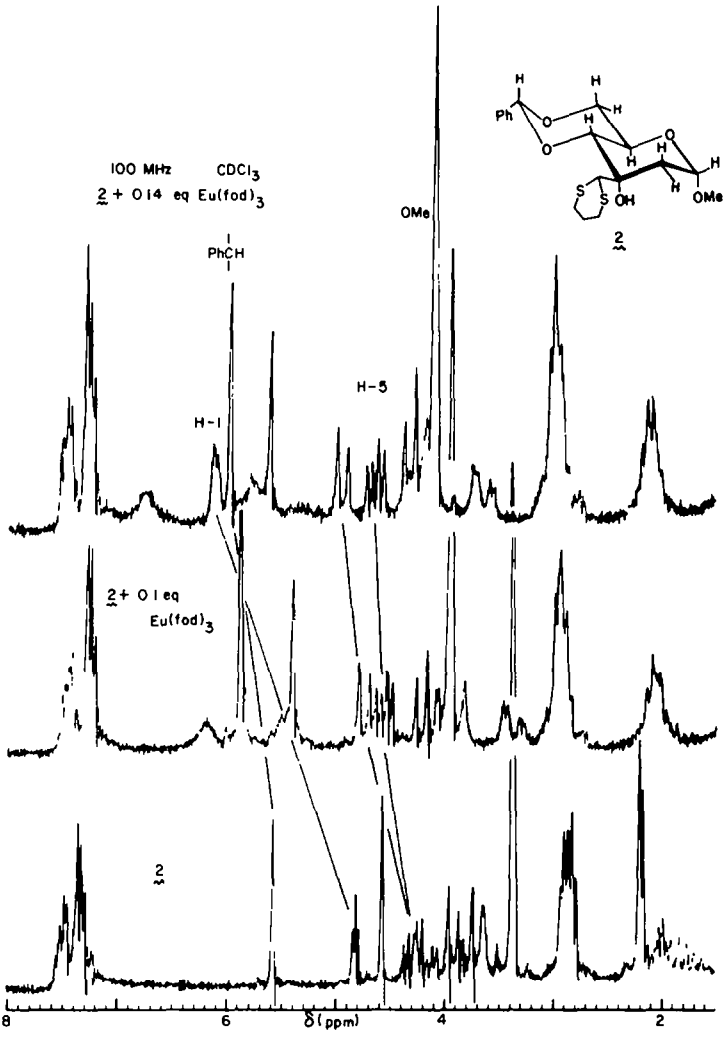

Fig 2. Unperturbed (lower) and progressively europium-shifted 100-MHz PMR spectra ot methyl 4.6-*O*-benzylidene-2-deoxy-3-*C*-(1.3-dithian-2-yl)-α-D-*ribo*-hexopyranoside (**2**) in chloroform-*d*.

lidene-β-D-arabinopyranoside (**3b**), a precursor that is oxidized to the 3-ulose (**3d**) in the preparation of **3**, provides reference data (Table 1) that can be seen to be uniformly at variance with compound **3**, thus suggesting that **3** has the *ribo* stereochemistry.

As this result was somewhat unexpected in the light of the well founded report of Burton, Overend, and Williams[14] that the addition of several different nucleophiles to the parent 3-ulose (**3d**) results in products having the *arabino* stereochemistry, it was necessary to prepare a 2-epimeric reference compound in order to ascertain if the discrepancies of induced shifts are conformational or configurational in origin. As specific replacement of H atoms by deuterium effectively removes the spin interactions in the PMR spectrum that result from the proton undergoing replacement, the derivative of the unbranched analogue that incorporates deuterium at the branch point affords an ideal reference compound because its spectrum can be expected to exhibit essentially the same multiplicities as the compound whose structure is at issue. Accordingly, methyl 3.4-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-2-ulose was reduced with sodium borodeuteride under conditions corresponding to those reported for the analogous preparation of benzyl 3,4-*O*-isopropylidene-β-D-ribopyranoside.[17] The resulting methyl 2-*C*-deuterio-3,4-*O*-isopropylidene-β-L-ribopyranoside (**3a**), which is of the opposite (L) configurational series from the D compounds **3** and **3b**, serves also to illustrate the principle that, in a symmetric environment, the properties of enantiomorphs are indistinguishable;

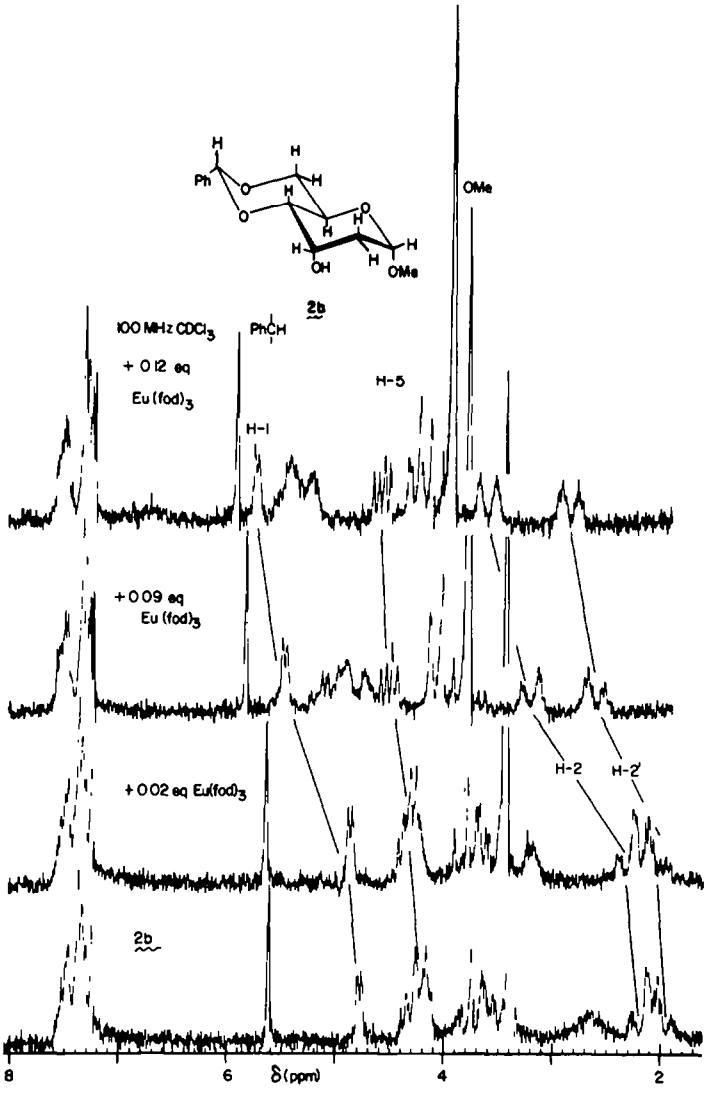

Fig 3. Unperturbed (lower) and progressively europium-shifted 100-MHz PMR spectra of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexopyranoside (**2b**) in chloroform-*d*.

if the spectra recorded for **3a** (Fig 6) had been determined in an optically active solvent or with a chiral[18] shift reagent, the results obtained by comparison of its shift gradients with those of compound **3** would have had little significance. As already noted, comparison of the data in Table 1 reveals major discrepancies between **3** and **3b** that signal a difference in configuration. In contrast, there is observed qualitative similarity and only modest, quantitative variations between shift gradients for the *ribo* glycoside and the branched-chain product **3**, allowing the *ribo* stereochemistry to be assigned with confidence to the latter. The slight quantitative differences between **3** and **3a** signal minor deviation from complete conformational uniformity and suggest that, for examples not constrained to conformational rigidity,[12] assignments based on comparisons with an epimeric pair of reference compounds are much more secure than interpretations with a single reference compound.

5-C-(*Benzoyloxymethyl*)-2,3-O-*cyclohexylidene*-1-O-p-*tolylsulfonyl*-1(R),2(S),3(S),5(R)-*cyclohexanetetrol*[15] (**4**). By graduated additions of Eu(fod)$_3$ to a solution of compound **4** in carbon tetrachloride, it was possible to obtain an almost completely separated, first-order NMR spectrum (Fig 7) for the polysubstituted, aliphatic ring. From the coupling data for these protons (Table 2; $J_{1,6'}$ large, $J_{4,6} \sim 1$ Hz) it is apparent that the low-field H-4 and H-6 signals are identifiable as equatorial

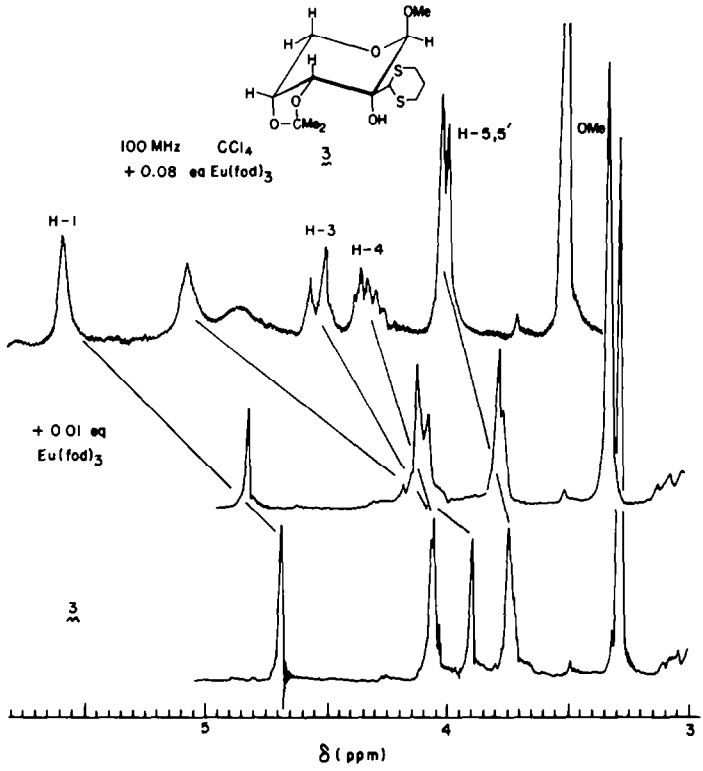

Fig 4. Unperturbed (lower) and progressively europium-shifted 100-MHz PMR spectra of methyl 2-*C*-(1,3-dithian-2-yl)-3,4-*O*-isopropylidene-β-D-ribopyranoside (3) in carbon tetrachloride.

protons, and H-1 is axially disposed. Accordingly, it is possible to specify for compound **4** the chair conformation illustrated.

The data of Table 1 reveal large shift-gradients for both of the exocyclic methylene protons, indicating that bridging between the hydroxyl group and O–5′ is strongly favored; the absence of asymmetrically substituted centers proximal to C-5 restricts the utility of information derived from this feature. It is, however, also recorded in Table 1 that the endocyclic methylene resonances exhibit different shift-gradients, increasing in the order H-4(eq) > H-4′(ax) ~ H-6(eq) > H-6′(ax). These two observations taken together suggest that an alternative favored site for bidentate coordination bridging from O–5 exists on the underside of the ring as drawn and proximal to H-4(eq); this secondary site is certainly O–3, the axially disposed acetal O atom of the isopropylidene group, rather than O–1 or O–2, both of which are in equatorial orientation. Thus the 5-OH group is *cis* to O–3, defining the stereochemistry of the tertiary center as (*R*).

General considerations. The treatment developed here for compounds **1**, **2**, **2a**, and **3** provides an approach that can be applied quite generally to any similar stereochemical problem that fulfils a few basic conditions, namely (*a*) that suitable reference compounds are available; (*b*) that the compounds can be dissolved in a noncoordinating solvent; (*c*) that a reasonable degree of conformational uniformity prevails throughout the series of examples related to the structure; and (*d*) that the same coordinating sites are present in each example in the series. The elucidation afforded for structure **4** is an atypical example in that sufficient information can be derived from the shifted PMR spectrum of the unknown compound itself to permit specification of the stereochemistry about the tertiary center.

Table 2. Coupling constants measured for 5-*C*-(benzoyloxymethyl)-2,3-*O*-cyclohexylidene-1-*O*-*p*-tolylsulfonyl-1(*R*),2(*S*),3(*S*),5(*R*)-cyclohexanetetrol (**4**) in CCl_4 at 100 MHz

Coupled protons *m*, *n*	$J_{m,n}$(Hz)	Coupled protons *m*, *n*	$J_{m,n}$(Hz)
1,2	6·0	1,6	4·6
2,3	6·0	1,6′	9·8
3,4	~ 4	6,6′	13·9
3,4′	3·7	4,6	~ 1
4,4′	16·0	5a′,5b′	11·0

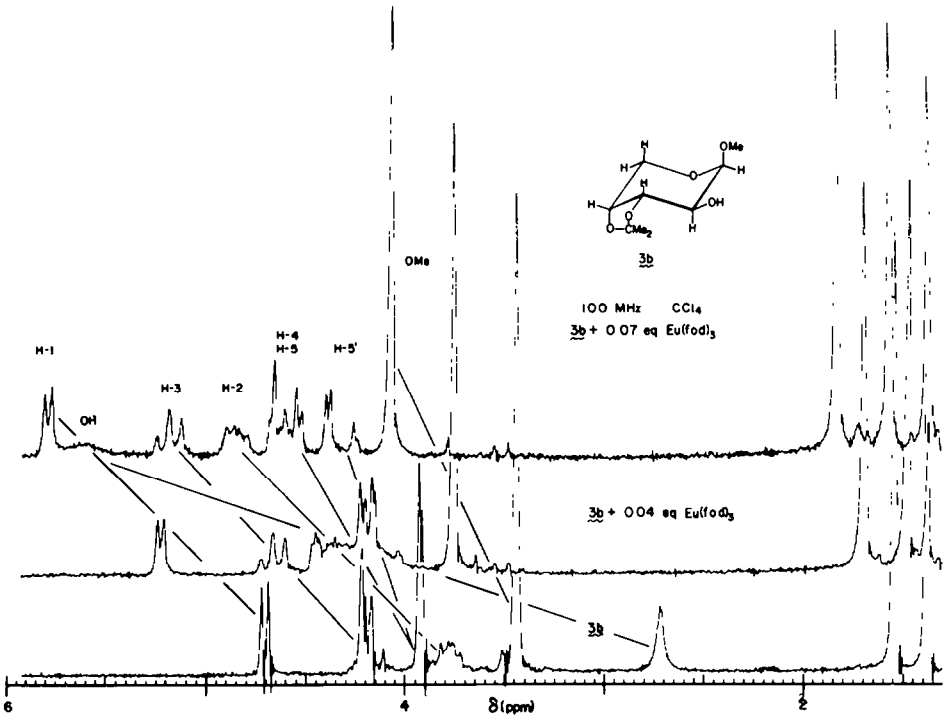

Fig 5. Unperturbed (lower) and progressively europium-shifted 100-MHz PMR spectra of methyl 3,4-*O*-isopropylidene-β-D-arabinopyranoside (**3b**) in carbon tetrachloride.

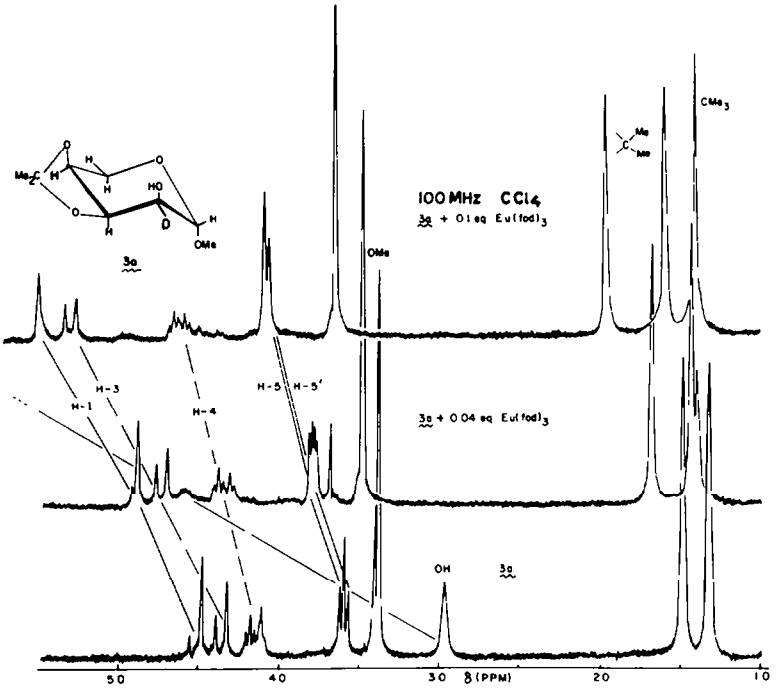

Fig 6. Unperturbed (lower) and progressively europium-shifted 100-MHz PMR spectra of methyl 2-*C*-deuterio-3,4-*O*-isopropylidene-β-L-ribopyranoside (**3a**) in carbon tetrachloride.

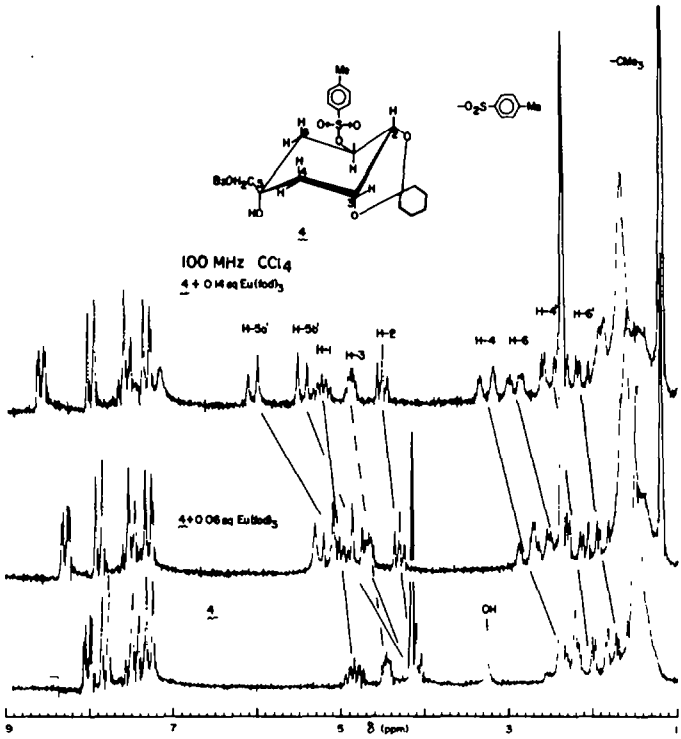

Fig 7. Uaperturbed (lower) and progressively europium-shifted 100-MHz PMR spectra of 5-*C*-benzyloxymethyl-2,3-*O*-cyclohexylidene-1-*O*-*p*-tolylsulfonyl-1(*R*), 2(*S*), 3(*S*), 5(*R*)-cyclohexanetetrol (**4**) in carbon tetrachloride.

In any application of this type, the inclusion of small amounts of competitive, coordinating impurities will have the effect of decreasing the measured value of the shift gradient. This factor is not critical for the application described here, as the ratios of shift-gradient values will remain approximately constant even though the absolute values are somewhat depressed. Thus the present method offers a convenient, general alternative to cyclization reactions,[19] electrophoresis of benzeneboronate or other complexes,[20] and infrared spectroscopy[20] as methods for determining the configuration at tertiary alcoholic centers in carbohydrate derivatives and other natural products. The structures determined here for **1**, **2**, **2a**, **3**, and **4** have been assigned independently by ^{13}C NMR spectroscopy.[21]

EXPERIMENTAL

100-MHz NMR spectra were recorded at ~ 30° on ~ 10% solns of each sample in CCl_4 when solubility permitted, otherwise in chloroform-*d*, by using a Varian HA-100 spectrometer in the frequency-sweep mode with ~ 5% Me_4Si added as internal reference and calibrant. Graduated amounts of a saturated solution of tris[1,1,1,2,-2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dionato]europium(III) ($Eu(fod)_3$) in CCl_4 were added dropwise (with vigorous mixing) between spectral determinations until sufficient information had been accumulated; relative concentrations of the tertiary alcohols and $Eu(fod)_3$ were verified by integration of the *t*-Bu resonance of the shift reagent.

Methyl 2-C-*deuterio*-3,4-O-*isopropylidene*-β-L-*ribopyranoside* (**3a**) *and methyl 2-C-deuterio*-β-L-*ribopyranoside.* Methyl 3,4-*O*-isopropylidene-β-L-*erythro*-pentopyranosid-2-ulose[14] (1 g) was reduced with 1·5 equivts of $NaBD_4$ according to the procedure of Horton, *et al*,[22] to yield syrupy compound[23] **3a**, which was identified immediately by PMR (Fig 6). Deacetonation with a trace of mineral acid in dichloromethane for 24 hr at ~ 25° afforded 350 mg (45%) of methyl 2-*C*-deuterio-β-L-ribopyranoside, m.p. 81°; $[\alpha]_D^{25}$ + 101° (*c* 1, H_2O); mass-spectral data, *m/e* 134 (5%, $M^+ - \cdot OCH_3$); Jackson and Hudson[24] reported m.p. 83°, $[\alpha]_D$ − 105° (H_2O) for methyl β-D-ribopyranoside.

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