2,6-Diacetamido-9-(tetra-*O*-acetyl-β-D-glucofuranosyl)purine.—Ethyl tetra-*O*-acetyl-1-thio-α-D-glucofuranoside (IIa) was converted to a sirupy tetra-*O*-acetyl-D-glucofuranosyl bromide by the method of Weygand and co-workers[19] and this derivative was converted to a nucleoside by the general method of Davoll and Lowy.[22] Crystalline ethyl tetra-*O*-acetyl-1-thio-α-D-glucofuranoside (IIa, 8.5 g.) was dissolved in absolute ether (90 ml.) and treated under magnetic stirring at room temperature with bromine (1.25 ml.). After 7 min. stirring, the amber solution was evaporated under reduced pressure; petroleum ether (b.p. 30–60°) was added and the mixture was twice evaporated to a dry sirup, 9.9 g. This product, dissolved in dry toluene, was added to an azeotropically dried mixture of 2,6-diacetamido-9-chloromercuripurine (10.1 g.),[22] cadmium carbonate (10 g.), Celite (5 g.),[24] and toluene (275 ml.), and the suspension was heated 2.5 hr. at reflux. Filtration of the hot suspension and collection of the material soluble in hot chloroform, followed by washing of the chloroform extract with 30% aqueous potassium iodide, then with water, and drying (sodium sulfate), gave a sirup, 13.63 g. (quantitative). Solid material was obtained by the addition of absolute ether to a concentrated ethanolic solution, m.p. 107–116°, $[\alpha]^{29}\text{D}$ +30 ± 3° (*c* 0.37, chloroform); absorption spectra data[23]: $\lambda_{\max}^{\text{EtOH}}$ 237, 264, 288 mμ; $\lambda_{\max}^{\text{KBr}}$ 3.15, 3.25, 3.35 (NH), 5.70–5.95 (ester carbonyl, amide carbonyl), 6.10–6.25, 6.60–6.90 (NH and purine ring), 7.25–7.35 (methyl hydrogen), 9.24–9.80 μ (C–O–C). This amorphous substance could not be obtained in analytical purity

Anal. Calcd. for $C_{23}H_{28}O_{11}N_6$: C, 48.92; H, 5.00; N, 14.89. Found: C, 48.26; H, 5.10; N, 12.74.

2-Acetamido-9-β-D-glucofuranosyladenine (VIa).—Partial deacetylation of 2,6-diacetamido-9-(tetra-*O*-acetyl-β-D-glucofuranosyl)purine (Va, 850 mg.) in absolute methanol (50 ml.) and *n*-butylamine (1.5 ml.)[25] by refluxing 5 hr. resulted in crystallization from the hot mixture. Pink needles separated at 0°, 380 mg. (81%). Recrystallization (carbon) from water gave colorless needles, m.p. 241–242° dec., $[\alpha]^{28}\text{D}$ −77 ± 8° (*c* 0.13, water); absorption spectra data[23]: $\lambda_{\max}^{H_2O}$ 226, 269 mμ; $\lambda_{\max}^{\text{KBr}}$ 2.98, 3.18 (OH, NH), 5.90 (amide), 6.10, 6.25, 6.38, 6.85 (NH_2, NH, and purine ring), 9.00, 9.15, 9.40, 9.60 μ (C–O–C, C–OH); X-ray powder diffraction data[26]: 8.85 s (3), 7.90 s (2), 4.93 m, 4.51 m, 3.97 s (1), 3.88 vw, 3.60 w, 3.48 vw, 3.38 w, 3.03 m, 2.92 vw, 2.85 vw, 2.69 vw, 2.61 vw, 2.45 vw, 2.36 vw, 2.32 vw, 2.18 vw, 1.95 w. This material moved as a single zone on paper chromatography,[23] R_{Ad} 0.61.

Anal. Calcd. for $C_{13}H_{18}N_6O_6$: C, 44.05; H, 5.12; N, 23.73. Found: C, 43.83; H, 5.19; N, 23.85.

Structural Investigations of Acetylated Sugar Phenylhydrazine Derivatives

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The n.m.r. spectra of the following compounds were investigated to ascertain the utility of this technique in assigning cyclic or acyclic structures to such derivatives: D-*arabino*-3,4,5,6-tetraacetoxy-1-phenylazo-*trans*-1-hexene (I), D-*arabino*-3,4,5,6-tetraacetoxy-1-(*p*-bromophenyl)azo-*trans*-1-hexene (II), D-*lyxo*-3,4,5,6-tetraacetoxy-1-phenylazo-*trans*-1-hexene (III), penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (IV), penta-*O*-acetyl-*aldehydo*-D-galactose *p*-nitrophenylhydrazone (V), penta-*O*-acetyl-D-mannose *p*-nitrophenylhydrazone (VI), D-glucose "α"-phenylhydrazone pentaacetate (VII), tetra-*O*-acetyl-D-*arabino*-hexose phenylosazone (VIII), and tetra-*O*-acetyl-D-*lyxo*-hexose phenylosazone (IX). It was found that the presence of a low field signal, due to a formyl proton on C-1, is indicative of an acyclic structure in sugar derivatives. Fischer's D-glucose "α"-phenylhydrazone pentaacetate has been so found to be 1-acetyl-1-phenyl-2-(tetra-*O*-acetyl-β-D-glucopyranosyl)-hydrazine. Definitive evidence for the chelate structure of phenylosazones has been obtained. Three striking examples of magnetic nonequivalence of two apparently equivalent protons due to asymmetry at an adjacent center have been found, all occurring in acyclic galactose derivatives. Optical rotatory dispersions of III, IV, V, VI, and VIII have been determined and analyzed.

The structure of the crystalline tetra-*O*-acetyl derivative isolated by Wolfrom and Blair[3] from the acetylation of D-mannose phenylhydrazone has been shown to be D-*arabino*-3,4,5,6-tetraacetoxy-1-phenylazo-*trans*-1-hexene (I) by means of n.m.r. spectroscopy[4] as applied to the *p*-bromophenyl analog, D-*arabino*-3,4,5,6-tetraacetoxy-1-(*p*-bromophenyl)azo-*trans*-1-hexene (II). The analysis of the n.m.r. spectrum of I (Fig. 1) itself is now reported (Table I), along with that of II for comparative purposes. In the spectrum of I, the quartet at τ 2.68, half buried in the phenyl multiplet, shows a coupling constant in common with the quartet at τ 3.25. The low field quartet is assigned to the C-1 proton, which is coupled with the C-2 and C-3 protons. The quartet at higher field is due to the C-2 proton, coupled with its adjacent protons. The allylic C-3 proton, coupled with the protons on C-1, C-2, and C-4, gives an octet at τ 4.08. The quartet at τ 4.37 is assigned to the C-4 proton and the multiplet centered at τ 4.78 to the C-5 proton. The C-6 protons give the multiplet centered at τ 5.80. The complexity of this multiplet is probably due to slight nonequivalence of the C-6 protons due to asymmetry at C-5.

It has been shown that D-*lyxo*-3,4,5,6-tetraacetoxy-1-phenylazo-*trans*-1-hexene (III), an analog of I and II, may be prepared[4] through elimination of 1 mole of acetic acid from penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone[5] (IV) by heating in aqueous ethanol solution. The analysis of the n.m.r. spectrum of III is tabulated in Table I. A doublet at τ 2.70 and a quartet at τ 3.29 were assigned to the C-1 and C-2 protons, respectively. Two masses of lines centered at τ 4.50 and 5.86 of relative areas 2:3 are due to the protons on C-3 and C-4 and those on C-5 and C-6, respectively. This spectrum differs from those of the previously discussed *arabino* analogs in that the C-3 and C-5 proton signals are shifted upfield and there is no observable coupling between the C-1 and C-3 protons. In general, however, this spectrum substantiates the previous assignments, as one may expect such differences as noted due to the difference in configuration.

The analysis of the n.m.r. spectrum (Fig. 2) of penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (IV), of proven acyclic structure,[5,6] is given in Table II.

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(1) Fellow of the Corn Industries Research Foundation.

(2) National Science Foundation Cooperative Graduate Fellow.

(3) M. L. Wolfrom and M. G. Blair, *J. Am. Chem. Soc.*, **68**, 2110 (1946).

(4) M. L. Wolfrom, A. Thompson, and D. R. Lineback, *J. Org. Chem.*, **27**, 2563 (1962).

(5) M. L. Wolfrom and C. C. Christman, *J. Am. Chem. Soc.*, **53**, 3413 (1931).

(6) J. Compton and M. L. Wolfrom, *ibid.*, 1157 (1934).

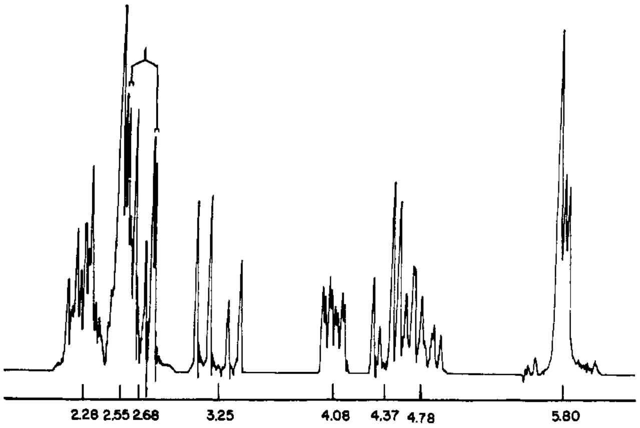

Fig. 1.—N.m.r. spectrum (τ) of D-*arabino*-3,4,5,6-tetraacetoxy-1-phenylazo-*trans*-1-hexene (I).

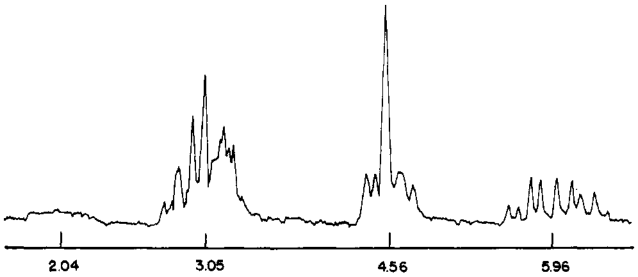

Fig. 2.—N.m.r. spectrum (τ) of penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (IV).

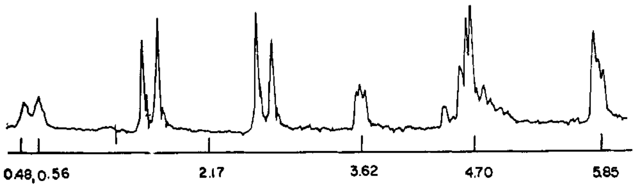

Fig. 3.—N.m.r. spectrum (τ) of penta-*O*-acetyl-*aldehydo*-D-mannose *p*-nitrophenylhydrazone (VI).

The N–H signal, broadened by the nitrogen quadrupole, is a very low broad line at τ 2.04. The complex multiplet at τ 3.05, of relative area six, includes the signals due to the aromatic protons and the C-1 proton. The C-2, C-3, C-4, and C-5 protons give a multiplet of relative area four at τ 4.56. The grouping of eight lines at τ 5.96 is the AB portion, the C-6 protons, of an ABX multiplet, the X proton, that on C-5, being buried in the multiplet at τ 4.56. The nonequivalence of the protons at C-6 arises from the asymmetry at C-5[7] and the imbalance of the populations of the possible rotamers about the C-5–C-6 bond. Analysis of this multiplet yields, in absolute magnitudes, $\delta_{6,6'} = 0.337$ p.p.m., $J_{6,6'} = 11.1$ c.p.s., $J_{5,6} = 5.2$ c.p.s., and $J_{5,6'} = 7.4$ c.p.s.[8]

Because of its insolubility in deuteriochloroform, difficulties were encountered in obtaining a suitable n.m.r. spectrum of penta-*O*-acetyl-*aldehyde*-D-galactose *p*-nitrophenylhydrazone (V), of proven[5] acyclic structure. A spectrum taken at high gain showed a fine structure very similar to the spectrum of IV, differing only slightly in chemical shifts of the multiplets and in the aromatic region. The C-1 aldehydic proton, coupled with the C-2 proton, gave a doublet at τ 3.00, $J_{1,2} = 4.0$ c.p.s. The aromatic protons gave a symmetrical A_2B_2 spectrum centered at τ 2.42. The C-2, C-3, C-4, and C-5 protons gave a multiplet at τ 4.50, very similar to the corresponding multiplet in the spectrum of IV. The C-6 protons were nonequivalent in this case also, giving a multiplet with several lines.

Mild acetylation of D-mannose *p*-nitrophenylhydrazone yielded a crystalline product whose analysis showed it to be the penta-*O*-acetyl derivative (VI). An analysis (Table II) of the n.m.r. spectrum (Fig. 3) of this crystalline substance conclusively proved that it was penta-*O*-acetyl-*aldehydo*-D-mannose *p*-nitrophenylhydrazone (VI). The two broad lines at τ 0.56 and 0.48 are assigned to the C-1 proton and the imino proton, respectively, since the latter line was found to disappear whenVI was exchanged by deuterium in deuterium oxide–deuteriochloroform. The aromatic protons gave an A_2B_2 spectrum centered at τ 2.17. The multiplet at τ 3.62 is due to the C-2 proton, and that at 5.85, the C-6 protons, which again seem slightly nonequivalent due to asymmetry at C-5. The C-3, C-4, and C-5 protons give the complex multiplet centered at τ 4.70.

In the n.m.r. spectra of aldehydes,[9] their semicarbazones,[10] 2,4-dinitrophenylhydrazones,[10] and oximes,[11] the formyl proton gives a signal at low field which is usually readily distinguished from the rest of the spectrum. The presence of such a low field signal in the spectra of sugar phenylhydrazones is indicative of a Schiff base structure, as in the spectra of V and VI. However, in some cases, as that of IV, the formyl proton signal is buried in the aromatic multiplet. In such a case, the presence or absence of an acyclic structure must be determined by other methods or by comparing the fine structure of the signals from the protons on the carbohydrate portion of the molecule to the corresponding signals in the spectra of a proven cyclic or acyclic structure of the same conformation.

Fischer[12] first prepared D-glucose "α"-phenylhydrazone. A cyclic structure for this compound was indicated by the isolation of 1-acetyl-1-phenylhydrazine from a hydrolyzate of its pentaacetate[13] and its inability to undergo the formazan reaction.[14] The n.m.r. spectrum of D-glucose "α"-phenylhydrazone was accordingly determined (Fig. 4, curve A) for comparison with proven acyclic analogs. The spectrum was quite similar to that of cyclic β-D-glucopyranose pentaacetate in corresponding regions. The phenyl group gave a signal at τ 2.75 of relative area five and two sharp lines at τ 8.01 and 8.06 were assigned to the methyl protons of the acetyl groups. A mass of lines centered at τ 5.09 comprised the signals attributed to protons on C-2, C-3, and C-4. The anomeric proton gave a broad line at τ 5.60, overlapping the signal attributed to the

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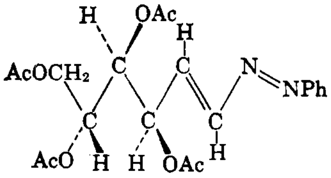
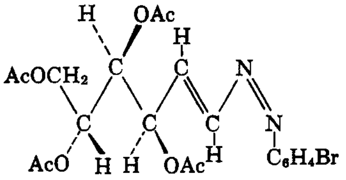
Table I

Nuclear Magnetic Resonance Spectral Data for Tetraacetoxy-1-phenylazo-*trans*-1-hexenes


I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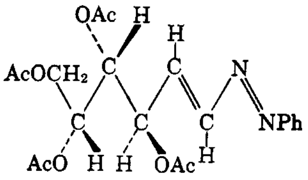
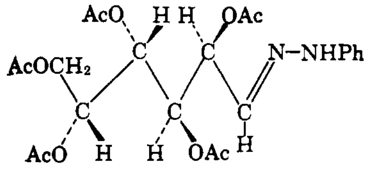
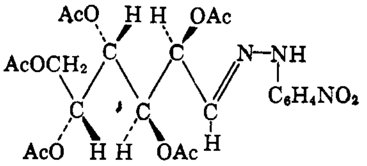

III

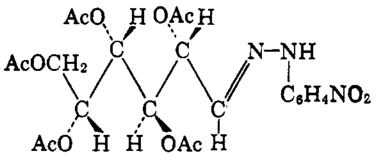
	I		II		III	
Protons on	Chemical shift, τ	Coupling constant, c.p.s.	Chemical shift, τ	Coupling constant, c.p.s.	Chemical shift, τ	Coupling constant, c.p.s.
Aromatic ring	2.28, 2.55		2.73	...	2.33, 2.75	...
C-1	2.68	$J_{1,2}$ = 13.5	2.99	$J_{1,2}$ = 12.0	2.70	$J_{1,2}$ = 10.5
C-2	3.25	$J_{1,3}$ = 1.0	3.50	$J_{1,3}$ = 1.0	3.29	$J_{2,3}$ = 6.0
C-3	4.08	$J_{2,3}$ = 6.0	4.23	$J_{2,3}$ = 5.0	...	
C-4	4.37	$J_{3,4}$ = 3.0		$J_{3,4}$ = 2.5	4.50	
C-5	4.78	$J_{4,6}$ = 9.0	4.70			
C-6	5.80		5.70		5.86	
Acetyl groups	7.87, 7.93, 7.97		7.92		8.09, 8.13, 8.14	

Table II

Nuclear Magnetic Resonance Spectral Data for Acyclic Phenylhydrazone Pentaacetates


IV


V


VI

Protons on	IV, chemical shift, τ	V, chemical shift, τ	VI, chemical shift, τ
Aromatic Ring	3.05		2.17
N	2.04	1.74	0.48
C-1	...	3.00	0.56
C-2			3.62
C-3, C-4, C-5	4.56	4.50	4.70
C-6	5.96	...	5.85
Acetyl Groups	7.92, 7.96, 7.98, 8.03	8.03, 8.05, 8.06, 8.07, 8.08	7.52, 7.99, 8.03

C-6 protons at τ 6.08. The C-5 proton gave a multiplet at τ 6.44 and the imino hydrogen gave a low broad line at τ 3.88. To confirm the assignment of this line to the imino hydrogen, a deuteriochloroform solution of VII was shaken overnight with a few drops of deuterium oxide, thus exchanging the imino hydrogen with deuterium. The spectrum of the resulting two-phase mixture (Fig. 4, curve B) had no signal at τ 3.88, the line assigned to the imino hydrogen. Further, the signal due to the C-1 proton was simplified to a doublet at τ 5.80, $J_{1,2}$ = 7.8 c.p.s. This is due to exchange of the *N*-deuterium atom in the wet solution or possibly because replacing the *N*-proton with deuterium reduces the spin coupling constant by the ratio of the gyromagnetic ratios of deuterium and hydrogen, about $^1/_7$. The magnitude of $J_{1,2}$ indicates that D-glucose "α"-phenylhydrazone exists in the β-D-pyranose form.[15] This VII may now be designated 1-acetyl-1-phenyl-2-(tetra-*O*-acetyl-β-D-glucopyranosyl)hydrazine.

It has been reported that hydrazones of simple aldehydes rearrange to a phenylazo structure on heating in alcohol solution.[16] It accordingly would appear possible that sugar osazones might have this type of structure since they are prepared in hot buffered acetic acid solutions. A phenylazo structure, in equilibrium with the classic Fischer structure, has indeed been proposed by Zerner and Waltuch[17] to account for the mutarotation of osazones. Engel,[18] however, found the ultraviolet spectra not in accord with such a situation. An analysis (Table III) of the n.m.r. spectrum of tetra-*O*-acetyl-D-*arabino*-hexose phenylosazone (VIII)[18–20] proves the presence of a formyl proton and a strongly hydrogen-bonded proton, thus confirming the chelate structure first proposed by Fieser and Fieser[21] and supported by chemical evidence adduced by Mester.[22] An isolated singlet far downfield at τ −2.32 is assignable to the chelated proton, and a singlet at τ 1.62 to the C-1 aldehydic proton. A multiplet centered at τ 2.80 comprised the aromatic proton signals. Complex multiplets at τ 4.25 and 4.70 are assigned to the C-3, C-4, and C-5 protons and the C-6 methylene group gives a multiplet at τ 5.70. Three sharp lines at τ 7.92, 7.96,

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[15] R. U. Lemieux, R. K. Kullnig, H. J. Bernstein, and W. G. Schneider, *J. Am. Chem. Soc.*, **79**, 1005 (1957); ref. 8, p. 395.

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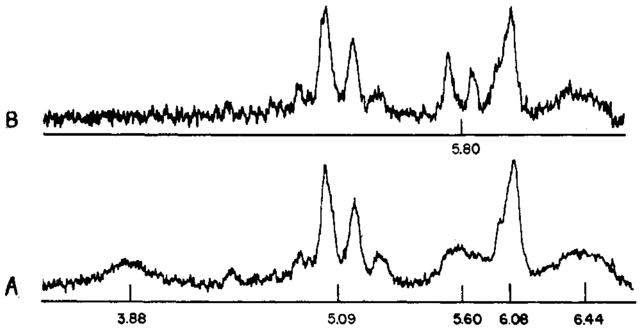


Fig. 4.—N.m.r. spectra (τ) of 1-acetyl-1-phenyl-2-(tetra-*O*-acetyl-β-D-glucopyranosyl)hydrazine (glucose "α"-phenylhydrazone pentaacetate, VII): A, deuteriochloroform solvent; B, deuteriochloroform–deuterium oxide solvent.

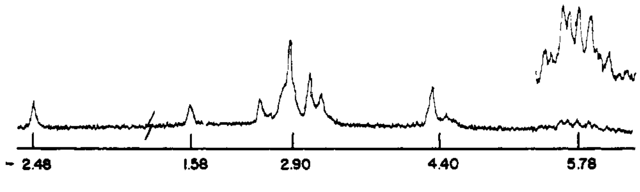


Fig. 5.—N.m.r. spectrum (τ) of tetra-*O*-acetyl-D-*lyxo*-hexose phenylosazone (X).

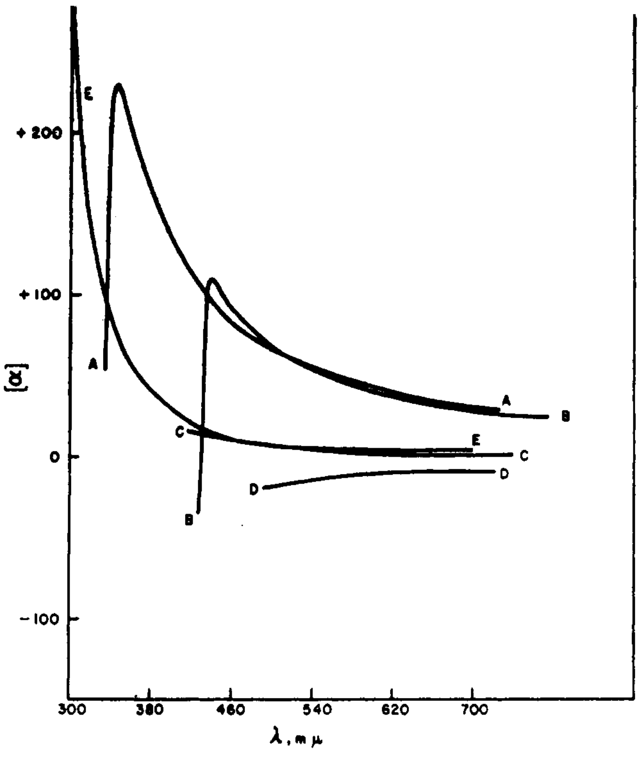
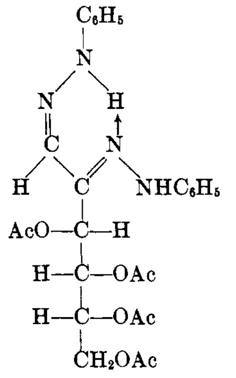


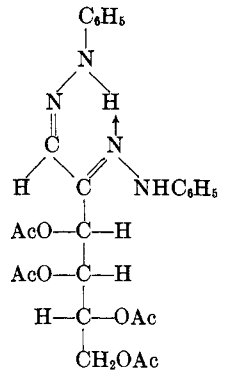
Fig. 6.—Optical rotatory dispersions at 28–29°, in acetonitrile (c 1.0), of penta-*O*-acetyl-*aldehydo*-D-galactose phenylhydrazone (IV, curve A), penta-*O*-acetyl-*aldehydo*-D-mannose *p*-nitrophenylhydrazone (VI, curve C), penta-*O*-acetyl-*aldehydo*-D-galactose *p*-nitrophenylhydrazone (V, curve B), D-*lyxo*-3,4,5,6-tetraacetoxy-1-phenylazo-*trans*-1-hexene (III, curve D) (c 0.5), and D-glucose "α"-phenylhydrazone pentaacetate (VII, curve E); Rudolph automatic recording spectropolarimeter, Model No. 260/655/850/810-614, Rudolph Instruments Engineering Co., Little Falls, N. J.

TABLE III

NUCLEAR MAGNETIC RESONANCE SPECTRAL DATA FOR PHENYL OSAZONE TETRAACETATES



VIII



IX

Protons on	VIII, chemical shift, τ	IX, chemical shift, τ
N (chelated)	−2.32	−2.48
Aromatic rings	2.80	2.90
C-1	1.62	1.58
C-3, C-4, C-5	4.25, 4.70	4.40
C-6	5.70	5.78
Acetyl groups	7.92, 7.96, 8.00	7.90, 7.95, 8.05

and 8.00 are assigned to the acetate methyl protons. The chelate structure also is indicated clearly by the n.m.r. spectrum (Fig. 5) of tetra-*O*-acetyl-D-*lyxo*-hexose phenylosazone (IX) (Table III).[20] As in two of the other galactose derivatives discussed in this paper, IV and V, the C-6 protons are magnetically nonequivalent. Calculations yield $\delta_{6,6'}$ = 0.372 p.p.m., $J_{5,6}$ = 3.7 c.p.s., $J_{5,6'}$ = 6.8 c.p.s., and $J_{6,6'}$ = 11.9 c.p.s. The apparently common occurrence of this phenomenon in acyclic galactose derivatives is worthy of note.

The optical rotatory dispersion curves for III, IV, V, VI, and VII in acetonitrile are shown in Fig. 6. A simple negative curve (D) and a simple positive curve (C), both referable to single Drude factors, were obtained for III and VI, respectively. Biot–Lowry plots of $1/[\alpha]$ against λ^2 yielded straight lines from which there can be located the optically active absorption bands at 312 mμ for III and 363 mμ for VI. These results compare with ultraviolet absorption at 303 mμ for III[4] and 370 mμ for VI. The curve obtained for VII (E) was complex but normal[23]; a Biot–Lowry plot was nonlinear. The curves for IV (A) and V (B) were complex and anomalous, not referable to single Drude factors.

Experimental

N.m.r. Spectra.—All spectra were taken at 60 Mc. in deuteriochloroform solution with a tetramethylsilane internal reference standard. The spectra of I, II, and VII were taken by Varian Associates. The spectra of III, IV, V, and VI were obtained on a Varian Associates HR-60 spectrometer and calibrated by the usual side-band technique. All other spectra were taken on a Varian Associates A-60 spectrometer and were calibrated by obtaining a second spectrum in chloroform and interpolating between the tetramethylsilane and chloroform lines. For purposes of brevity, the acetate methyl group protons are not shown in the figures.

Penta-*O*-acetyl-*aldehydo*-D-galactose Phenylhydrazone.—This substance was prepared by the acetylation of D-galactose phenylhydrazone as described by Wolfrom and Christman[5], $[\alpha]^{24}\text{D}$ +46° (c 2, acetonitrile, optical rotatory dispersion shown in Fig. 6, curve A); $\lambda_{\max}^{\text{EtOH}}$ 280, 302.5 (shoulder), 372.5, 550 mμ ($\epsilon_{\max}$ 1.82×10^4, 1.135×10^4, 339, 234, respectively); n.m.r. spectrum shown in Fig. 2; X-ray powder diffraction pattern[24]: 8.65 m,

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[23] T. M. Lowry, "Optical Rotatory Power," Longmans Green and Co., New York, N. Y., 1935, p. 142.

[24] Interplanar spacing, Å., Cu Kα radiation. Relative intensities, estimated visually: s, strong; m, medium; w, weak; v, very. Strongest lines numbered, 1 strongest.

7.99 w, 6.81 s, 6.03 vs (1), 5.36 s (2), 4.79 w, 4.57 m, 4.01 w, 3.59 m, 3.43 s (3), 3.11 vw, 3.02 vw, 2.92 w, 2.82 w.

Penta-*O*-acetyl-*aldehydo*-D-galactose *p*-Nitrophenylhydrazone.—This substance was prepared by the acetylation of D-galactose *p*-nitrophenylhydrazone[25] as described by Wolfrom and Christman,[5] $[\alpha]^{24}$D +41° (*c* 2, acetonitrile, optical rotatory dispersion in Fig. 6, curve B); $\lambda_{\max}^{\text{EtOH}}$ 375 and 550 mμ ($\epsilon_{\max}$ 2.34×10^4 and 266, respectively); X-ray powder diffraction pattern[24]: 12.63 w, 9.41 s (2), 7.20 w, 6.33 vs (1), 5.75 w, 5.40 w, 5.15 w, 4.65 w, 4.15 m, 3.92 s (3), 3.68 m, 3.53 vw, 3.40 w, 3.27 vw, 2.73 vw.

Penta-*O*-acetyl-*aldehydo*-D-mannose *p*-Nitrophenylhydrazone.—This substance was prepared by the acetylation of D-mannose *p*-nitrophenylhydrazone[25] according to the procedure of Wolfrom and Christman.[5] The sirupy product was dissolved in 50 ml. of benzene and chromatographed, in equal portions, on two columns (75 × 240 mm.) filled with Magnesol–Celite[26] (5:1 by weight) and developed with 1400 ml. of benzene–2–methyl-2-propanol (100:1 by volume). Extrusion and streaking with alkaline permanganate solution revealed the presence of two zones 90–175 and 220–230 mm. from the column top. The zones were excised, twice extracted with acetone, filtered; the solvent was removed under reduced pressure and the resulting sirups were crystallized from ethanol. Both zones gave the same bright yellow crystalline material as identified by melting point and mixture melting point, 3.47 g., m.p. 130–131°, $[\alpha]^{27}$D −16.0° (*c* 4, pyridine), +4.5° (*c* 2, acetonitrile, optical rotatory dispersion shown in Fig. 6 curve C); $\lambda_{\max}^{\text{EtOH}}$ 370 (shoulder) and 540 mμ ($\epsilon_{\max}$ 1100 and 166, respectively); n.m.r. spectrum shown in Fig. 3; X-ray powder diffraction pattern[24]: 12.40 w, 9.85 m, 8.12 m, 6.58 s (2), 6.13 vw, 5.36 vs (1), 5.01 w, 4.70 s (3), 4.33 w, 3.99 m, 3.73 m, 3.47 w, 3.25 w, 3.09 vw, 2.88 m, 1.98 vw.

Anal. Calcd. for $C_{12}H_{12}O_7N_3(CH_3CO)_5$: C, 50.29; H, 5.14; N, 8.00; CH_3CO, 10.74 ml. of 0.1 *N* NaOH for 100 mg. Found: C, 50.57; H, 5.50; N, 7.71; CH_3CO (as *O*-Ac),[20] 10.25 ml.

1-Acetyl-1-phenyl-2-(tetra-*O*-acetyl-β-D-glucopyranosyl)hydrazine.—D-Glucose "α"-phenylhydrazone was prepared according to the method of Stempel,[12b] m.p. 145–150°. This hydrazone was then acetylated in the manner described by Behrend and Reinsberg,[13] m.p. 151–153°, $[\alpha]^{32}$D +20° (*c* 2.0, chloroform), +9.0° (*c* 2.0, pyridine), +2.0° (*c*, 2.0, acetonitrile, optical rotatory dispersion shown in Fig. 6, curve E); n.m.r. spectrum shown in Fig. 4; $\lambda_{\max}^{\text{EtOH}}$ no absorption between 285 and 600 mμ; $\lambda_{\max}^{\text{KBr}}$ 3.1, 3.4, 5.7 (carbonyl), 6.1, 6.3, 6.5, 6.7, 7.0, 7.3, 7.9, 8.1–8.3 (acetate), 9.1, 9.4, 9.6, 10.2, 11.0, 11.9, 12.5, 13.1, 13.9, 14.3, 15.5 μ; X-ray powder diffraction pattern[24]: 10.78 w, 9.61 m (3), 8.85 m, 6.71 vw, 5.40 s (1), 4.82 w, 4.51 m, 4.23 w, 3.87 s (2), 3.56 vw. Hofmann[27] reported m.p. 152–153° and $[\alpha]$D +11.97° (pyridine) for this material while Behrend and Reinsberg[13] reported m.p. 151° and $[\alpha]$D +17.5° (pyridine).

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The Synthesis of the *t*-Butyl 1-Thio-D-glucosides and of 2,4-Dinitrophenyl 1-Thio-β-D-glucopyranoside. The Reaction of Some 1-Thio-D-glucosides with Mercury Salts of Carboxylic Acids

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Both anomeric *t*-butyl 1-thio-D-glucopyranosides and *t*-butyl 1-thio-D-glucofuranosides, as well as 2,4-dinitrophenyl 1-thio-β-D-glucopyranoside, have been synthesized. The behavior of some of these thioglucosides with mercury salts of carboxylic acids has been investigated and a tentative mechanism of the formation of 1-*O*-acylaldoses by this pathway is proposed.

Earlier investigations in this laboratory[1-4] have shown that various 1-thioaldose derivatives (dithioacetals and alkyl 1-thioglycosides) undergo metathetical reactions with silver and mercury salts. Thus, ethyl 1-thio-β-D-glucopyranoside is converted into a mixture of the anomeric 1-*O*-mesitoyl-D-glucopyranoses when treated with silver mesitoate[1] (silver 2,4,6-trimethylbenzoate), and the condensation of 5-*O*-benzoyl-2-deoxy-D-*erythro*-pentose diisopropyl dithioacetal with chloromercuri-6-benzamidopurine leads (after the removal of masking groups) to a mixture of the anomeric 9-(2-deoxy-D-*erythro*-pentofuranosyl)adenines. In the studies of the behavior of ethyl 1-thioaldosides with silver salts of carboxylic acids,[1,4] prolonged boiling in acetonitrile was found necessary to effect complete reaction, although an ethyl 1-thioaldofuranoside[4] obviously reacted more readily than did an ethyl 1-thioaldopyranoside.[1] Under these conditions, acyl migrations (for example, conversion of 1-*O*-benzoyl-α-D-glucopyranose to 2-*O*-benzoyl-D-glucose) take place and the procedure is obviously less than ideal for inserting labile substituents at C-1 in an aldose. Pedersen and Fletcher[4] noted that mercuric acetate reacts with ethyl 5-*O*-benzoyl-1-thio-β-L-arabinofuranoside more readily than does silver benzoate. In seeking methods whereby this reaction can be carried out under comparatively mild conditions, we have, therefore, now turned our attention to some mercury salts of carboxylic acids, and, for glycosides, have used *t*-butyl 1-thio-β-D-glucopyranoside (II), *t*-butyl 1-thio-α-D-glucofuranoside (X), and 2,4-dinitrophenyl 1-thio-β-D-glucopyranoside (XIV) in the hope of revealing any influence of the electronegativity of the aglucon on the nature of the reaction.

Although 2-methyl-2-propanethiol (*t*-butyl mercaptan) is a readily available substance, no *t*-butyl thioglycosides appear to have been reported in the litera-

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