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-

(1) K. Stolte, *Beitr. Chem. Physiol. Pathol.*, **11**, 19 (1908).
(2) M. I. Taha, *J. Chem. Soc.*, 2468 (1961).
(3) C. A. Lobry de Bruyn, *Rec. Trav. Chim.*, **18**, 77 (1899).
(4) S. Fujii, R. Kikuchi, and H. Kushida, *J. Org. Chem.*, in press.
(5) Nmr spectrum was measured with Varian A-60 60-Mcps nmr spectrometer. Tetramethylsilane (τ 10.00) was used as the internal reference standard.

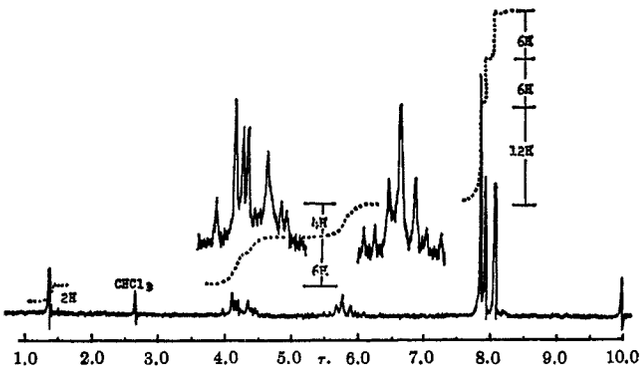
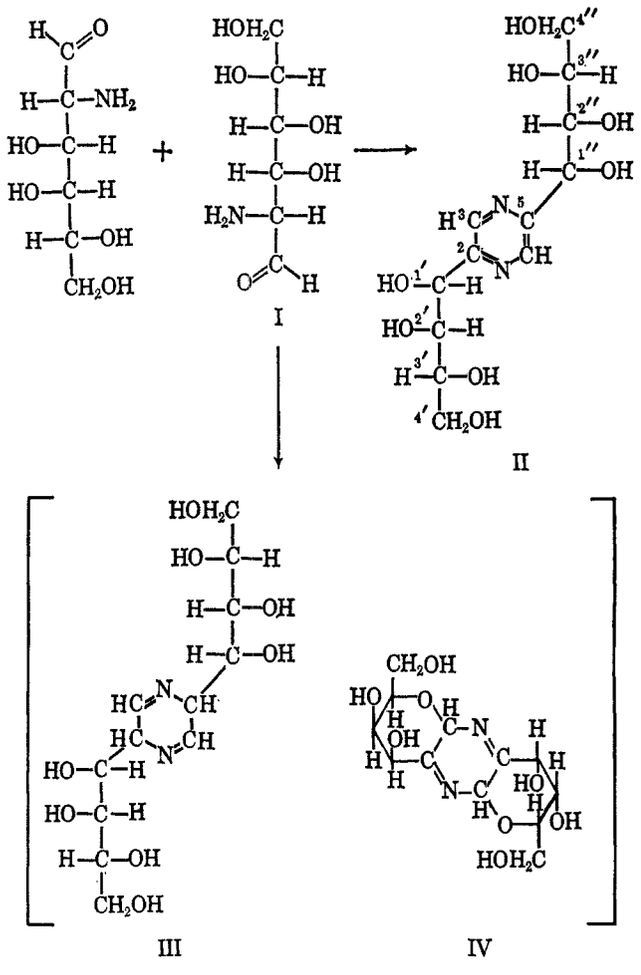


Figure 1.—Nmr spectrum of 2,5-(D-*lyxo*-tetraacetoxybutyl)-pyrazine.

SCHEME I



galactose) appears as a low field singlet, τ 1.04, as in the case of fructosazine. This fact supports the structure II, for in the structure III the proton at C-3 would appear as a doublet through coupling with the proton at C-2. The integral value of protons appears between τ 4.0 and 6.0, corresponding to six methine protons at C-1′, C-2′, C-3′, C-1″, C-2″, C-3″, and four methylene protons at C-4′, C-4″, and between τ 7.8 and 8.2, corresponding to 24 protons of eight acetyl groups. These data exclude the possibility of structure III and IV. (See Scheme I.)

Experimental Section[6]

Tagatosazine.—Thirty grams of 2-amino-2-deoxy-D-galactose hydrochloride was suspended in 150 ml of hot methanol containing 3.6 g of sodium, and after shaking, sodium chloride deposited was filtered off. The filtrate was warmed to 60–65° in water bath under reflux and oxygen was bubbled into the solution for 6 hr. After allowing to stand overnight, this reaction mixture was dissolved in 500 ml of water and passed through an Amberlite infrared-120 (H^+) column (3 × 70 cm). The eluate together with washings was neutralized with Dowex 1 × 8 (HCO^-), 200–400 mesh, and the resin was removed by filtration. After treatment with charcoal, the solution was concentrated *in vacuo* to a syrup. This syrup was dissolved in small amount of methanol, and ethanol was added to this solution to turbidity. Then crystals were deposited; the yield was 2.2 g (9.6%). Recrystallization from water and ethanol furnished pure crystals, mp 198° dec, $[\alpha]^{20}D$ −14.5° (*c* 1.0, water), $\lambda_{max}^{H_2O}$ 274 mμ.

Anal. Calcd for $C_{12}H_{20}N_2O_8$: C, 45.00; H, 6.29; N, 8.75. Found: C, 44.92; H, 6.55; N, 8.68.

2,5-Bis(D-*lyxo*-tetraacetoxybutyl)pyrazine.—This compound was prepared according to the method reported by Taha,[2] for fructosazine octaacetate, by acetylation of tagatosazine (220 mg) with acetic anhydride and pyridine. Recrystallization from acetone and petroleum ether afforded pure crystals, in the yield of 270 mg (61%): mp 143°; $[\alpha]^{11}D$ −3.6° (*c* 1.0, chloroform); ν_{max}^{Nujol} 1740 (C=O), 1230, 1060, and 870 cm^{-1}. For nmr spectrum, see Figure 1.

Anal. Calcd for $C_{28}H_{36}N_2O_{16}$: C, 51.22; N, 5.53; N, 4.27. Found: C, 51.18; H, 5.53; N, 4.25.

2,5-Dimethoxycarbonylpyrazine (Pyrazine-2,5-dicarboxylic Acid Dimethyl Ester) from Tagatosazine.—Tagatosazine (500 mg) was treated with potassium permanganate according to the method of Mager and Berends,[7] and 70 mg of pyrazine-2,5-dicarboxylic acid thus gained was converted to 2.5-dimethoxycarbonylpyrazine by boiling in methanolic hydrogen chloride. Recrystallization from methanol gave 58 mg of pure product: mp 168°; the over-all yield, 19.4%; ν_{max}^{Nujol} 1720 (C=O), 1286, 1153, 1030 (C—O—C), 968, 830 (C=CH), and 763 cm^{-1}.

Anal. Calcd for $C_8H_8N_2O_4$: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.03; H, 4.19; N, 13.98.

No depression in the melting point was observed when this material was mixed with a sample of the authentic one from fructosazine, and they showed the identical infrared spectrum.

(6) All melting points are uncorrected.

(7) H. I. X. Mager and W. Berends, *Rec. Trav. Chim.*, **77**, 827 (1958).

An Unusual Wittig Reaction with Benzil

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The reaction of benzil with triphenylphosphine-phenylmethylene, according to Parrick,[1] leads to unilateral condensation, giving *cis*- and *trans*-1,2,3-triphenyl-1-propen-3-one. In a study of synthetic routes to pseudo-aromatic, polycyclic ring systems, we have investigated the reactions of the bisphosphorane (III), derived from 1,8-bis(bromomethyl)-naphthalene (I) *via* (II) (Chart I). Since the only reaction of III which had been reported so far, was its oxidative transformation to acenaphthylene,[2] condensations with benzaldehyde and 2-naphthaldehyde were studied. 1,8-Distyrylnaphthalene (IV, Ar = C_6H_5) and 1,8-di-[β-(2-naphthyl)vinyl]naphthalene (IV, Ar = 2-$C_{10}H_7$) were obtained.[3] In the reaction with benzil, however, a yellow-greenish hydrocarbon $C_{38}H_{22}$ (mp

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(2) H. J. Bestmann, H. Haeberlein, and O. Kratzer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 226 (1964); J. Bestmann, *ibid.*, **4**, 830 (1965).

(3) The configuration of the compounds, IV, has not been elucidated; the infrared spectrum indicates that at least one of the double bonds (and probably both) has the *trans* configuration, which would have been expected under the experimental conditions used.