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SPECIFICALLY MERCURATED CARBOHYDRATE DERIVATIVES: MODELS FOR DETERMINATION OF THE STEREOSPECIFIC DEPENDENCIES OF MERCURY-199 N.M.R. PARAMETERS*†

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ABSTRACT

The proton and natural-abundance carbon-13 nuclear magnetic resonance spectra of a series of methyl 2-deoxy-2-mercuri-D-pyranosides have been measured and analysed. The ^{199}Hg–^{1}H and ^{199}Hg–^{13}C couplings, which were readily obtained from the ^{199}Hg satellite peaks, delineate the angular dependence of ^{3}J and ^{4}J couplings.

INTRODUCTION

As a continuation of a longstanding programme of using suitably substituted carbohydrate derivatives to evaluate the stereospecific dependencies of heteronuclear n.m.r. parameters[2–6], we now report data for a series of specifically mercurated derivatives that delineate the angular dependencies of several sets of mercury–proton and mercury–carbon coupling constants.

The seven stable isotopes of mercury have atomic weights of 196, 198, 199, 200, 201, 202, and 204, respectively; hence, any mercury derivative is a mixture of seven isotopically different compounds. Of the seven isotopes, only ^{199}Hg is effectively magnetic (16.86% abundant, spin 1/2); as a result, the resonances of the ^{1}H and ^{13}C nuclei of those molecules that bear a ^{199}Hg substituent close enough to experience spin coupling appear as a series of doublets. In practice these transitions are observed as a series of satellite peaks located symmetrically about, and having 10% of the intensity of, the resonances of those molecules that are substituted by the other mercury isotopes. Providing that the ^{1}H (or ^{13}C) n.m.r. spectrum of the compound of interest is reasonably well dispersed, it is a straightforward matter to identify the various satellite peaks and thereby determine the magnitudes of the ^{199}Hg–^{1}H (or ^{199}Hg–^{13}C) coupling constants. If the magnitudes of the ^{1}H–^{1}H coupling constants

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allow assignment of the overall conformation of the molecules, these experiments may permit the determination of the angular dependence of the ^{199}Hg couplings.

In the present study, we have used the well-known methoxymercuration reaction to synthesise a range of methyl 2-deoxy-2-mercuri-D-aldopyranosides in order to study their ^{1}H and natural-abundance ^{13}C n.m.r. spectra. Because these spectra are so well dispersed, we have been able to detect ^1J, ^2J, ^3J, ^4J, and ^5J couplings and have been able to assign stereospecific dependencies to several of these sets of couplings. This work was preceded by studies elsewhere of several series of organomercury derivatives, including two specifically mercurated derivatives[7]. We shall discuss some of these literature data later.

RESULTS AND DISCUSSION

The compounds studied here were prepared by the known methoxymercuration reaction[8] of four glycals, namely tri-*O*-acetyl-D-glucal (1), tri-*O*-acetyl-D-galactal (2), di-*O*-acetyl-D-xylal (3), and di-*O*-acetyl-D-arabinal (4). We discuss in detail here the spectral assignments for only one, representative compound; all other assignments were made by the same general procedures.

Treatment[8] of 1 with mercuric acetate in methanol gave a mixture of two products, which were treated with sodium chloride and separated by fractional crystallisation. The ^{1}H n.m.r. spectrum of one of these products (5), shown in Fig. 1, confirms that 5 has the structure methyl 3,4,6-tri-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-glucopyranoside. Although it is not possible to identify every individual ^{199}Hg satellite in that spectrum, sufficient of them are clearly resolved to permit complete assignment. In this context, it is important to note that each ^{199}Hg satellite must

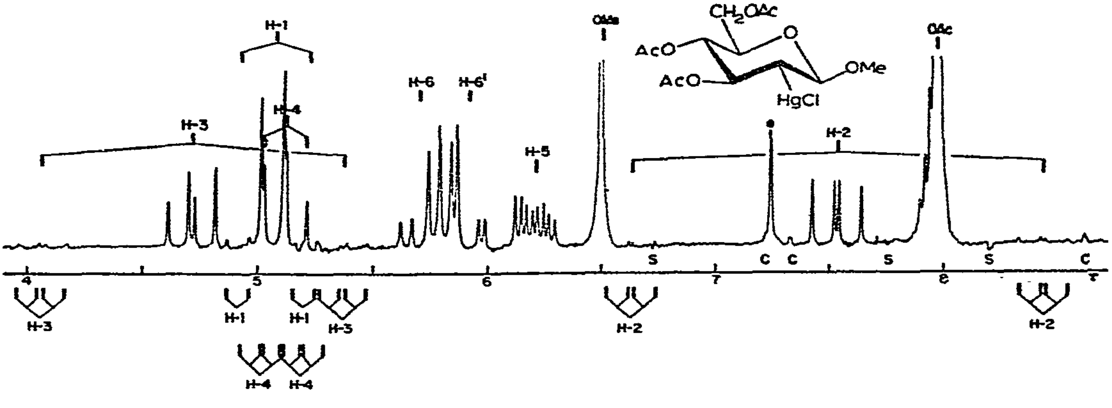


Fig. 1. Proton n.m.r. spectrum (100 MHz) of methyl 3,4,6-tri-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-glucopyranoside (5) in acetone-d_6 solution [NT 250, 65 μsec (90° pulse), AT 4 sec, SW 1000 Hz, 8K data points]. The general assignments are given above the spectrum and those of the ^{199}Hg satellites are given below the spectrum. (Note: Spinning sidebands are marked S, ^{13}C satellites are marked C and the peak marked * is residual H_2O in the solvent.)

evidence the same ^{1}H–^{1}H coupling constants as the equivalent ^{1}H resonance of the molecules that contain a non-magnetic isotope of mercury; it follows then, that careful measurement of the ^{1}H–^{1}H couplings provides important evidence in support of a particular satellite assignment. This concept clearly proves that the lowest-field satellite resonance at τ 4.72, which shows splittings of 11.7 and 8.9 Hz, must correspond to H-3, rather than the formerly[7] reported assignment to H-2, which would require splittings of 11.7 and 9.7 Hz.

For some of the other derivatives, it was necessary to study the ^{1}H n.m.r. spectra in several different solvents in order to assign all ^{199}Hg–^{1}H couplings; the spectra shown in Fig. 2 illustrate this point. The small, solvent-dependent variations in the shifts of H-4 and H-1 afford little assistance in assigning the normal proton resonances, but they greatly facilitate identification of the ^{199}Hg satellites.

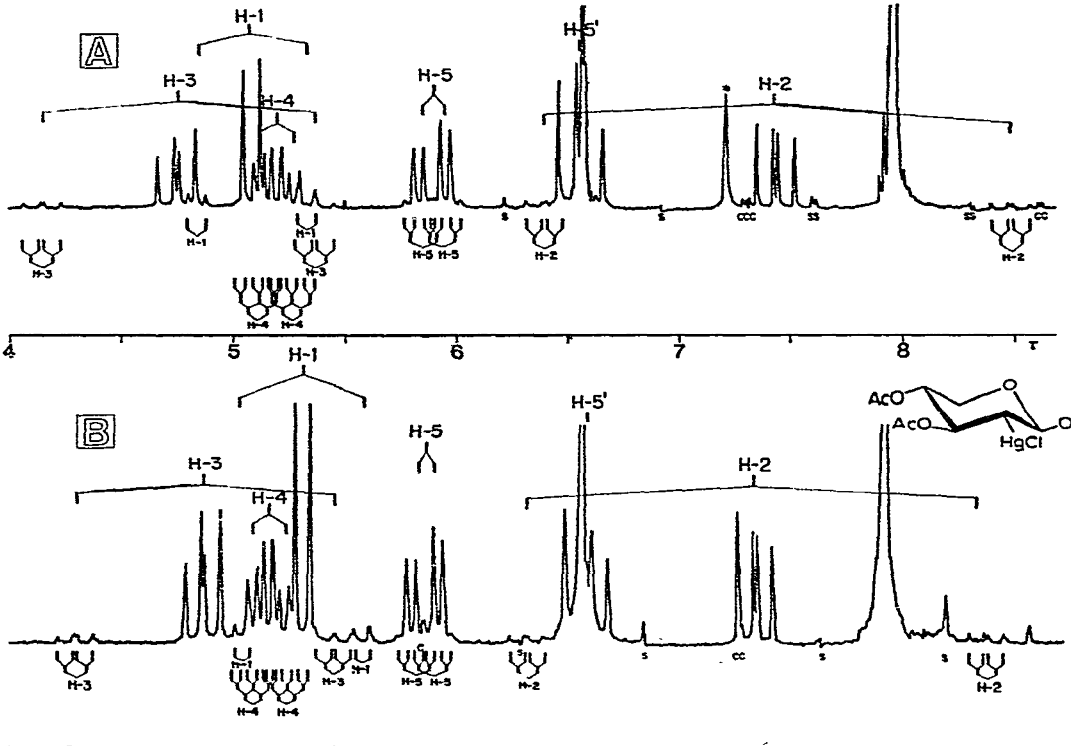


Fig. 2. Proton n.m.r. spectrum (100 MHz) of methyl 3,4-di-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-xylopyranoside (8); A, in acetone-d_6 solution and B, in chloroform-d solution. The assignments of the normal and of the ^{199}Hg satellite resonances are shown above and below the spectra, respectively. (Note: Spinning sidebands are marked S, ^{13}C satellites are marked C, and the residual H_2O is marked by *.)

Observation and assignment of the ^{199}Hg satellites of the ^{13}C resonances of 5 presented no great problem as the ^{13}C shifts are so well dispersed. The principal difficulty was simply the assignment of the ^{13}C resonances themselves and, in accord with our previous experiences, this was most rapidly accomplished by selective proton-decoupling (see Experimental Section); the spectra shown in Figs. 3 and 4 illustrate this technique. Assignments of the ^{199}Hg satellites could then be made by identifying those sets of satellites that were symmetrically disposed with respect to each of the principal resonances.

The ^{1}H chemical shifts and ^{1}H–^{1}H coupling constants observed for the derivatives **5–10** are summarised in Table I. The values are unexceptional, and in every instance they confirm both the gross stereochemistry of the products as well as their nominal conformations.

The ^{199}Hg–^{1}H couplings are listed separately in Table II. The values of the ^{2}J couplings vary between ~164 and 215 Hz, and, apart from a solvent dependence, there is no obvious, systematic reason for the observed variations. The ^{3}J couplings are more interesting. Three derivatives (**6**, **7**, and **9**) have a *trans*-antiparallel relation-

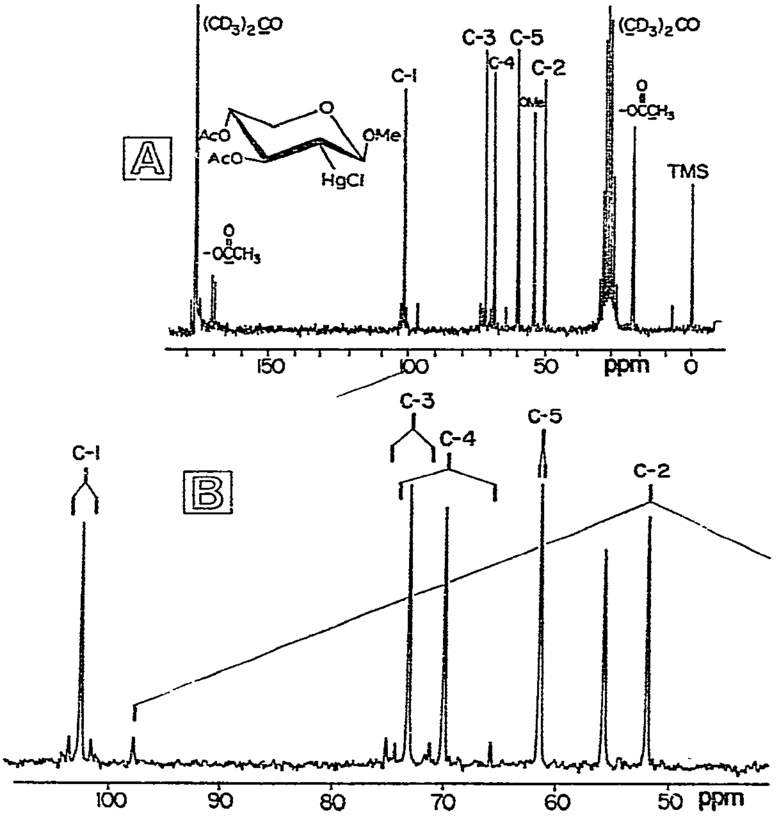


Fig. 3. The natural abundance, carbon-13 n.m.r. spectrum (20 MHz) of methyl 3,4-di-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-xylopyranoside (**8**) in acetone-d_6 solution: A, a complete spectrum (4 KHz sweep width); B, an expanded portion, showing the resonances of the ring carbon atoms, together with their ^{199}Hg satellites. Note the well resolved satellites of the C-1 and C-4 resonances; the splitting of the C-5 resonance was observed in the original spectrum as poorly defined shoulders.

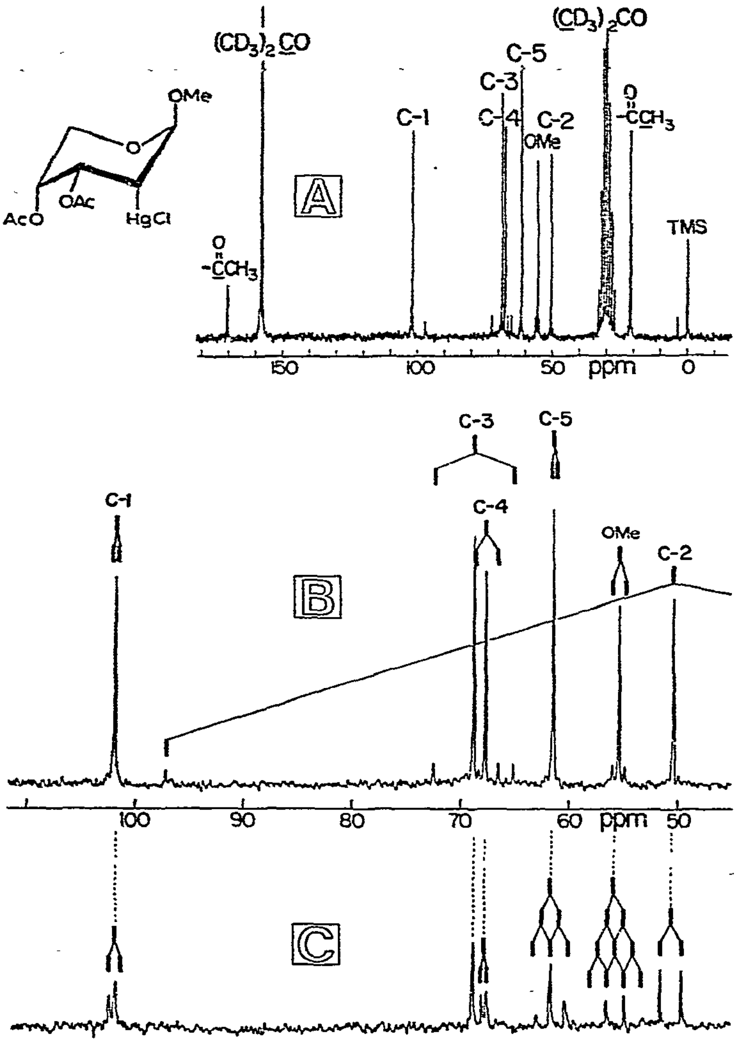


Fig. 4. Proton-decoupled, natural abundance, carbon-13 n.m.r. spectra of methyl 3,4-di-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-ribopyranoside (9) in acetone-d_6 solution: A, a complete (4 KHz sweep width) spectrum; B, an expanded portion showing the resonances of the ring-carbon atoms; C, the same expanded portion measured during selective irradiation of the H-3 resonance (at 5.78 p.p.m. to low field of Me_4Si) in order to identify the C-3 resonance. The multiplicities of the other resonances, which are only partially decoupled, are indicated diagrammatically.

ship between the ^{199}Hg–C-2 bond and the C-3–H-3 bond and they exhibit a substantially larger coupling (410–460 Hz) than that (110–131 Hz) observed for the examples (**5**, **8**, and **10**) having a gauche relationship of the two bonds.

This observation confirms other reports[9] that the gross angular-dependence of these couplings parallels that well documented for other vicinal ^{1}H-C–C-X couplings. More-detailed consideration of the couplings listed in Table II shows that the parallel-

TABLE I

PROTON MAGNETIC RESONANCE DATA FOR CHLOROMERCURIAL DERIVATIVES[a]

Compound	*H-1* $J_{1,2}$ $J_{1,3}$	*H-2* $J_{2,3}$ $J_{2,4}$	*H-3* $J_{3,4}$	*H-4* $J_{4,5}$ $J_{4,5'}$	*H-5* $J_{5,6}$ $J_{5,6'}$	*H-5'* $J_{5,5'}$	*H-6* $J_{6,6'}$	*H-6'*	*OMe*	*OAc*
5	5.06[b] (9.7)[c]	7.54 (11.7)	4.72 (8.9)	5.21 (9.8)	6.21 (5.0) (2.7)		5.71 (11.9)	5.92	6.50	7.98(2)[d], 7.99
6	4.77 (1.3) (0.6)	6.70 (5.6) (0.4)	4.24 (9.1)	4.94 (9.1)	[e]		[e]	[e]	6.65	8.01, 7.97, 7.96
7	4.62 (1.1) (0.7)	7.09 (5.5) (0.8)	4.21 (3.4)	4.62 (0.6)	[f]		[f]	[f]	6.64	8.04, 7.99, 7.79
8	5.09 (7.6)	7.43 (9.3)	4.75 (7.6)	5.20 (4.4) (7.6)	5.89	6.55 (11.7)			6.58	7.97, 7.95
9	4.81 (1.6) (0.7)	7.12 (5.2) (1.0)	4.22 (3.7)	4.83 (1.6) (2.5)	5.94	6.25 (12.9)			6.65	8.02, 7.83
10	5.21 (9.3)	7.20 (12.3)	4.72 (3.2)	4.78 (2.1) (1.5)	5.95	6.26 (13.3)			6.50	8.01, 7.91

[a] Measured as 0.3 molar solutions in acetone-d_6. [b] Chemical shifts (τ). [c] Coupling constants (Hz) in parentheses. [d] Number of acetate groups having identical shifts. [e] ABC system, τ 5.6–6.1. [f] ABC system, τ 5.6–6.0.

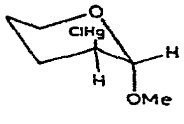
TABLE II

PROTON–MERCURY COUPLING CONSTANTS FOR CHLOROMERCURIAL DERIVATIVES[a]

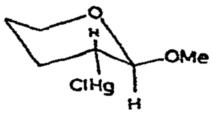
Compound	*Solvent*	*H-1*	*H-2*	*H-3*	*H-4*	*H-5*	*H-5'*	*H-6*	*H-6'*
5	acetone-d_6	30.2	181.0	131	17.5	0		0	0
	$CDCl_3$[b]	29	179	216	[c]	0		0	0
6	acetone-d_6	84	215	418	11	[c]		[c]	[c]
	$CDCl_3$	84	193	414	10	0		0	0
	C_6D_6	85	[c]	410	10.5	0		0	0
7	acetone-d_6	89	201.8	457.5	8.3	[c]		[c]	[c]
	$CDCl_3$	85.8	176.3	447.8	10.5	[c]		[c]	[c]
	C_6D_6	87.4	181.0	443.8	9.2	[c]		[c]	[c]
8	acetone-d_6	49.2	207.5	121	[c]	9	0		
	$CDCl_3$	53.4	206.2	115.5	15.5	8.0	[c]		
	C_6D_6[d]	59.8	215.0	110.2	10.8	10.8	0		
9	acetone-d_6	81.0	201	432	10–11	0	6.0		
	$CDCl_3$	80.7	164	433.6	11	0	5.1		
	C_6D_6[b]	81.5	177.0	432.4	12	0	[c]		
10	acetone-d_6	32.3	194.6	117.2	43.2	10.8	0		

[a] Concentrations were 0.3 molar, unless otherwise stated; couplings are expressed in Hz. [b] 0.2 molar. [c] Indeterminate. [d] 0.25 molar.

ism with ^{1}H-C–C-^{1}H couplings extends further. The vicinal couplings of ^{199}Hg to H-1 are systematically smaller than those to H-3, probably as a result of the electronegativity of the ring-oxygen atom. Further, the couplings to H-1 exhibit the well known configurational dependence, associated here with the orientation of the C-1–O-5 bond relative to the C-2–^{199}Hg bond. Thus, those compounds (**6**, **7**, and **9**) having the partial configuration **A** give larger couplings (81–89 Hz) than those found (29–49 Hz) for the compounds (**5**, **8**, and **10**) having the partial configuration **B**.

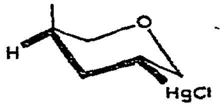


A



B

Another set of rationalizable ^{199}Hg–^{1}H couplings are those across four bonds to H-4; compound **10**, which has the "planar-M" (1,3-diequatorial) relationship (C) between the C-2–Hg and C-4–H-4 bonds, gives a larger coupling (43 Hz) than the other compounds, which have either the axial–axial (**6**) or axial–equatorial (**5**, **7**, **8**, and **9**) orientations. This again precisely parallels the dependence of the analogous ^{1}H-C–C-^{1}H couplings, and it would be of interest to determine the relative signs of these couplings.



C

A five-bond coupling between ^{199}Hg and H-5 is seen for compounds **8** and **10**, in which both H-5 and the mercury atom are equatorially disposed in the favored conformer; no equivalent coupling is observed for **9**, in which the C-2–Hg bond is axial, nor for **5** or **6**, in which the C-5–H-5 bond is axial. Such mercury–proton couplings over five bonds are normally observed only in arylmercury compounds[10].

The ^{13}C n.m.r. parameters for derivatives **5**–**10** are summarised in Table III. The chemical shifts show the trends that are now familiarly associated with spectra of peracetylated methyl hexopyranosides. The anomeric-carbon resonance appears downfield of all other ring-carbon signals, the shift of α-anomers falling ~2.2 p.p.m. to low field of the β-anomer counterparts. The equatorially oriented methyl groups each give a resonance at ~56.5 p.p.m., whereas the resonances of the axially oriented groups appear near 55.3 p.p.m.

The C-2 resonances are all shifted substantially (~17 p.p.m.), to high field of the other ring-carbon signals, and their field position is intermediate between that of an acetylated sugar and a deoxy sugar.

TABLE III

CARBON-13 CHEMICAL SHIFTS[a] AND CARBON-13–MERCURY-199 COUPLING CONSTANTS[b] MEASURED FOR CHLOROMERCURIAL COMPOUNDS IN ACETONE-d_6

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	$-OCH_3$	$-OCOCH_3$	$-OCOCH_3$
5	103.42	54.63	75.73	71.71	72.80	63.22	56.72	21.17, 20.66, 20.66	171.46, 170.68, 170.09
	(49.2)	(1855.5)	(120.4)	(225.2)	(8.2)	(11.2)	0		
6	101.09	56.20	72.04	71.15	69.10	63.35	55.22	21.12, 20.65, 20.65	170.65, 170.25, 170.12
	(12.3)	(1853.7)	(135.3)	(53.3)	0	0	(23.4)		
7	101.70	49.22	68.94	66.33	67.47	62.97	55.30	20.97, 20.97, 20.60	170.58, 170.06, 169.76
	(11.0)	(1879.7)	(148.4)	(36.2)	0	0	(24.9)		
8	103.00	52.56	73.79	70.67	62.15		56.39	21.21, 20.86	171.14, 170.13
	(39.7)	(1825.2)	(76.9)	(168.8)	~8[c]		0		
9	101.88	50.37	68.71[d]	67.62[d]	61.49[d]		55.43	21.08, 21.08	170.06, 169.94
	(9.0)	(1870.3)	(146.4)	(48.8)	~4[c]		(22.5)		
10	104.04	52.68	73.06	69.39	65.19		56.40	21.10, 20.86	170.59, 170.41
	(53.8)	(1837.3)	(116.7)	(144.4)	~5[c]		0		

[a] Expressed as p.p.m. downfield from Me_4Si. [b] In parentheses, measured in Hz. [c] Observed as shoulders on main peak. [d] Assignments not definite.

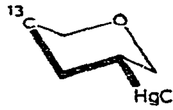
The ^{13}C–^{199}Hg couplings exhibit a number of interesting variations. The ^{1}J couplings appear to be relatively insensitive to their surroundings. The only obvious, systematic variation occurs when both the chloromercuri group and the acetoxyl group at C-4 occupy axial dispositions, as in 7 and 9, the coupling constant (1870–1880 Hz) being slightly larger than for other configurations (1825–1856 Hz).

Two-bond couplings, on the other hand, are very sensitive to environment. In a previous study by Kitching, Anet, and coworkers[11], it was concluded that electronegative oxy-functions appreciably increase coupling to the oxygenated carbon atom of organomercurials. On this basis, one would expect the geminal coupling of ^{199}Hg to C-1 to be larger than the coupling to C-2, whereas, in fact, the reverse is true. Both sets of results presumably result from the effect of increased electronegativity on negative coupling-constants.

More surprising, perhaps, is the fact that the geminal coupling to C-1 is invariably smaller for the *trans*-diaxial adducts than for the *trans*-diequatorial adducts. In both instances, the mercury atom maintains a *gauche* relationship with one of the oxy-functions on C-1 and a *trans* relationship with the other.

Such phenomena are not uncommon in ^{13}C n.m.r. spectroscopy; studies of substituted cyclopropanes[12] and halogenated ethylenes[13] have shown that J_{CCH}, is more positive, namely, of smaller magnitude, for the protons further away from the electronegative substituents. In these mercurated sugars, such distances appear to be approximately equal in both configurations. A similar situation occurs in aralkylmercury compounds[14], in which $J_{\mathrm{Hg-C-H}}$ is often different for the two protons of a methylene group bonded to mercury. The results most relevant to this study, however, are those of Kitching, Anet, and coworkers[11] on methoxymercuration products of cyclohexene. They found that an axial and an equatorial mercury atom couple differently to a vicinal carbon atom bearing an equatorial methoxyl group. As their values are the reverse of what the configuration at C-2 alone would predict, the configuration at C-1 is obviously important as well. Our data for the mercury-199 couplings to C-3 support their[11] findings, as $^{2}J_{\mathrm{Hg,C\text{-}3}}$ is slightly larger in those compounds having an axial chloromercuri group than in those having an equatorial one.

As anticipated, the ^{3}J couplings of ^{199}Hg to C-4 exhibit a dependence such that a *trans*-antiparallel relationship between the C-2–Hg and C-3–C-4 bonds (as in **D**)



D

E

gives a substantially larger coupling than the gauche relationship (**E**). Data for the hexopyranose derivatives 6 and 7 suggest that the magnitude of the gauche coupling is also dependent on the orientation of the acetoxyl substituent at C-4.

Several interesting, long-range couplings were also observed. Evidence of ^{4}J

couplings was found in the form of "shoulders" on either side of the C-5 resonance or, as in the spectrum of **5**, as distinct peaks. A more-definitive series of ^4J couplings involved the anomeric methoxyl carbon resonance; a *trans*-diaxial relationship as in **6**, **7**, and **9**, correlates with a substantial coupling (~23 Hz), whereas no coupling was detected for the gauche relationship.

An observed $J_{Hg,C\text{-}6}$ coupling, probably the first example in monoalkyl mercurials of a carbon–mercury coupling over five bonds, is exhibited by the fully equatorial product **5**. This isomer also exhibits a trend that appears to be common among organomercury derivatives[10,11,15], namely, an alternation in absolute magnitude of ^nJ coupling constants as "n" increases, superposed on a general decreasing trend. Thus,

$$^3J_{C\text{-}4,Hg} > {}^2J_{C\text{-}3,Hg} \text{ and } {}^2J_{C\text{-}1,Hg}, \text{ whereas } {}^5J_{C\text{-}6,Hg} > {}^4J_{C\text{-}5,Hg}.$$

At this point, it would be profitable to compare the results obtained here with those extant in the literature for other monoalkylmercury derivatives. To this end, the reader is referred to a recent comprehensive review article by Petrosyan and Reutov[16] on the n.m.r. spectroscopy of organomercury compounds.

Although the "Karplus" type of relationship evident in the vicinal proton–mercury coupling constants reported here is similar both in form and magnitude to that observed by Kreevoy and Schaefer[9], the vicinal carbon–mercury couplings observed differ significantly in magnitude from the values published by Kitching and coworkers[11]. The data[11] for eight alkylmercuric acetates show a Karplus type of relationship, the coupling constants being $J \simeq 275$ Hz when the dihedral angle is $\simeq 180°$ and $\simeq 75$ Hz when the angle is $\simeq 60°$; in cyclohexylmercury compounds a *trans*-antiplanar disposition of the C-3–C-2 and C-1–Hg bonds gives $J_{Hg,C\text{-}3}$ 184 Hz and a *gauche* relationship between these bonds gives $J_{Hg,C\text{-}3}$ 102 Hz. Our couplings are 144–225 Hz for a nominal 180° dihedral angle and 36–53 Hz for a nominal 60° angle. It is obvious from all of the foregoing data that vicinal carbon–mercury couplings are very sensitive to the orientation of nearby substituents, and it does not seem profitable to speculate further at this juncture.

According to Anet and coworkers[17], the absence of a chemical-shift difference between the γ-carbon atoms of two cyclohexylmercuric acetates, one having an equatorial acetoxymercuri group and the other an axial group, indicates a lack of steric compression in these molecules. This is consistent with the slight preference of the acetoxymercuri group for the axial disposition. It was thus of interest to see whether the introduction of chloromercuri substituents into the monosaccharides examined here had caused any steric compression, as evidenced by the ^{13}C-shifts.

If we consider the two derivatives (**5** and **6**) derived from D-glucal triacetate, we see that there is an upfield shift of only 0.56 p.p.m. in the C-4 resonance of the diaxial adduct **6** as compared with the diequatorial adduct **5**. At the same time, the change from an equatorial methoxyl group to an axial one leads to upfield shifts of 3.69 and 3.70 p.p.m. in the C-3 and C-5 resonances, respectively. Apparently, the chloromercuri group causes only slight, steric compression in this instance, much less than that caused by the methoxyl group. To place these numbers in some perspective, it should be remembered that an axial methyl group causes an upfield shift of 5 p.p.m. in the γ-carbon atoms of a cyclohexane ring[18]. Similarly, in the pyranose series, a comparison[19] of the ^{13}C spectra of the methyl 2,3,4,6-tetra-*O*-acetyl-D-glycopyranoside analogues of compounds **6** and **5** shows an upfield shift of 2.3 p.p.m. in the C-4 resonance as a result of the change in the configuration of the *O*-acetyl group at C-2.

On the other hand, compounds **9** and **10**, which have an axial acetate substituent on C-4, show an upfield shift of 1.77 p.p.m. in the C-4 resonance between the diequatorial adduct and the diaxial adduct, the shift differences in the C-3 and C-5 resonances being 4.35 and 3.70 p.p.m., respectively. Thus, as expected, there is greater steric compression in these molecules between C-4 and its substituents and the mercury substituent at C-2.

It is also possible, however, that the axial C-4 acetoxyl group coordinates weakly with the axial mercury atom. Kiefer *et al.*[20] have studied intramolecular coordination in monoalkyl mercurial derivatives. Although they did not test the acetate group, they did show that in addition to such basic donor groups as hydroxyl and dimethylamino, much weaker "basic" substituents such as chloride and bromide may exhibit intramolecular coordination with mercury. Unfortunately, our data cannot be compared directly to theirs, as they were studying such interactions by examining conformational changes.

Hatton, Schneider, and Siebrand have examined the effect of solvent coordination on proton–mercury and carbon–mercury coupling-constants in monoethylmercurials[21]. Other workers have studied such phenomena in dialkyl and diarylmercury compounds[21,22]. A comparison of the coupling-constant data for compounds **6** and **7** with that in the literature might lead to the inference that intramolecular coordination is occurring; however, such a conclusion appears unjustified, because large differences in coupling constants also occur between compounds **8** and **10**, in which no such coordination is possible.

Better evidence for such an effect is found in the chemical-shift data. In a comparison of compound **6** and compound **7**, the resonance of C-2 occurs 6.98 p.p.m upfield; C-3, 3.10 p.p.m. upfield; and C-4, 4.82 p.p.m. upfield. These are very large effects, indeed. Of course, some changes in these chemical shifts may be attributed solely to the change in configuration at C-4 without invoking intramolecular coordination. To measure this effect, it is only necessary to compare the data for the two diequatorial adducts **8** (which has an equatorial C-4 acetoxyl group), and **10**, which has an axial one; here the C-2 resonance moves 0.12 p.p.m. downfield, and is thus essentially unchanged, C-3 moves only 0.73 p.p.m. upfield, and C-4 moves only 1.28 p.p.m. upfield. Alternatively, comparison with the data of Bock and Pedersen[19] for methyl tetra-*O*-acetyl-α-D-glucopyranoside and for methyl tetra-*O*-acetyl-α-D-galactopyranoside reveals that all the ^{13}C resonances move upfield but by only1.2, 2.8, and 1.1 p.p.m. for C-2, C-3, and C-4, respectively.

Another way to consider the data is to look at the total upfield shifts for all six ring-carbon atoms. The difference in this sum is 16.29 p.p.m. for compounds 6 and 7 and only 7.4 p.p.m. for the fully acetylated methyl glycopyranosides. Clearly, then, we are not looking at a strictly additive effect. The chemical shifts of certain protons also change significantly, the H-2 resonance moving 0.39 p.p.m. upfield and the H-4 signal, 0.32 p.p.m., downfield.

The inference then, is that an axial chloromercuri group appears to create very little steric compression in the sugar ring, but an axial acetoxyl group contributes somewhat more. When both groups are axial, however, there is a very large effect on the carbon chemical shifts and a significant effect on the proton shifts. This effect may be due either to greatly increased steric compression or to a change in electron densities or bond hybridizations as a result of the intramolecular coordination of the axial mercury atom by an axial C-4 acetoxyl group.

Throughout this discussion we have assumed that the pyranoses strongly favor their nominal chair-conformations. Close examination of the proton–proton coupling constants and proton shifts shows no evidence for substantial conformational inhomogeneity, even for compound **8**, some of whose carbon–mercury and proton–mercury coupling constant values might lead one to suspect such inhomogeneity.

EXPERIMENTAL

General methods. — All solutions were concentrated with a Buchi rotary evaporator at a bath temperature below 30°. Melting points were determined with a Thomas–Hoover "Unimalt", capillary m.p. apparatus and are uncorrected. T.l.c. was performed on plates coated with silica gel G (Sigma Chemical Co., St. Louis, Mo.) using the solvent systems 2:1 ether–toluene and butanone–water (azeotrope). Spots were detected by spraying with 30% sulfuric acid in ethenol and heating on a hot plate.

N.M.R. measurements. — All ^1H n.m.r. measurements were made at 100 MHz with a Varian XL-100-15 instrument fitted with a Varian 620 L (16K) computer and a Linc Tape Unit (Model CO600). The ambient probe-temperature was 35°.

TABLE IV

CONDITIONS USED FOR MEASUREMENTS OF CARBON-13 SPECTRA

Compound	*Concentration*	*NT*[a]	*PD*[b]	*Assignment*[c]
5	0.2M	41,000	0.6	[d]
6	0.5M	34,000	0.6	[e]
7	0.5M	43,000	0.7	[d]
8	0.3M	34,000	0.7	[d]
9	0.34M	28,000	0.7	[d]
10	0.3M	52,000	0.7	[f]

[a] Number of transients. The pulse duration was 10 μsec, corresponding to a 45° pulse. The acquisition time was 1.023 sec. [b] Pulse delay (sec). [c] Assignments were made by selective proton decoupling in the designated solvent. [d] In acetone-d_6. [e] In benzene-d_6. [f] No assignment made.

The ^{13}C n.m.r. measurements were made at 20 MHz with a Varian CFT-20 (16K) instrument fitted with an Anadex Line Printer (Model DP-753). The conditions used for the various measurements are summarised in Table IV. Selective proton-decoupling experiments were performed by replacing the noise-modulated decoupler (supplied with the instrument) by a unit based on a Hewlett–Packard frequency synthesiser. The frequency output of the synthesiser was locked to that of the spectrometer via the 1-MHz output at J532 of the CFT-20 instrument. The proton decoupling-frequency required (79.542526 MHz) for selective decoupling of the carbon resonance of the tetramethylsilane was then found by trial and error. Chemical shifts of the proton resonances measured from the 100 MHz spectra were converted into frequency-offset values for the decoupler operating at ~80 MHz.

The solvents used for the n.m.r. measurements were all purchased from Norell Chemical Company (Landisville, N.J.) and were used as received: $CDCl_3$ (99.8%), $(CD_3)_2CO$ (99.5%), and C_6D_6 (99.5%).

Syntheses. — The reagents used were as follows: mercuric acetate (Alfa Inorganics, Beverly, Mass.) was dried over potassium hydroxide in a vacuum desiccator before use. Methanol (Matheson, Coleman and Bell, Norwood, Ohio) was dried over anhydrous calcium sulfate. D-Glucal triacetate (Aldrich, Milwaukee, Wisconsin), recrystallised from ethanol–light petroleum, had m.p. 52.5–54°, and was vacuum-dried before use. D-Galactal triacetate (Terochem Laboratories Ltd., Edmonton, Canada) was supplied as a 70% solution in benzene and was evaporated to a syrup prior to use. D-Xylal diacetate (Sefochem, Esnek Hayarden, Israel) was used as received, even though t.l.c. showed it to be substantially impure. D-Arabinal diacetate (Raylo Chemicals Ltd., Edmonton, Canada) was received as an oil that was essentially pure.

The methoxymercuration reactions followed the various literature procedures reasonably closely and only brief descriptions are given here.

Reaction of D-*glucal triacetate* (1). — Following the method of Inglis and Schwarz[24], methyl 3,4,5-tri-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-glucopyranoside (5) was obtained as white crystals, m.p. 172–174° {lit. values[24], 172–174° from ethanol and[8] 177–178° from methanol}, by storing the original mixture at 0° overnight. When the mother liquors were concentrated to "cloudiness" and stored for several days at 0°, crystalline masses of methyl 3,4,6-tri-*O*-acetyl-2-chloromercuri-2-deoxy-α-D-mannopyranoside (6) were obtained. Recrystallised from ethanol–acetone, 6 had m.p. 131–132° (lit. value[24] 112–114° from ethyl acetate–light petroleum).

Reaction of D-*galactal diacetate* (2). — The acetoxymercuri derivative obtained by the method of Takiura and Honda[8] was converted directly into methyl 3,4,6-tri-*O*-acetyl-2-chloromercuri-2-deoxy-α-D-talopyranoside (7). Three recrystallisations from methanol gave 7 as white crystals, m.p. 114–117° {lit. value[8] 120–121° from methanol}.

Reaction of D-*xylal diacetate* (3). — Because the starting material was so impure, only the known crystalline product of the reaction was isolated. The methyl 3,4-di-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-xylopyranoside (8) was recrystallised from methanol–diisopropyl ether as white crystals, m.p. 163–165°, (lit.[8] 167–168° from methanol).

Reaction of D-*arabinal diacetate* (**4**). — The two crystalline acetoxymercuri adducts obtained from the mixture were separately converted into their chloromercuri analogs. Methyl 3,4-di-*O*-acetyl-2-chloromercuri-2-deoxy-β-D-ribopyranoside (**9**) was obtained as white crystals from methanol, m.p. 141–143° {lit.[8] 142–142.5°}, from methanol and methyl 3,4-di-*O*-acetyl-2-chloromercuri-2-deoxy-α-D-arabinopyranoside (**10**) as white crystals from methanol, m.p. 208–211° (lit. value[8] 212.5°, from methanol).

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