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Preliminary communication

The angular dependence of the ^{1}H–^{199}Hg and ^{13}C–^{199}Hg coupling constants of specifically mercurated sugars

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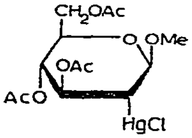
As part of a continuing programme on the use of carbohydrate derivatives as model systems for determining[1-3] the stereospecific dependencies of heteronuclear magnetic resonance parameters, we now report results obtained from the known[4] products (**1**,**2**) of the methoxy-mercuration of D-glucal triacetate.



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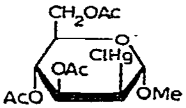


2

Mercury has seven stable isotopes: atomic weights 196, 198, 199, 200, 201, 202, and 204; two of these, ^{199}Hg (16.86%, spin 1/2) and ^{201}Hg (13.24%, spin 3/2), are magnetic in the n.m.r. sense. Only the former is of concern here since it splits into doublets the ^{1}H- and ^{13}C-resonances with which it couples; as a result, the transitions of those molecules bearing a ^{199}Hg-substituent generally appear as satellite peaks located symmetrically about, and each with 10% of the intensity of, the resonances of those molecules which contain the other mercury isotopes.

TABLE I

^{1}H–^{199}Hg COUPLING CONSTANTS (Hz)[a] FOR 1 AND 2 IN ACETONE-d_6 SOLUTION

Compound	*Proton*			
	H-1	*H-2*	*H-3*	*H-4*
1	30	181	131	17.5
2	84	215	418	11

[a] Measured with a Varian XL-100 (15) spectrometer operating at 100 MHz in the F.t. mode at 35°.

TABLE II

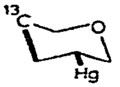
^{13}C-CHEMICAL SHIFTS[a] AND ^{13}C–^{199}Hg COUPLING CONSTANTS (Hz, IN PARENTHESES) FOR 1 AND 2 IN ACETONE-d_6 SOLUTION

Compound	*C-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*OMe*
1[b]	103.42 (49.2)	54.63 (1855.5)	75.73 (120.4)	71.71 (225.2)	72.80 (8.2)	63.22 (11.2)	56.72 *d*
2[c]	101.09 (12.3)	56.20 (1853.7)	72.04 (135.3)	71.15 (53.3)	69.10 *d*	63.35 *d*	55.22 23.4

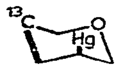
[a] Measured at 32.6° with a Varian CFT-20 instrument operating at 20 MHz; 45° pulse, 10μsec; AT, 1.023 sec; PD, 0.6 sec. Shift values, with respect to internal Me$_4$Si, and assignments confirmed by selective proton decoupling. [b] 0.2M; NT, 41,000. [c] 0.5M; NT, 34,000. [d] Indeterminate.

Tables I and II summarise the coupling constants obtained from the ^{1}H- and ^{13}C- n.m.r. spectra of methyl 3,4,6-tri-*O*-acetyl-2-(chloromercuri)-2-deoxy-β-D-glucopyranoside [**1**, m.p. 172–174° (from ethanol–acetone)] and methyl 3,4,5-tri-*O*-acetyl-2-(chloromercuri)-2-deoxy-α-D-mannopyranoside [**2**, m.p. 131–132° (from ethanol–acetone)].

Immediately obvious is the pronounced angular dependence of the ^{1}H–^{199}Hg couplings, which appears to conform with the general pattern predicted by Karplus[5]. The couplings of the anomeric protons also show a configurational dependence analogous to that previously documented for the corresponding proton[6], fluorine[1], and phosphorus[2] couplings. The angular dependence of the *vicinal* ^{13}C-couplings is clearly depicted in the partial structural formulae **1a** and **2a**.



1a (Φ ~180°)



2a (Φ ~60°)

Both these dependencies are in good accord with previous studies[7] of *mono*alkyl mercury derivatives; the difference between our value for the H-2–^{199}Hg coupling of **1** and that given by Horton *et al.*[8] is easily explicable.

The particular suitability of carbohydrate derivatives for heteronuclear studies of this kind is further exemplified by the wealth of other couplings listed in the Tables. These couplings, and those of other mercurated carbohydrates, will be discussed in detail elsewhere.

ACKNOWLEDGMENTS

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