STEREOCHEMISTRY OF THE METHOXYMERCURATION OF GLYCAL ACETATES

K. TAKIURA AND S. HONDA
Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka-fu (Japan)
(Received June 14th, 1971; accepted in revised form October 14th, 1971)

ABSTRACT

The methoxymercuration of the acetates of D-glucal, D-galactal, L-arabinal and D-xylal was studied by n.m.r. spectroscopy, and by stereoselective demercuration with thiourea, as well as by reductive demercuration with sodium borohydride. It is considered to be a *trans*-addition to the double bond to yield isomeric methyl glycosides having mercury attatched to C-2. The proportion of diaxial to diequatorial addition is strongly affected by the protecting groups at C-4 and C-5.

INTRODUCTION

In spite of the accumulation of information concerning addition reactions to unsaturated sugars, oxymercuration[1–4] has received relatively scant attention. It is a quantitative reaction, proceeding under mild conditions, and the resulting addition products may be important intermediates for carbohydrate synthesis. This article presents a stereochemical investigation of the methoxymercuration of the acetates of D-glucal, D-galactal, L-arabinal and D-xylal. It also describes the demercuration of the addition products with thiourea, and with sodium borohydride.

RESULTS AND DISCUSSION

The methoxymercuration of glycal acetates with mercuric acetate proceeded smoothly, and t.l.c. indicated that the reaction was complete after 2 h at room temperature. The n.m.r. spectra of the reaction mixtures, from which excess methanol and the acetic acid liberated had been removed by evaporation, provided useful information concerning the number of isomeric products. A single signal for methoxyl protons was observed at τ 6.64 in the reaction with D-galactal triacetate, whereas two methoxyl-proton signals were observed (at τ 6.4–6.7) with the acetates of D-glucal, L-arabinal, and D-xylal, indicating that two *O*-methyl derivatives of isomeric acetoxymercurial derivatives had been formed (Table I).

These isomers were separated by fractional crystallization from methanol–isopropyl ether, and the physical properties of the isolated products are recorded in Table II. The n.m.r. data obtained at 100 MHz are recorded in Table III. Of the seven products, compounds **3–7**, are new. Although compound **2** has been briefly

TABLE I

DETERMINATION BY N.M.R. SPECTROSCOPY OF THE PERCENTAGES OF ISOMERIC ACETOXYMERCURIAL PRODUCTS FORMED

Glycal acetate used	*Mercurial product*	*Chemical shift (τ) of OMe protons*	*Formed Percent*
D-Glucal triacetate	1	6.47	45
	2	6.65	55
D-Galactal triacetate	3	6.64	100
L-Arabinal diacetate	4	6.47	35
	5	6.63	65
D-Xylal diacetate	6	6.55	76
	7	6.60	24

TABLE II

YIELDS AND PHYSICAL PROPERTIES OF THE ACETOXYMERCURIAL PRODUCTS ISOLATED

Mercurial product	*Yield (%)*	*M.p. (°C)*	$[\alpha]_D$ (°) *in chloroform*
1	47[a]	159[b]	+9.5[c] (24°, *c* 1.0)
2	53	syrup	−13.4 (27°, *c* 1.0)
3	92	60–61	+19.2 (21°, *c* 1.0)
4	35	199–200	−5.6 (21°, *c* 0.9)
5	58	147–147.5	+21.4 (20°, *c* 1.1)
6	74	151–152	−41.4 (20°, *c* 1.1)
7	26	syrup	−22.4 (18°, *c* 1.4)

[a]lit.[2] 45%. [b]lit.[2] 161–162°. [c]lit.[2] +9.9° (31°, *c* 9.5, methanol).

reported[1], its structure remains uncertain. The structure of compound **1** has been established[1,2,11].

The acetoxymercurial products were quantitatively converted into halomercurial analogs whose properties are listed in Table IV.

$$\text{R–HgOAc} \xrightarrow{\text{NaX}} \text{R–HgX} \quad (\text{X:Cl, Br, I})$$

The mercurial derivatives underwent stereoselective demercuration with thiourea in methanol at room temperature (Table V), and syrupy products were obtained from **1**, **4**, and **6** in nearly quantitative yield after reaction for 2 h. After reaction for 5 h, compounds **2**, **3** and **7** gave only poor yields of crude, syrupy products purification of which was unsuccessful. The mercurial derivative **5** gave no product, even after reaction for 5 h.

In their i.r. spectra, the demercuration products from **1**, **4**, and **6** showed weak absorption at 1650–1660 cm^{-1} (C=C), characteristic of pseudoglycal derivatives, together with intense absorption at 1740 cm^{-1} (C=O). The n.m.r. spectra of the products from **1**, **4**, and **6** indicated that one acetoxyl group and one acetoxymercuri

TABLE III

N.M.R. PARAMETERS OF ACETOXYMERCURIAL PRODUCTS, MEASURED AT 100 MHz IN CHLOROFORM-*d*

Mercurial product	*Chemical shifts (τ) and multiplicities[a] of signals*									
	H-1	*H-2*	*H-3*	*H-4*	*H-5'[b]*	*H-5[b]*	*H-6[b]*	*H-6'[b]*	*OMe*	*OAc[c]*
1	5.37d	7.38t	4.80q	5.02t		6.2–6.5m	5.77q	5.79q	6.48s	7.90(1) 7.92(2) 7.95(1) 7.97 (1)
2	4.95d	6.58q	4.34q	5.03t		6.2–6.5m	5.81q	5.85q	6.67s	7.92(1) 7.98(3)
3	4.94d	7.16q	4.32q	4.63d		———	5.4–6.4m	———	6.67s	7.75(1) 7.98(2) 8.03(1)
4	5.49d	7.08q	4.88q	4.84q	6.10q	5.91q			6.49s	7.88(1) 7.97(1) 8.01(1)
5	4.98d	7.13q	4.32q	4.80q	6.12q	6.09q			6.66s	7.83(1) 7.98(2)
6	5.39d	7.38q	4.88q	5.16sx	6.81q	5.88q			6.57s	7.94(1) 7.97(1) 8.00(1)
7	5.23d	6.87q	4.62q	5.22sx	—5.9–6.2m—				6.58s	7.90(1) 7.93(1) 7.96(1)
	Absolute values of spin–spin coupling constants (Hz)									
	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$	
1	9.8	11.6	8.6	8.6			4.6[d]	3.0[d]	12.2[d]	
2	1.1	5.5	8.9	8.9			4.7[d]	2.9[d]	12.3[d]	
3	1.1	5.5	3.2	0.0			[e]	[e]	[e]	
4	9.6	13.3	3.0	1.7[d]	0.7[d]	13.4[d]				
5	1.3	5.2	3.0	1.6[d]	2.2[d]	13.3[d]				
6	7.9	10.0	8.2	4.4	3.7	11.6				
7	6.1	4.0	6.5	[f]	[f]	[f]				

[a]Multiplicities are designated: d, is doublet; t, triplet; q, quartet; sx, sextet; m, multiplet. [b]The C-5 proton resonating at lower field is designated H-5, and that resonating at higher field is designated H-5'. The C-6 proton resonating at lower field is designated H-6, and that resonating at higher field is designated H-6'. [c]The numbers in parentheses indicate number of acetoxyl groups. [d]Calculated by ABX analysis. [e]Unresolved ABC system. [f]Unresolved ABX system.

TABLE IV

PHYSICAL PROPERTIES OF HALOMERCURIAL DERIVATIVES

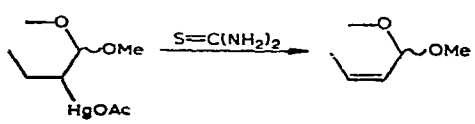
Mercurial derivative	*Appearance*			*M.p.* (°C)		
	Cl	*Br*	*I*	*Cl*	*Br*	*I*
1	needles	needles	plates	177–178[a]	178–179[b]	172–173[c]
2	syrup[d]	syrup	syrup	[e]		
3	needles	needles	prisms	120–121	117–118	130–130.5
4	needles	needles	needles	212.5	202–203	182–182.5
5	needles	needles	needles	142–142.5	164.5–165.5	167–168
6	needles	prisms	leaflets	167–168	156–157	157–158
7	syrup	syrup	syrup			

[a]lit.[1] 172–174°, lit.[2] 172–173°. [b]lit.[1] 176–178°. [c]lit.[3] 170–170.5°. [d]lit.[1] crystals. [e]lit.[1] 112–114°.

group had been eliminated from each mercurial precursor, whereas the methoxyl group remained present in all products. Two olefinic-proton signals were also observed at τ 3.9–4.1. The mass spectrum of the product from **1** gave essentially the same pattern as did methyl 4,6-di-*O*-acetyl-2,3-didehydro-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside[6,7], although minute variations of abundance were observed for minor fragment-ions, because of the slight difference in operating conditions. The mass spectra of the products from **4** and **6** gave identical patterns, and fragment-ions having *m/e* 172, 171, 142, 141, 129, 113, 111, 100, 99, 83, 81, and 69 corresponded to the molecular ion, and the ions c1′ (d1′), g1, c1″, d2, d3, c2″, g2, r1, r2, c2″ and c3′ of

TABLE V

DEMERCURATION OF THE ACETOXYMERCURIAL DERIVATIVES WITH THIOUREA



Mercurial precursor	*Reaction time (h)*	*Pseudoglycal derivative*	
		Yield (%)	$[\alpha]_D$ (°) *in chloroform*
1	2	89	+124.0 (27°, *c* 1.6)[a]
2	5	20	—
3	5	3	—
4	2	88	−74.0 (21°, *c* 1.2)
5	5	0	—
6	2	92	+164.3 (19°, *c* 1.2)
7	5	13	—

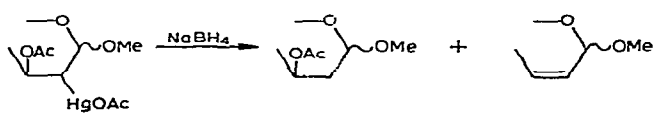
[a]+153.7 (31°, *c* 1.6, benzene). lit.[5] methyl 4,6-di-*O*-acetyl-2,3-didehydro-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside, +142 (20°, *c* 3.0, benzene).

methyl 4,6-di-*O*-acetyl-2,3-didehydro-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside, respectively[6]. The analytical data for these products are in accord with those calculated for the acetates of the methyl glycosides of pseudoglycals. Although the specific rotation of the product from **1** (+124.0° in chloroform, +153.7° in benzene) differed somewhat from the value reported (+143° in benzene[5]) for methyl 4,6-di-*O*-acetyl-2,3-didehydro-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside, the di-*p*-nitrobenzoate of the deacetylated product was identical with methyl 2,3-didehydro-2,3-dideoxy-4,6-di-*O*-*p*-nitrobenzoyl-β-D-*erythro*-hex-2-enopyranoside[5] by m.p. and microanalysis. Thus, demercuration with thiourea is considered to effect elimination of mercuric acetate between the acetoxymercuri group at C-2 and the adjacent acetoxyl group at C-3.

With sodium borohydride in methanol, all of the mercurial derivatives underwent almost instantaneous reductive demercuration to give 2-deoxy sugar derivatives in high yield (Table VI). These were converted into the parent 2-deoxy sugars by deacetylation in methanolic sodium methoxide, with subsequent mild hydrolysis.

TABLE VI

REDUCTIVE DEMERCURATION OF ACETOXYMERCURIAL DERIVATIVES WITH SODIUM BOROHYDRIDE

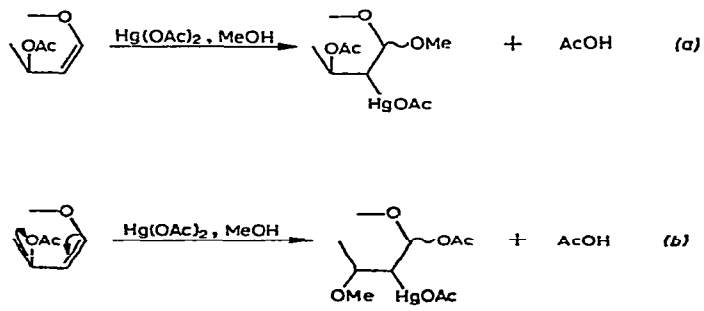


Mercurial precursor	*2-Deoxy sugar product*				*Pseudoglycal derivative*
	Yield (%)	*M.p.* (°C)	$[\alpha]_D$ (°) *in chloroform*	*Chemical shift of OMe* (τ)	*Yield* (%)
1	75	99–99.5[a]	−27.4 (22°, *c* 1.0)[b]	6.49	8
2	76	syrup	+100.5 (20°, *c* 1.0)	6.64	0
3	90	syrup	+143.0 (18°, *c* 1.0)	6.64	0
4	73	73–73.5	−11.7 (21°, *c* 1.0)	6.49	9
5	73	syrup	+193.6 (19°, *c* 1.1)	6.64	0
6	75	syrup	−121.9 (19°, *c* 1.0)	6.55	8
7	78	syrup	+16.7 (18°, *c* 1.0)	6.64	0

[a]lit.[1] 96–98°. [b]lit.[1] −24° (22°, *c* 1).

Pseudoglycal derivatives were formed as additional by-products from compounds **1**, **4**, and **6**.

Generally, oxymercuration is regarded as an addition reaction to unsaturated linkages, and hence the methoxymercuration of glycal acetates should proceed by addition to the 1,2-double bond, as in (*a*) of Scheme I. However, another type of reaction (*b*) is possible, since, in the presence of nucleophiles, the acetoxyl group at C-3 of glycal acetates is labile and easily released to generate a carbonium ion at C-3,



Scheme I

as in the well established allylic rearrangement of glycal acetates[8]. Deprotection of the demercuration products, however, provided evidence that the latter route is not operative; n.m.r.-spectral examination for methoxyl protons and identification by paper chromatography indicated that the products were not the 3-methyl ethers of 2-deoxy sugars, but only the parent 2-deoxy sugars. In consequence, it can be concluded that the methoxymercuration of glycal acetates proceeds through route (*a*), and that the mercurial products are methyl glycosides having mercury attatched to C-2.

The conformations of the acetoxymercurial products can be determined from the n.m.r. data in Table III, by considering the angular dependence of vicinal, spin–spin coupling-constants. The products obtained from the acetates of D-glucal, D-galactal, and L-arabinal (**1–5**) appear to exist in the *C1* conformation in chloroform-*d* solution. The large $J_{2,3}$ and $J_{3,4}$ values and small $J_{4,5}$ and $J_{4,5'}$ values of compound **6**, one of the two isomers obtained from D-xylal diacetate, accord with a *B2* conformation. For the other isomer from D-xylal diacetate (compound **7**), the *1B* or *2B* conformation appears feasible, although the coupling between H-4 and the C-5 methylene protons is unknown.

Since axial anomeric protons in pyranoses generally resonate at higher field than equatorial ones[9], and an analogous relationship has been reported with methoxyl protons in methyl pyranosides[10], the C-1 methoxyl group is evidently axial in compounds **2**, **3**, **5**, and **7**, and equatorial in **1**, **4**, and **6**. The chemical shifts of the methoxyl protons of the 2-deoxy sugar derivatives also accord with this correlation. Furthermore, the specific rotations of the 2-deoxy sugar derivatives indicate that the derivatives from **2**, **3**, **4**, and **7** are α anomers, and the others are β anomers, in agreement with the foregoing conformational evidence.

The $J_{1,2}$ and $J_{2,3}$ spin–spin coupling constants provide important information concerning the configuration at C-2. Both couplings are large for compounds **1**, **4** and **6**, indicating the triaxial orientation of H-1, H-2, and H-3. Small $J_{1,2}$ values and moderate $J_{2,3}$ values observed for **2**, **3**, and **5** indicate that H-2 is equatorial. The configuration of **7** at C-2 is not definitely established, although H-2 appears to be equatorial rather than axial.

The stereoselectivity of demercuration with thiourea was also indicative of the configuration at C-2. Since demercuration with thiourea is considered to involve elimination of mercuric acetate between C-2 and C-3, and the ring conformation and orientation of the acetoxyl group at C-3 in compounds **1** and **2** (a pair of isomers obtained from D-glucal triacetate) is regarded to be the same, the difference of reactivity between the two isomers on demercuration is attributable to the configuration at C-2. The structure of **1** can be deduced easily, from the unequivocal X-ray analysis of the corresponding chloromercuri derivative, to be methyl 2-acetoxymercuri-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside in the *C1* conformation[11], and this means that the 2-acetoxymercuri group in **1** is oriented equatorially. Accordingly, the acetoxymercuri group in the less reactive counterpart (**2**) is assigned in axial disposition. This rule of diequatorial elimination was applied to the other mercurial derivatives, and the acetoxymercuri groups at C-2 was assigned in axial disposition for **3** and **5**, and equatorial for **4** and **6**. Although the conformational difference between **6** and **7** must not be neglected, it is plausible that the acetoxymercuri group at C-2 of **7** should be axial rather than equatorial. Thus, the results obtained from stereoselective demercuration are concordant with the assignment based on n.m.r. data.

The presumed ring conformations and configurations at C-1 and C-2 are summarized in Table VII. It may be concluded that methoxymercuration of these

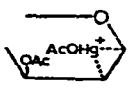
TABLE VII

PRESUMED CONFORMATIONS AND CONFIGURATIONS OF THE ACETOXYMERCURIAL PRODUCTS

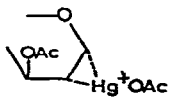
Mercurial compound	*Apparent conformation*	*Configuration*		*Proposed structure*
		OMe at C-1	*HgOAc at C-2*	
1	*C1*(D)	equatorial	equatorial	methyl 2-acetoxymercuri-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranoside
2	*C1*(D)	axial	axial	methyl 2-acetoxymercuri-2-deoxy-3,4,6-tri-*O*-acetyl-α-D-mannopyranoside
3	*C1*(D)	axial	axial	methyl 2-acetoxymercuri-2-deoxy-3,4,6-tri-*O*-acetyl-α-D-talopyranoside
4	*C1*(L)	equatorial	equatorial	methyl 2-acetoxymercuri-2-deoxy-3,4-di-*O*-acetyl-α-L-arabinopyranoside
5	*C1*(L)	axial	axial	methyl 2-acetoxymercuri-2-deoxy-3,4-di-*O*-acetyl-β-L-ribopyranoside
6	*B2*(D)	equatorial	equatorial	methyl 2-acetoxymercuri-2-deoxy-3,4-di-*O*-acetyl-β-D-xylopyranoside
7	*1B* or *2B* (D)	axial	axial	methyl 2-acetoxymercuri-2-deoxy-3,4-di-*O*-acetyl-α-D-lyxopyranoside

glycals proceeds through diaxial addition for compounds **2**, **3**, **5**, and **7**, and by diequatorial addition for **1**, **4**, and **6**; some uncertainty remains for **7**. The proportion of diaxial to diequatorial product was increased by introduction of axial acetoxyl groups at C-4, and was decreased by the presence of an equatorial acetoxyl group at C-5. It is noteworthy that, in the case of D-galactal triacetate, only diaxial addition occurred (giving compound **3**). Again, the boat-like conformations of the mercurial derivatives from D-xylal diacetate are considered possible. These abnormal conformations may be attributed to a possible interaction between the mercury atom and the carbonyl function of the C-4 acetoxyl group.

Adopting the intermediate "mercurinium ion" theory[12], diaxial and diequatorial adducts are expected from the mercurinium ions, *A* and *B*, respectively. The protecting groups at C-4 and C-5 play an important role, presumably through carbonyl–mercury interaction, in controlling the proportion of mercurinium ions formed at either side of the double bond.



A



B

EXPERIMENTAL

General. — Melting points were determined on a hot stage with a Yanagimoto micro melting-point apparatus and are uncorrected. Specific rotations were determined in a 1-dm tube. I.r. spectra were observed with a Hitachi EPI G-2 i.r. spectrophotometer. N.m.r. spectra were measured at 100 MHz on a JNM-4H spectrometer for the acetoxymercurial derivatives, and at 60 MHz on a Hitachi R-20B spectrometer for the other compounds. Spin-decoupling experiments were conducted with a R-201SD proton spin-decoupler operating in the frequency-sweep mode, and chemical shifts are expressed on the τ scale for 10% solutions in chloroform-*d* at 25° with tetramethylsilane as the internal standard. The spin–spin coupling constants of the methylene protons in the acetoxymercurial derivatives were calculated by ABX analysis, except for compound **6**. The other spin–spin coupling constants are the direct peak-spacings. Mass spectra were obtained with a Hitachi RM-60 instrument at an ionization potential of 70 eV, and at an ion-source temperature of 240°. T.l.c. was performed on microscope slides coated with Wakogel B-5, by using the solvent systems 7:3 benzene–ethyl acetate for the mercurial derivatives and 1:1 ether–*n*-hexane for the demercuration products. Spots were visualized by spraying with sulfuric acid, followed by heating the plates in an oven. Descending paper chromatography (p.c.) was carried out on Whatman No. 1 filter paper with *n*-butanol–acetic acid–water (4:1:5, upper phase, solvent *A*) and *n*-butanol–pyridine–water (6:4:3, solvent *B*) at 25°. The spots were detected by alkaline silver nitrate[13]. 2-Deoxy sugars were detected also with cysteine–sulfuric acid[14] as pink spots. R_G values represent the mobility relative to D-glucose. G.l.c. was performed with a Hitachi K-23 instrument equipped with a

hydrogen-flame ionization detector. A stainless-steel column (2 m) containing SE-30 was used at 120°, and the carrier gas (nitrogen) was regulated at a flow rate of 60 ml/min. Microanalysis for carbon and hydrogen in the mercurial derivatives was performed with a modified Yanagimoto MC-2 apparatus equipped with a gold net to remove mercury vapour. Mercury was determined cheletemetrically by the method described by Kinoshita *et al.*[15]. All evaporations were effected below 40° under diminished pressure.

Glycal acetates. — The acetates of L-arabinal and D-xylal were obtained from the corresponding acetylated pentosyl bromides by treatment with zinc dust[16]. The acetates of D-glucal and D-galactal were prepared from the corresponding hexoses in one operation[17]. The crude products were purified from peracetylated sugars by column chromatography on Wakogel C-200 with 7:3 benzene–ethyl acetate as eluant.

N.m.r. spectra of reaction mixtures from the methoxymercuration of glycal acetates. — Mercuric acetate (Wako Pure Chemicals Co. Ltd., 0.1 mmole) and the respective glycal acetates (0.1 mmole) were dissolved in abs. methanol (0.5 ml) and the solutions were kept for 2 h at 25°. T.l.c. of the reaction mixtures showed that the glycal acetates had disappeared completely, and the products were detected at the base line. The reaction mixtures were evaporated to dryness, and n.m.r. spectra were recorded at 60 MHz with the resultant samples.

Methoxymercuration of glycal acetates. — Mercuric acetate (10.0 mmole) and glycal acetates (10.0 mmole) were dissolved in abs. methanol (20 ml), and the solutions were kept for 2 h at room temperature. After refrigeration overnight, the reaction mixtures were fractionated as follows. The yields of crude products and physical properties of the purified products are summarized in Table II. The i.r. spectra of all of the products gave intense absorption bands at 1570–1630 cm^{-1} (C=O of HgOAc) and at 1725–1742 cm^{-1} (C=O of OAc).

Methoxymercuration of D-*glucal triacetate.* — The reaction mixture was evaporated to dryness, and the residual syrup was redissolved in hot methanol (2 ml), and boiling isopropyl ether (40 ml) was added. Upon storage, followed by refrigeration, crystals of **1** separated. Recrystallization from methanol afforded needles.

Anal. Calc. for $C_{15}H_{22}HgO_{10}$: C, 32.00; H, 3.94; Hg, 35.64. Found: C, 32.18; H, 4.01; Hg, 35.94.

The mother liquor of **1** was evaporated to dryness to give syrupy **2**. Attempted crystallization from various solvents was unsuccessful.

Methoxymercuration of D-*galactal triacetate.* — The reaction mixture was evaporated to dryness, and the resulting solid mass was redissolved in hot methanol (2 ml), and boiling isopropyl ether (40 ml) was added. Upon storage, followed by refrigeration, crystals of **3** separated. Recrystallization from methanol afforded large plates.

Anal. Calc. for $C_{15}H_{22}HgO_{10}$: C, 32.00; H, 3.94, 35.64. Found: C, 32.22; H, 3.97; Hg, 35.94.

Methoxymercuration of L-*arabinal diacetate.* — The mercurial derivative **4** separated from the reaction mixture as fine crystals, which were collected and recrystallized from methanol to give needles.

Anal. Calc. for $C_{12}H_{18}HgO_8$: C, 29.36; H, 3.70; Hg, 40.87. Found: C, 29.56; H, 3.64; Hg, 40.99.

The filtrate from **4** was evaporated to dryness. The residue was redissolved in hot methanol (2 ml), and boiling isopropyl ether (40 ml) was added. Upon storage, followed by refrigeration, crystals of **5** separated, which were collected and recrystallized from methanol to give prisms.

Anal. Calc. for $C_{12}H_{18}HgO_8$: C, 29.36; H, 3.70; Hg, 40.87. Found: C, 29.62; H, 3.77; Hg, 40.97.

Methoxymercuration of D-*xylal diacetate.* — Part of the product **6** separated from the reaction mixture. The filtrate was evaporated to dryness, and the residue was redissolved in hot methanol (2 ml), and boiling isopropyl ether (40 ml) was added. Upon storage followed by refrigeration, a second crop was obtained. The combined crops were recrystallized from methanol to give needles.

Anal. Calc. for $C_{12}H_{18}HgO_8$: C, 29.36; H, 3.70; Hg, 40.87. Found: C, 29.67; H, 3.92; Hg, 41.09.

The filtrate from the second crop was evaporated to dryness to give syrupy **7**, which failed to crystallize from various solvents.

Conversion of the acetoxymercurial derivatives into halomercurial analogs. — The acetoxymercurial derivatives (1 mmole) were dissolved in methanol (3 ml) and M aqueous solutions of sodium halides (1 ml) were added. Upon storage followed by refrigeration, crystals of the halomercurial derivatives separated almost quantitatively; these were collected and recrystallized from methanol.

Demercuration of the acetoxymercurial derivatives with thiourea. — The aceoxymercurial derivatives (2.0 mmoles) and thiourea (10.0 mmoles) were dissolved in abs. methanol (20 ml), and the solutions were kept at room temperature. At intervals, the reaction solutions were monitored by t.l.c.. The fast-moving spots of the demercuration products, giving a deep violet color ($R_F \sim 0.7$), were observed after reaction for 2 h with **1**, **4**, and **6**, whereas only faint spots were detected after reaction for 5 h with **2**, **3**, and **7**. No demercuration products were detected from **5**, even after reaction for 5 h. Wakogel C-200 (1 g) was added to the reaction mixtures, and the mixtures were evaporated to dryness in a rotary evaporator. The products adsorbed on resulting gels were resolved on a Wakogel C-200 column (1.5 × 30 cm). The yields of the syrupy pseudoglycal derivatives are summarized in Table V. T.l.c. of all of the products gave single spots, and g.l.c. indicated that the products from **1**, **4**, and **6** were homogeneous (retention time relative to D-glucal triacetate: 0.58, 0.091, and 0.098, respectively), but the products from other mercurials were contaminated with some impurities. Attempted purification of the latter products by column chromatography with various solvent systems was unsuccessful. The specific rotations of the products from **1**, **4**, and **6** are also recorded in Table V; ν_{max}^{film} of the products from **1**, **4**, and **6**: 1740 cm (strong, C=O of OAc), 1650–1660 cm^{-1} (weak, C=C); n.m.r. data (60 MHz): the product from **1**, τ 3.93 (2-proton broadened singlet, H-2 and H-3), 4.72 (1-proton quartet, H-4), 4.87 (1-proton singlet, H-1), 5.6–6.0 (3-proton multiplet, H-5, H-6, and H-6'), 6.49 (3-proton singlet, OMe), 7.87 (6-proton singlet, OAc); the product

from **4**, τ 4.09 (2-proton singlet, H-2 and H-3), 4.44 (1-proton triplet, H-4), 5.16 (1-proton triplet, H-1), 4.1-4.3 (2-proton multiplet, H-5 and H-5'), 6.56 (3-proton singlet, OMe), 7.93 (3-proton singlet, OAc); the product from **6**, τ 3.93 (2-proton doublet, H-2 and H-3), 5.0–5.2 (1-proton multiplet, H-4), 5.10 (1-proton singlet, H-1), 5.6–6.3 (2-proton multiplet, H-5 and H-5'), 6.56 (3-proton singlet, OMe), 7.91 (3-proton singlet, OAc); mass-spectrometric data: the product from **1**, *m/e* 244, 243, 213, 185, 183, 171, 153, 142, 141, 139, 129, 113, 112, 111, 110, 109, 101, 100, 99, 97, 87, 85, 84, 83, 82, 81, 71, 70, 69, 62, 57, 55, 54, 53, 43, 40, and 39; the products from **4** and **6** (identical patterns), *m/e* 172, 171, 142, 141, 130, 129, 113, 112, 111, 101, 100, 99, 98, 97, 87, 85, 84, 83, 82, 81, 73, 72, 71, 70, 69, 68, 59, 57, 55, 53, 52, 51, 45, 44, and 43. Analytical data for the products from **1**, **4** and **6** are recorded in Table VIII.

TABLE VIII

ANALYTICAL DATA OF THE PSEUDOGLYCAL DERIVATIVES

Mercurial product	*Formula*	*Calc.*		*Found*	
		C	*H*	*C*	*H*
1	$C_{11}H_{16}O_6$	54.09	6.60	54.24	6.56
4	$C_8H_{12}O_4$	55.80	7.03	55.97	6.99
6	$C_8H_{12}O_4$	55.80	7.03	55.80	7.16

The product from **1** (268 mg, 1.10 mmole) was dissolved in 0.05M methanolic sodium methoxide and the solution was kept in a refrigerator for 1 h. T.l.c. showed that the starting material had disappeared completely and a spot of the deacetylated product was detected at the starting line. The reaction solution was deionized by passing through small columns of Amberlite IR-120 (H^+) followed by Amberlite IRA-400 (OH^-), and evaporated to dryness to give a syrup; $[\alpha]_D^{27}$ +71.1° (*c* 3.5, methanol); R_G 3.34 (solvent *A*). The syrup was dissolved in dry pyridine (7 ml) and *p*-nitrobenzoyl chloride (390 mg, 2.10 mmole) was added. After being kept for one day at room temperature, followed by refrigeration overnight, the reaction solution was evaporated to dryness to give a crystalline mass, which was taken up in chloroform (10 ml). The chloroform layer was washed with 0.5M sulfuric acid (10 ml), with saturated aqueous sodium hydrogen carbonate, (20 ml), and finally with water. The chloroform layer was dried over calcium chloride and evaporated to dryness to give the crystalline di-*p*-nitrobenzoate of the methyl glycoside of pseudoglucal (386 mg, 100%). Recrystallization from methanol afforded needles, m.p. 132–133° (lit.[5] 130–132°); $[\alpha]_D^{29}$ +164.1° (*c* 2.7, chloroform); n.m.r. data (60 MHz): τ 1.77 (4-proton singlet, aromatic protons), 1.79 (4-proton singlet, aromatic protons), 3.88 (2-proton broadened singlet, H-2 and H-3), 4.44 (1-proton quartet, H-4), 4.87 (1-proton singlet, H-1), 5.3–5.7 (3-proton multiplet, H-5, H-6 and H-6'), 6.48 (3-proton singlet, OMe).

Anal. Calc. for $C_{21}H_{18}N_2O_{10}$: C, 55.02; H, 3.96; N, 6.11. Found: C, 54.95; H, 3.97; N, 5.94,

Reductive demercuration of the acetoxymercurial product with sodium borohydride. — The mercurial products (2.0 mmoles) were dissolved in abs. methanol (20 ml) and sodium borohydride (100 mg) was added in small portions with cooling. In all cases, immediate precipitation of mercury was observed, and t.l.c. of the reaction mixtures showed the presence of fast-moving spots of 2-deoxy sugar derivatives having R_F 0.5–0.6. In the cases of **1**, **4**, and **6**, faint spots of pseudoglycal derivatives having R_F ~0.7 were also detected. Wakogel C-200 (1 g) was added to the reaction mixtures, which were then evaporated to dryness in a rotary evaporator. Application of the resulting gels to a Wakogel C-200 column (1.5 × 30 cm) impregnated with ether–*n*-hexane, followed by fractionation of the demercuration products with this solvent system, afforded the results summarized in Table V; n.m.r. data of the 2-deoxy sugar derivatives (60 MHz): τ 7.8–8.1 (9 protons for the products from **1**, **2**, and **3**; 6 protons for the products from **4**, **5**, **6**, and **7**, OAc), τ 6.4–6.7 (3-proton singlet, OMe), τ ~8 (2-proton multiplet, H-2 and H-2'), τ 4–7 (other ring-protons). The analytical data of the 2-deoxy sugar derivatives are recorded in Table IX.

TABLE IX

ANALYTICAL DATA FOR 2-DEOXY SUGAR DERIVATIVES

Mercurial precursor	*Formula*	*Calc.*		*Found*	
		C	*H*	*C*	*H*
1	$C_{13}H_{20}O_8$	51.31	6.63	51.12	6.55
2	$C_{13}H_{20}O_8$	51.31	6.63	51.65	6.55
3	$C_{13}H_{20}O_8$	51.31	6.63	51.57	6.60
4	$C_{10}H_{16}O_6$	51.72	6.94	51.88	6.96
5	$C_{10}H_{16}O_6$	51.72	6.94	51.88	7.11
6	$C_{10}H_{16}O_6$	51.72	6.94	51.63	6.99
7	$C_{10}H_{16}O_6$	51.72	6.94	51.98	6.96

A portion of each 2-deoxy sugar derivative was deacetylated in 0.05M methanolic sodium methoxide for 2 h at room temperature. After deionization with resins, the reaction solution was evaporated to dryness. The residual syrup was heated in 5mM sulfuric acid for 2 h at 60°, and the hydrolyzate was neutralized with barium carbonate. The precipitate was removed by centrifugation, and the supernant was evaporated to dryness to give a syrup. The n.m.r. spectra of all of the syrupy products gave no signals of methoxyl protons; R_G values of the products (solvent *A*): from **1** and **2**, 1.70 (authentic 2-deoxy-D-*arabino*-hexose, 1.70); from **3**, 1.55 (authentic 2-deoxy-D-*lyxo*-hexose, 1.55); from **4** and **5**, 1.94 (authentic 2-deoxy-L-*erythro*-pentose, 1.94); from **6** and **7**, 2.02 (authentic 2-deoxy-D-*threo*-pentose, 2.02); R_G values of the products (solvent *B*): from **1** and **2**, 1.38 (authentic 2-deoxy-D-*arabino*-hexose, 1.38); from **3**, 1.26 (authentic 2-deoxy-D-*lyxo*-hexose, 1.26); from **4** and **5**, 1.40 (authentic 2-deoxy-L-*erythro*-pentose, 1.41); from **6** abd **7**, 1.51 (authentic 2-deoxy-D-*threo*-pentose, 1.51). The authentic sample of 2-deoxy-D-*arabino*-hexose

was purchased from the Sigma Chemical Co., Authentic samples of 2-deoxy-D-*lyxo*-hexose[18], 2-deoxy-L-*erythro*-pentose[19] and 2-deoxy-D-*threo*-pentose[20] were prepared from the corresponding glycals.

Pseudoglycal derivatives were identified by comparative mass spectrometry with the demercuration products formed by thiourea.

ACKNOWLEDGEMENT

The authors wish to thank Dr. Y. Terawaki for recording the 100-MHz n.m.r. spectra.

REFERENCES

1 G. R. INGLIS, J. C. P. SCHWARZ, AND L. MCLAREN, *J. Chem. Soc.*, (1962) 1014.
2 P. T. MANOLOPOULOS, M. MEDNICK, AND N. N. LICHTIN, *J. Amer. Chem. Soc.*, 84 (1962) 2203.
3 J. H. LEFTIN AND N. N. LICHTIN, *Israel J. Chem.*, 3 (1965) 107.
4 J. P. MARSH, C. W. MOSHER, E. M. ACTON, AND L. GOODMAN, *Chem. Commun.*, (1967) 973.
5 A. ROSENTHAL AND J. N. C. WHYTE, *Can. J. Chem.*, 46 (1969) 2245.
6 A. ROSENTHAL, *Carbohyd. Res.*, 8 (1968) 61.
7 R. J. FERRIER AND N. VETHAVIYASAR, *Carbohyd. Res.*, 13 (1970) 269.
8 R. J. FERRIER, *Adv. Carbohyd. Chem.*, 20 (1965) 67.
9 R. U. LEMIEUX, R. K. KULLING, H. J. BERNSTEIN, AND W. G. SCHNEIDER, *J. Amer. Chem. Soc.*, 80 (1958) 6098.
10 L. D. HALL, *Adv. Carbohyd. Chem.*, 19 (1964) 68; A. KONOWAL AND A. ZAMOJSKI, *Rocz. Chem.*, 44 (1970) 1607.
11 H. W. W. EHRLICH, *J. Chem. Soc.*, (1962) 509.
12 H. J. LUCAS, F. R. HEPNER, AND S. WINSTEIN, *J. Amer. Chem. Soc.*, 61 (1939).
13 N. E. TREVELYAN, D. P. PROCTER, AND J. S. HARRISON, *Nature*, 166 (1950) 444.
14 J. G. BUCHANAN, *Nature*, 168 (1951) 1091.
15 S. KINOSHITA AND K. HOZUMI, *Microchem. J.*, 8 (1964) 79.
16 P. A. LEVENE AND T. MORI, *J. Biol. Chem.*, 83 (1929) 803.
17 B. HELFERICH, E. N. MULCAHY, AND H. ZIEGLER, *Chem. Ber.*, 87 (1954) 233.
18 W. G. OVEREND, F. SHAFIZADEH, AND M. STACEY, *J. Chem. Soc.*, (1951) 992.
19 R. E. DERIAZ, W. G. OVEREND, M. STACEY, E. G. TEECE, AND L. F. WIGGINS, *J. Chem. Soc.*, (1949) 1879.
20 W. G. OVEREND, F. SHAFIZADEH, AND M. STACEY, *J. Chem. Soc.*, (1952) 255.