gamated zinc[9] (15.0 g), 3.0 g (0.012 mole) of 1,[3] 50 ml of ethanol, and 25 ml of concentrated HCl were refluxed for 6 hr, an additional 20 ml of concentrated HCl being added after 3 hr. The reaction mixture was decanted from the remaining zinc amalgam, diluted with 100 ml of water, made strongly alkaline with 20% NaOH, and extracted with four 100-ml portions of ether. The combined ether extracts were washed once with water, dried ($MgSO_4$), filtered, and concentrated to give a dark red liquid (1.5 g) which was dissolved in benzene and was chromatographed on neutral alumina (Merck No. 71707) wet with benzene. The column was eluted with benzene, benzene–ether, and ether–methanol. The eluate fractions yielded 0.28 g of a colorless liquid, 1,2,3,4-tetrahydro-5,6-dimethoxynaphthalene, the infrared spectrum of which was identical with that of an authentic sample; 0.26 g of a yellow liquid, 5,6-dimethoxy-1-naphthylamine **6**, which crystallized on standing; and 0.5 g of a highly impure dark oil which showed bands in the N—H stretching region of its infrared spectrum. Recrystallization of **6** from ethanol gave small, colorless prisms, mp 97.5–98°. An infrared spectrum of **6** ($CHCl_3$) showed a doublet at 2.90 and 2.97 μ (NH_2 stretching) and a strong band at 6.20 μ (NH_2 deformation). A nmr spectrum of **6** ($CDCl_3$) showed a pair of singlets at δ 3.90 and 3.95, superimposed upon a broad band between δ 3.7 and 4.3 (eight protons), and a series of broad, overlapping signals between δ 6.4 and 7.8 (five protons).

Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 71.10; H, 6.49; N, 7.11.

A hydrochloride salt of **6** was prepared in ether and was recrystallized from ethanol, mp 254–255° dec.

Anal. Calcd for $C_{12}H_{14}ClNO_2$: C, 60.13; H, 5.89; Cl, 14.79; N, 5.84. Found: C, 60.40; H, 5.95; Cl, 15.31; N, 5.93.

1,2,3,4-Tetrahydro-5,6-dimethoxynaphthalene (3).—This compound was obtained by a modification of the method employed by Stork[10] to prepare 1,2,3,4-tetrahydro-6-methoxynaphthalene. A mixture of 117.4 g (0.625 mole) of 1,2-dimethoxynaphthalene,[11] 2 ml of glacial acetic acid, and 20 ml of Raney nickel catalyst W-2[12] in 400 ml of anhydrous ethanol was hydrogenated in a Parr shaker apparatus at a maximum pressure of 45 psig. Approximately 4 days was required for completion of the hydrogenation. The product was isolated by filtration from the catalyst, concentration of the filtrate under reduced pressure, and distillation, to give 115.5 g (96%) of a colorless liquid, bp 81–83° (0.45 mm), $n^{25}D$ 1.5379, d^{20} 1.060. Schroeter and co-workers[13] reported synthesis of this compound by another route, bp 137–138° (12 mm). Vapor phase chromatographic analysis indicated 96% of the product to be a single component. A nmr spectrum (CCl_4) showed a multiplet centered at δ 1.70 (four protons), a multiplet centered at δ 2.65 (four protons), a pair of singlets at δ 3.70 and 3.73 (six protons), and a series of bands between δ 6.5 and 7.2 (two protons).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 75.20; H, 8.29.

Attempted Clemmensen Reduction of 2-Amino-3,4-dihydro-1(2H)-naphthalenone Hydrochloride (5).—Amalgamated zinc (50 g), 10.0 g (0.051 mole) of 5,[14] 150 ml of ethanol, and 50 ml of concentrated HCl were refluxed 6 hr, an additional 25 ml of concentrated HCl being added after 3 hr. The reaction mixture was decanted from the remaining amalgam, diluted with 250 ml of water, made strongly alkaline with 20% NaOH, and extracted with four 250-ml portions of ether. The combined ether extracts were washed once with water, then were dried ($MgSO_4$). Filtration and concentration of the filtrate under reduced pressure gave 5.1 g of a dark red liquid which was dissolved in benzene and chromatographed as previously described for the Clemmensen reaction mixture of **1**. The eluate fractions yielded 1.7 g (25%) of 1,2,3,4-tetrahydronaphthalene and 1.5 g (21%) of 1-naphthylamine (identified by comparing their infrared spectra with those of authentic samples) and 0.9 g of a highly impure, dark green liquid, which showed weak bands in the N—H stretching region of its infrared spectrum. The alkaline aqueous solution from which 1,2,3,4-tetrahydronaphthalene and 1-naphthylamine had been extracted was made strongly acidic with concentrated HCl, but extraction of this solution with ether failed to provide any identifiable product.

Rearrangement of 2-Amino-3,4-dihydro-1(2H)-naphthalenone Hydrochloride (5) in Ethanol–Hydrochloric Acid.—A solution of 2.0 g (0.01 mole) of **5** in 100 ml of ethanol and 20 ml of concentrated HCl was refluxed for 6 hr. The reaction mixture was cooled, then was made strongly alkaline with 20% NaOH, and was extracted with three 100-ml portions of ether. The combined ether extracts were swirled with $MgSO_4$ for 10 min, then were filtered and concentrated under reduced pressure to give 0.95 g of a yellow-brown liquid which was dissolved in benzene and immediately chromatographed as previously described. The eluate fractions yielded 0.17 g (12%) of 1-naphthylamine (the infrared spectrum of which was superimposable upon that of an authentic sample), and a variety of unidentifiable substances, all of which showed similar infrared spectra: multiple absorption bands in the 2.7–3.1-μ region (N—H and/or O—H stretching) and a broad band in the 5.8–6.2-μ region (C=N and/or C=O stretching).

5,6-Dimethoxy-1-naphthylamine (6).—A modification of the method of Bauer and Hewitson[15] was employed. 3,4-Dihydro-5,6-dimethoxy-1(2H)-naphthaleneone oxime (**7**,[3] 5.0 g, 0.023 mole) was heated in a mixture of 2.5 ml of acetic anhydride and 20 ml of glacial acetic acid for 10 min at 110°, then anhydrous HCl was passed through the solution for 30 min, while maintaining the temperature at 100°. The reaction mixture was cooled overnight in a refrigerator and the gray crystals which separated were collected on a filter. These were washed twice with 10-ml portions of anhydrous ethanol and were air dried to yield 0.6 g (13%) of 5,6-dimethoxy-1-naphthylamine hydrochloride, mp 253–255° dec. An infrared spectrum (Nujol) was superimposable upon a similar spectrum of the hydrochloride salt of the product of the attempted Clemmensen reduction of **1**. The hydrochloride salt obtained above was warmed gently in 5% Na_2SO_3, and the resulting solution was extracted with chloroform, dried ($MgSO_4$), and filtered. The solvent was removed from the filtrate under reduced pressure and the residue was recrystallized repeatedly from ethanol (charcoal), to afford white crystals of 5,6-dimethoxy-1-naphthylamine (**6**), mp 97–98°. An infrared spectrum ($CHCl_3$) of this product was superimposable upon a similar spectrum of the free base form of the amino product isolated from the attempted Clemmensen reduction of **1**.

Acknowledgment.—We acknowledge with thanks the helpful discussions with Professor Ludwig Bauer, University of Illinois, regarding the Semmler–Wolff reaction.

(9) Prepared by shaking 15 g of clean mossy zinc with a solution of 1.5 g of mercuric chloride in 15 ml of water and 15 ml of 5% HCl, followed by thorough washing with water.

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The Conformational Inversion of D-Mannopyranosides Caused by Certain Aglycons

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D-Mannopyranose is found in nature as a constituent of certain polysaccharides, of nucleotides, and of certain glycoproteins. The elucidation of the conformation of D-mannopyranose moiety in these molecules will be very important in studying their structures, biosyntheses, and biological functions. Both α- and β-D-mannopyranoses are believed to have C1 conforma-

TABLE I

CHEMICAL SHIFTS OF METHINE AND METHYLENE PROTONS (δ)

		Chemical shifts[a] (integral of protons)											
		H-1		H-2		H-3		H-4		H-5			
Compd	Solvent	a	e	a	e	a	e	a	e	a	e	Ha-6	Hb-6
I	$CDCl_3$[b]	6.50 d		5.95 q		5.09 q		5.52 t		←4.14–4.86c (3 H)→			
II	D_2O	6.32 d		←3.66–4.70c (6 H)→									
IV	$CDCl_3$		4.60 d	5.51 q	←4.93–5.39c (2 H)→					3.75[c]	←4.20–4.38c (2 H)→		
VI	$CDCl_3$		5.66 d	←5.17–5.59c (3 H)→						←3.63–4.50c (3 H)→			
VIII[d]	$CDCl_3$	5.91 d		5.50 q	5.70 q		5.33[c]			3.82[c]		4.32 q	4.16 q
IX[d]	$CDCl_3$		6.32 d	5.43 q	5.70 q		5.33 t			4.15[c]		4.30 q	4.18 q
X	$CDCl_3$	6.66 d		←5.87–6.32c (3 H)→						←4.32–4.91c (3 H)→			
XI	$CDCl_3$		5.47 d	←4.54–4.97c (4 H), 3.68–4.22c (2 H)→									
XII	$CDCl_3$	6.20 d		←5.10–5.87c (3 H)→						←3.90–4.32c (3 H)→			

[a] For compounds I and II, the position numbers 1, 2, 3, 4, 5, and 6 should be taken to mean 1′, 2′, 3′, 4′, 5′, and 6′, respectively; d, doublet; t, triplet; q, quarter; c, complex, overlapping, or incompletely resolved multiplet; a, axial; e, equatorial. [b] There was no significant change of the proton signals as measured in pentadeuteriopyridine and in various mixtures of deuteriochloroform and benzene. [c] A multiplet center. [d] Reported by Horton and Turner.[4e]

TABLE II

FIRST-ORDER COUPLING CONSTANTS OF METHINE PROTONS[a]

	Coupling constants (cps)[b]			
Compd	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$
I	8.7	3.3	3.7	3.7
II	6.5	c	c	c
IV	1.0	2.5	c	c
VI	1.3	c	c	c
VIII[c]	1.1	3.0	9.5	9.0
IX[c]	1.6	3.0	10.0	9.4
X	1.5	c	c	c
XI	1.5	c	c	c
XII	7.5	c	c	c

[a] Measured in the solvents described in Table I. [b] For compounds I and II, the position numbers 1, 2, 3, and 4 should be taken to mean 1′, 2′, 3′, and 4′, respectively; c, the coupling constants could not be determined because of complex, overlapping, or incompletely resolved multiplets. [c] Reported by Horton and Turner.[4e]

tion as predicted on the basis of optical rotatory data[1,2] and the Reeves' conformational instability factors.[3] The conformation has also been confirmed with the derivatives by the nmr spectral analysis,[4] but Lemieux and Morgan[5] have recently reported 1C conformation for *N*-(3′,4′,6′-tri-*O*-acetyl-2′-deoxy-2′-iodo-α-D-mannopyranosyl)pyridinium perchlorate.

In the course of the synthesis of 1,2-*cis* glycosides,[6] we observed by nmr and infrared spectral analyses a conformational inversion of D-mannopyranosides from C1 to 1C by modifying the aglycons. The present paper describes the evidences for the conformational inversion. The derivatives of D-mannopyranose examined are as follows: 7-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyl)theophylline (I), 7-α-D-mannopyranosyltheophylline (II), 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-mannopyranose (III), methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (IV), methyl 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranoside (V), *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (VI), *p*-tolyl 2,3,4,6-tetra-*O*-acetyl-D-mannopyranosylamine (VII), 1,2,3,4,6-penta-*O*-acetyl-β-D-mannopyranose (VIII), 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl bromide (IX), and 1,2,3,4,6-penta-*O*-benzoyl-β-D-mannopyranose (X). In addition to these compounds, 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (XI) and 7-(2′,3′,4′,6′-tetra-*O*-acetyl-β-D-glucopyranosyl)-theophylline (XII) were examined.

Spin–Spin Coupling Constants of Methine and Methylene Protons.—The signals of the ring hydrogens in the nmr spectra were assigned in the usual manner. The chemical shifts of methine and methylene protons are given in Table I, and the first-order coupling constants are given in Table II. As shown in Figure 1, the H-1′ signal in I appears at δ 6.50 as doublet of $J_{1',2'} = 8.7$ cps, which indicates[7–9] the diaxial orientation of H-1′ and H-2′ with a projected angle of *ca.* 180° between the C-1′ and C-2′ carbon–hydrogen bonds. The H-2′ signal appears at δ 5.95 as quartet through coupling with H-1′ and with H-3′. The small value (3.3 cps) of the $J_{2',3'}$ indicates the axial–equatorial orientation of H-2′ and H-3′. The H-3′ signal in I is observed at δ 5.09 as quartet with $J_{3',4'} = 3.7$ cps, which indicates a projected angle of *ca.* 60° between the C-3′ and C-4′ carbon–hydrogen bonds. The H-4′ signal in I is observed at δ 5.52 as triplet with a small spacing of 3.7 cps between the lines, due to equal coupling with the equatorial protons at C-3′ and at C-5′. Owing to the equatorial orientation of the hydrogen at C-2′ in the C1 conformation of D-mannopyranose, the value of $J_{1',2'}$ should be small, without the distinction of α- and β-D configurations. Therefore, the large values of $J_{1',2'}$ in I and II exclude the possibilities of α- and β-D-mannopyranosides in C1 conformation and of the β-D anomer in 1C conformation, and are in good agreement with α-D anomer in 1C conformation. The α-D configuration is also confirmed with the ORD curve of II. The small values of $J_{2',3'}$, $J_{3',4'}$, and $J_{4',5'}$ in I fully support the 1C conformation. On the other hand, the small values of $J_{1,2}$ and $J_{2,3}$, and the large values of $J_{3,4}$ and $J_{4,5}$ in other com-

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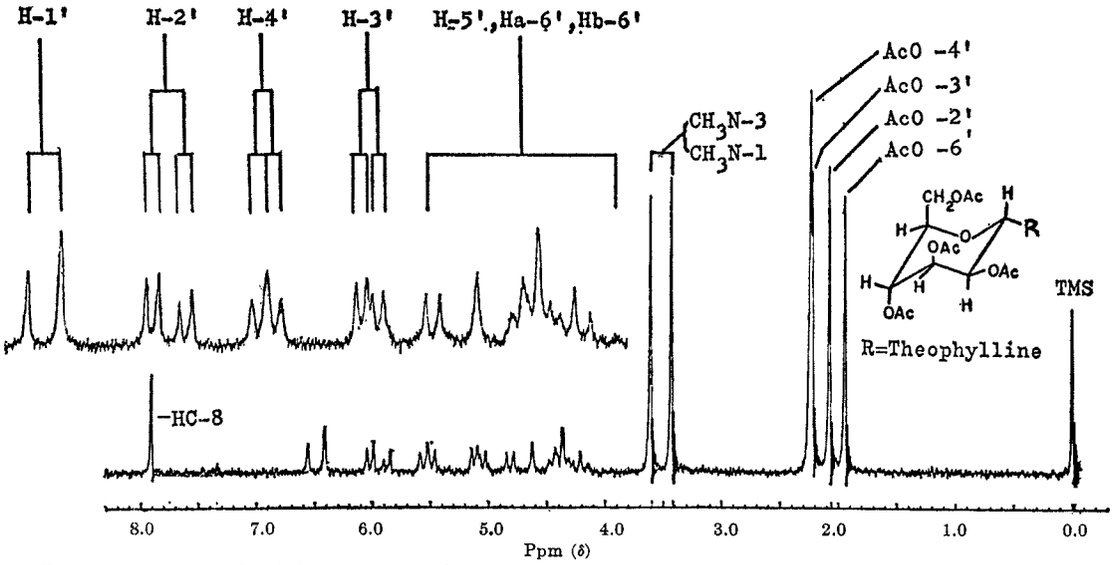

Figure 1.—The nmr spectrum of 7-(2′,3′,4′,6′-tetra-*O*-acetyl-α-D-mannopyranosyl)theophylline (I) recorded at 60 Mc in $CDCl_3$.

pounds examined are in good agreement with the theoretical values of the C1 conformation.

Chemical Shifts of Acetate-Methyl Signals.—Equatorial acetate-methyl signals (δ 2.11–2.02) in pyranose ring had been confirmed to shift to smaller δ values than those of axial ones (δ 2.19–2.15),[5,8–14] and acetate-methyl signals on axial and equatorial orientations above the plane of D-hexopyranose ring had been confirmed to shift to relatively a little smaller δ values than those on their orientations below the plane of pyranose ring.[10,13] This tentative rule was applied to the assignment of acetate-methyl signals of the acetylated derivatives to be examined. As shown in Table III, two acetate-methyl signals of axial orientation and one signal of equatorial one appear in I: the two axial signals were assigned to the acetate-methyl signals at C-3′ and C-4′ and one equatorial signal to that at C-2′. The acetate-methyl signals in other compounds examined are in good agreement with those of C1 conformation having one axial orientation at C-2 and two equatorial ones at C-3 and C-4. Therefore, these acetate-methyl signals in I fall within the range expected as 1C conformation.[5,8–14]

C–H Deformation Vibration at the Anomeric Carbon in the Infrared Spectra.—It had been found by the infrared spectral analysis to be able to distinguish the orientation of anomeric hydrogens due to the axial and equatorial C–H deformation vibrations at the anomeric carbon and equatorial C–H deformation vibrations other than the anomeric one.[15–17] The analytical results are shown in Table IV. Compounds I and II show absorption bands in the range from 890 to 895 cm^{-1}, indicating the axial orientation of C–H at the anomeric carbon. On the other hand, IV, X, and XI show absorption bands in the range from 840 to 860 cm^{-1}, indicating the equatorial orien-

TABLE III

CHEMICAL SHIFTS OF ACETATE-METHYL PROTONS[a]

	Chemical shifts (δ)[b]							Presumed conformation
	AcO-2		AcO-3		AcO-4			
Compd	a	e	a	e	a	e	AcO-6	
I		2.06	2.14		2.16		1.93	1C
III[c]		2.06	2.14		2.16			1C
IV	2.20			2.70		2.01	2.00	C1
V[d]	2.15			2.10		2.04	1.99	C1
VI	2.23			2.08		2.07	2.03	C1
VII	2.23			2.02		2.02	2.00	C1
XI	2.13		2.11		2.15			1C
XII		2.06		2.02		2.06	1.90	C1

[a] Measured in $CDCl_3$. The assignments of the acetate-methyl resonances are carried out only on the basis of the empirical rule as described in the text. Recently, D. Horton has shown that the acetate-methyl resonance in the highest field to the C_6 substituents may be erroneous (150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965) but the exact assignment is not definitely settled. [b] For the compound I, the position numbers 2, 3, 4, and 6 should be taken to mean 2′, 3′, 4′, and 6′, respectively; a, axial; e, equatorial. [c] Reported by Hall and Hough.[10] [d] Reported by Sowden, Bowers, Hough, and Shute.[13]

TABLE IV

ABSORPTION BANDS IN THE INFRARED SPECTRA OWING TO THE C–H DEFORMATION VIBRATION AT ANOMERIC CARBON (cm^{-1})[a]

	Deformation vibration		
	Anomeric C–H		
Compd	Axial[b]	Equatorial[c]	Other equatorial C–H
I	895 (m)	...	870 (w)
II	890 (m)	...	880 (w)
IV	...	860 (m)	875 (w)
X	...	840 (w)	883 (w)
XI	...	840 (w)	880 (m)

[a] m, moderate absorption; w, weak absorption. [b] Reported value: 891 ± 7.[15,16] [c] Reported value: 844 ± 8.[15,16] [d] Reported value: 880 ± 8.[15,16] Recently the C–H deformation vibration at C-1 has been amended. A vibration of the whole grouping at the aromeric carbon atom has been found to be responsible for each of these bands, but the exact nature of the vibration is still not definitely settled.[17]

(10) L. D. Hall and L. Hough, *Proc. Chem. Soc.*, 382 (1962).
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tation of C–H at the anomeric carbon. These data also support the 1C conformation for I and for II.

All of these data described above fully support the 1C conformation for I and for II, and are inconsistent with any other conformational assignments.

As an essential factor for the conformational inversion, Lemieux and Morgan[5] suggested that a quaternized nitrogen on axial orientation at the anomeric carbon might be necessary for the inversion arising from the electrostatic interaction between the C-1 to N and C-5 to O bonds. From our observation, it is clear that methyl, *p*-nitrophenyl, and bromine molecules as aglycon on axial orientation at the anomeric carbon of D-mannopyranose have no effect on the conformational inversion, and that theophylline molecule as aglycon, on the other hand, has effect on the inversion. In due consideration of these data and of the existing states of pyranoses in natural products, it seems that there might be a relationship between the configurations and molecular weights of substituents on axial orientation and the conformational inversion. But this problem will have to be studied further, in viewpoint of the mechanism and biological meanings.

Experimental Section

All nmr spectra were recorded at 60 Mc with a Varian A-60 spectrometer at its normal operating temperature, and chemical shifts in the nmr spectra were expressed on δ scale in parts per million downfield displacement from tetramethylsilane or sodium 2,2-dimethyl-2-silapentane-5-sulfonate as internal standard. All infrared spectra were measured with a Shimadzu AR-6 spectrophotometer (sodium chloride optics). All compounds were examined in Nujol as phase. An ORD curve was measured with an optical rotatory dispersion recorder (Model ORD/UV-5, Japan Spectroscopic Co., Ltd.). Paper chromatographic examination was carried out on Toyo Roshi No. 51 filter paper by the descending technique, using 1-butanol–water (86:14, v/v) as developing solvent. All melting points are uncorrected.

7-(2′,3′,4′,6′-Tetra-*O*-acetyl-α-D-mannopyranosyl)theophylline (I).[18]—Syrupy 1,2,3,4,6-penta-*O*-acetyl-D-mannopyranose (3.9 g) was treated with theophylline (1.8 g) in an oil bath at 150–160° in the presence of about 0.1 g of freshly fused zinc chloride according to the procedure previously reported.[19,20] The reaction product was dissolved in a small volume of boiling methanol. Unreacted theophylline, which was immediately precipitated, was removed by filtration. The filtrate was allowed to stand in a refrigerator to produce a crystalline product. The product was recrystallized from ethanol: yield 2.1 g (41%); mp 136°; $[\alpha]^{22}D$ +39° (*c* 1.0, $CHCl_3$); R_f 0.77; ν_{max}^{Nujol} 1760 (OAc), 1705 (C=O), and 1550 (C=N) cm^{-1}.

Anal. Calcd for $C_{21}H_{26}N_4O_{11}$: C, 49.41; H, 5.13; N, 11.00. Found: C, 49.16; H, 5.26; N, 11.18.

7-α-D-Mannopyranosyltheophylline (II).—Deacetylation of I was carried out in methanol saturated with ammonia, according to the usual procedure. The reaction product was recrystallized from water: mp 199–200°; $[\alpha]^{22}D$ +86° (*c* 1.0, H_2O); R_f 0.21–0.22; ν_{max}^{Nujol} 3300 (OH), 1700 (C=O), and 1545 (C=N) cm^{-1}; $\lambda_{max}^{H_2O}$ 275 mμ (ϵ_{max} 7.6 × 10^3); ORD (*c* 1.0, H_2O), 17°, $[\phi]_{700}$ +219°, $[\phi]_{600}$ −301°, $[\phi]_{500}$ +356°, $[\phi]_{400}$ +793°, $[\phi]_{350}$ +1230°, and $[\phi]_{300}$ +2330°.

Anal. Calcd for $C_{13}H_{18}N_4O_7$: C, 45.61; H, 5.30; N, 16.37. Found: C, 45.73; H, 5.43; N, 16.17.

The other compounds examined were prepared according to each of the authorized methods: methyl 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranoside (V),[21] mp 161°, $[\alpha]^{22}D$ −46° (*c* 1.0, $CHCl_3$); *p*-nitrophenyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (VI),[22] mp 156–157°, $[\alpha]^{22}D$ +103° (*c* 1.5, $CHCl_3$); *p*-tolyl-2,3,4,6-tetra-*O*-acetyl-D-mannopyranosylamine (VII),[23] mp 127–128°; 1,2,3,4,6-penta-*O*-benzoyl-β-D-mannopyranose (X),[24] mp 147–148°; and 2,3,4-tri-*O*-acetyl-1,6-anhydro-β-D-glucopyranose (XI),[25] mp 111°, $[\alpha]^{22}D$ −55° (*c* 2.0, $CHCl_3$). The nmr spectral data of III,[10] of IV,[13] of VIII,[4a] and of IX[4a] are obtained from the reported ones, respectively.

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(18) The α configuration was assigned from the data of the nmr spectra of I and II and of the ORD curve of II.
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Tagatosazine. A Condensation Product Prepared from 2-Amino-2-deoxy-D-galactose

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Fructosazine,[1] 2,5-bis(D-*arabino*-tetrahydroxybutyl)-pyrazine, is a condensation product of 2 moles of 2-amino-2-deoxy-D-glucose (D-glucosamine), and has been previously prepared from 2-amino-2-deoxy-D-glucose in aqueous solution[2] and in methanol solution.[3] It is also prepared from 2-amino-2-deoxy-D-mannose and an evidence is offered that 2-amino-2-deoxy-D-glucose is epimerized to 2-amino-2-deoxy-D-mannose under the alkaline conditions besides the condensation to the fructosazine.[4]

It is expected that 2-amino-2-deoxy-D-galactose would similarly produce the corresponding pyrazine derivative, 2,5-bis(D-*lyxo*-tetrahydroxybutyl)pyrazine, designated as tagatosazine. This compound has been obtained actually by heating 2-amino-2-deoxy-D-galactose in methanolic alkaline solution. The product has the similar composition as fructosazine but the melting point, 198° dec, and rotatory power, $[\alpha]^{20}D$ −14.5° (*c* 1.0, water), are different from the corresponding physical constants, mp 237° and $[\alpha]^{20}D$ −84.1°, of fructosazine. The infrared spectra of both pyrazine derivatives differ from each other.

Tagatosazine and fructosazine gave the identical oxidative cleavage product, pyrazine-2,5-dicarboxylic acid, which was characterized by converting into the methyl ester. By acetylation with acetic anhydride and pyridine, tagatosazine was converted to the octaacetate, mp 143°, $[\alpha]^{11}D$ −3.6° (*c* 1.0, chloroform). These constants differ from those of fructosazine octaacetate, mp 174°, $[\alpha]^{11}D$ −7.2° (*c* 1.0, chloroform). The infrared spectra of both octaacetates do not overlap each other.

The nmr spectrum[5] of tagatosazine octaacetate is given in Figure 1. The C-3 proton of the pyrazine system (C-1 hydrogen of the 2-amino-2-deoxy-D-

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