acid 4-N-oxide samples showed the identical R_f values[12] and developed color by ferrosulfate.[13]

2-(D-*arabino*-Tetraacetoxybutyl)pyrazine 4-N-Oxide (3a).—A mixture of 5.0 g of **3** prepared from **2**, 100 ml of dry pyridine and 100 ml of acetic anhydride was warmed at about 50° to a solution with stirring. After keeping it at room temperature overnight, the solution was poured into 1000 ml of ice water. The aqueous mixture was extracted three times with 100 ml of chloroform, and the chloroform layer was washed twice with 100 ml of 2 *N* hydrochloric acid, twice with a 100 ml of saturated aqueous sodium hydrogen carbonate, and twice with a 100 ml of water. The solution was dried with anhydrous magnesium sulfate and concentrated *in vacuo*, giving 7.6 g (85.5%) of white needles by adding a little ether. Washing these with ethanol and ether and recrystallization from methanol and ethanol gave mp 142°; $[\alpha]^{28}D$ −6.82 → −2.79° (after 24 hr) (*c* 1.0 CHCl); ir (Nujor) 1050, 1270 (N→O), 1230 (C—O), 1600 (C=N), 1750 cm^{-1} (C=O); uv max (MeOH) 268 mμ; for nmr data, see Table I.

Anal. Calcd for $C_{16}H_{20}N_2O_9$: C, 50.00; H, 5.52; N, 7.29. Found: C, 50.06; H, 5.72; N, 7.48.

According to the procedures described above, 2.0 g of 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 4-N-oxide (**3**) prepared from 2-amino-2-deoxy-D-mannose oxime (**6**) was acetylated to yield 2.2 g (61.8%) of tetraacetate. Analyses, infrared spectra, and mixture melting points showed that this acetate was identical with the acetylated compound **3a** prepared from 2-amino-2-deoxy-D-glucose oxime (**2**).

Registry No.—Glyoxal, 107-22-2; **2**, 21537-55-3; **3**, 21537-56-4; **3a**, 21537-57-5; ; **4**, 874-54-4; **6**, 21537-58-6.

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Di-*O*-bromoethylidene-D-mannitol Formation[1]

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The stereochemistry and structure of 1,2-*O*-bromoethylidene-D-mannitol and its role in the reaction pathway leading to 1,2:5,6-di-*O*-bromoethylidene-D-mannitol were studied. Nmr spectroscopy established that monoacetal formation was from the outset an equilibrium-controlled reaction, giving a 65:35 *cis/trans* ratio. Previously reported work pointed out the high proportion of *cis* rings in the diacetal formation, *ca.* 67:33 *cis,cis/cis,trans*. When the latest results are coupled with earlier data, the reaction pathway can be explained. Monoacetal formation is equilibrium controlled and the subsequent diacetal formation is kinetically controlled and irreversible because of insolubility. Examination of molecular models suggested that the *cis* preference in the second ring closure may be accounted for by a long-range directional effect transmitted through hydrogen bonding. The unreported 3,4,5,6-tetra-*O*-methyl-D-mannitol was prepared as its crystalline 1,2-di-*O*-*p*-tolylsulfonyl ester.

From the acid-catalyzed condensation of bromoacetaldehyde diethyl acetal and D-mannitol two diacetals[3] were isolated. These diacetals were shown to be *cis*-1,2:*cis*-5,6-di-*O*-bromoethylidene-D-mannitol and the related *cis*-1,2:*trans*-5,6 isomer; no *trans,trans* isomer was found. The *cis,cis* isomer constituted approximately twice the amount of the *cis,trans* isomer. In the 1,3-dioxolane ring the greater stability of the *cis* over the *trans* isomer has been demonstrated for 2,4-dimethyl-1,3-dioxolane[4,5] and 4-benzyloxymethyl-2- bromomethyl-1,3-dioxolane.[5] 1,3-Dioxolane formation proceeds through an initial kinetic phase where *cis* stereochemistry predominates, and a subsequent equilibrium phase where the *cis/trans* ratio resides around 60:40.[4,6] However, with terminal diols no significant kinetic phase was noted.[6] If the diacetal pathway were equilibrium controlled and assuming a 60:40 *cis/trans* ratio, the predicted ratios would be *cis,cis/cis,trans/trans,trans* 36:48:16, which are very much at variance with the results. This variance suggested that somewhere along the mannitol → monoacetal → diacetal pathway a kinetically controlled step was operating, yielding preferentially a *cis*-1,3-dioxolane. Since both ring closures would involve terminal hydroxyl groups, no kinetic preference was expected. Accordingly, the preparation of the monoacetal was carried out and its function in the pathway was investigated to clarify this question of a kinetic preference of terminal hydroxyl groups.

Results

On dissolving D-mannitol and bromoacetaldehyde diethyl acetal (BEA) in 3–12 *N* hydrochloric (or sulfuric) acid, exploratory investigations established that a mono-*O*-bromoethylidene-D-mannitol formed rapidly. With a molar ratio of 1:1 mannitol–BEA, a moderate amount of di-*O*-bromoethylidene-D-mannitols[3] precipitated from solution. By altering the ratio to 10:1 mannitol–BEA, diacetal precipitation was avoided, but, since separating the excess mannitol proved time consuming, a compromise ratio of 2–4:1 mannitol–BEA was commonly used. After the reaction mixture was worked up and the solid was recrystallized to constant melting range, 1,2-*O*-bromoethylidene-D-mannitol (**1**), mp 151–153°, was isolated which, on reaction with acetic anhydride in pyridine, gave a crystalline tetra-*O*-acetyl ester, **1**-Ac_4, mp 76–78° (Figure 1). Both *p*-toluenesulfonyl chloride and methanesulfonyl chloride in pyridine gave products that were crystalline at ice-bath temperature, but, since they liquefied on warming to room temperature, they were not investigated further. Periodate oxidation (3.1–3.4 equiv) confirmed the structural assignment of the acetal bonds in **1**.

Chromatographic techniques—paper, tlc, gas, ion exchange (borate)—failed to separate **1**. Multiple ascent

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(2) This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

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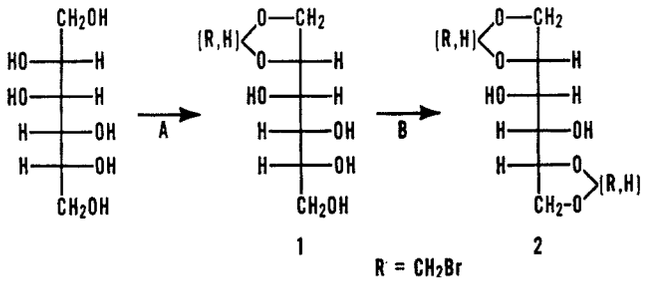

Figure 1.—Di-*O*-bromoethylidene-D-mannitol formation.

tlc on the 3,4,5,6-tetra-*O*-acetyl-1,2-*O*-bromoethylidene-D-mannitol revealed two overlapping comet-shaped spots. Nmr spectroscopy of **1** and its tetraacetate revealed two triplets in the δ 5 area. Previous work[3] assigned the *cis* structure to the upfield triplet and the *trans* structure to the downfield triplet. Decoupling experiments established that the two doublets near δ 3.5 were coupled with these triplets, the inner doublet and triplet and outer doublet and triplet being respectively coupled. Integration of nmr curves in the δ 5 area resulted in a 65:35 *cis/trans* ratio, close to the ratio reported[4,5] for other 1,3-dioxolanes.

Kinetic studies on the monoacetal formation, followed by nmr, revealed no kinetic preference. Experiments conducted to follow the conversion of monoacetal into diacetal were inconclusive in that, shortly after blending, the diacetals precipitated from solution; nmr spectra could not be obtained. This precipitate compared in composition and melting point to the diacetals prepared[3] by direct reaction.

Discussion

When considering the sum of reaction A + B (Figure 1) in light of the information presented, a rational explanation for the pathway was that reaction A was equilibrium controlled and reaction B was not only kinetically controlled but also irreversible because of product insolubility. If reaction B was kinetically controlled to yield a *cis*-1,3-dioxolane and it was also irreversible, the *cis,cis/cis,trans* **2** ratio (~2:1) would approximate the *cis/trans* **1** ratio (~1.8:1). However, since reaction B involved a terminal hydroxyl group, no kinetic preference for a *cis* structure was anticipated. In some manner the first acetal seemed to exert a directional effect on the introduction of the second acetal.

In Figure 2 (**M** being C_1–C_4 in *O*-bromoethylidene-D-mannitol) shows a reasonable, but by no means exclusive, reaction pathway. Loss of ethanol from the protonated acetal to give a transoid oxonium ion,[7] followed by a rapid nucleophilic addition of the C_5 hydroxyl group to this oxonium ion, would rationalize the results if the product was removed from further reaction by precipitation. Loss of ethanol in this scheme would be the rate-determining step, hydroxyl addition and precipitation being irreversible. Consequently, structures that occurred before the protonated acetal were considered in explaining the *cis* preference. Structures A and B in Figure 3 would have a hydrogen bond to assist in their stabilization. Newman projections point out the preferred *trans* relationship both of the two bulky groups, $BrCH_2$ and C_6, and of the ethoxy and an electron pair. Since the C_5 hydroxyl is spatially close to its addition site in the oxonium ion, a minimum of molecular reorganization would be needed for ring closure. A minimal reorganization supports the view that this closure is kinetically controlled. Examination of space-occupying models, however, offer no clear choice between structures A or B.

(7) F. S. Al-Jeboury, N. Baggett, A. B. Foster, and J. M. Webber, *Chem. Commun.*, 222 (1965).

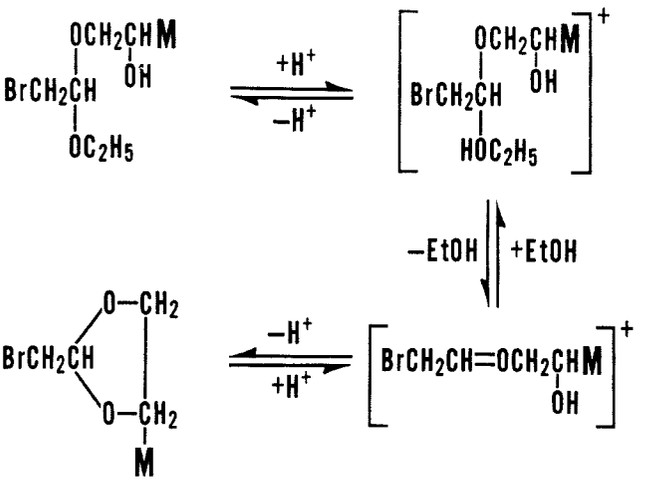

Figure 2.—Postulated reaction scheme. M signifies unshown portion of mannitol chain in **1**.

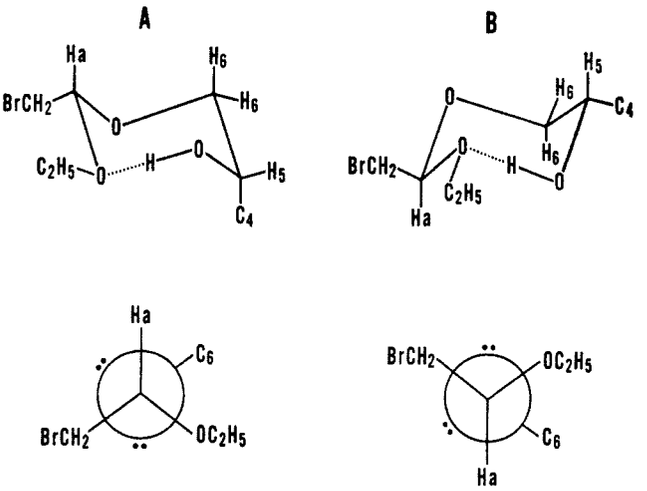

Figure 3.—Schematic line structure and Newman projection of an intermediate (see text). C_1–C_3 not shown.

Models of *cis* or *trans* **1** (not shown) indicate that one spatial arrangement might be preferred. A hydrogen bond between the C_2 oxygen and the C_4 hydroxyl group gives a compact structure. If this hydrogen bond is reasonably stable, it limits the position of the C_3 hydroxyl group. If the C_3, C_4, and C_5 hydroxyl groups are allowed to form a "hydrogen bond cluster" and if the transoid oxonium ion $[BrCH_2CH{=}OC_2H_5]^+$ can be fitted onto this cluster with a minimum of steric interaction, structure A (Figure 4) is the better arrangement. If the above conditions prevail, structure A will yield a *cis* isomer.

The unreported 3,4,5,6-tetra-*O*-methyl-D-mannitol was prepared as a crystalline 1,2-di-*O*-*p*-tolylsulfonate. Compound **1** was subjected to catalytic hydrogenolysis over Pd–C in ethanolic sodium hydroxide to give a crystalline 1,2-*O*-ethylidene-D-mannitol, which was methylated with sodium hydride and dimethyl sulfate. The methylated product, a syrup which could not be made

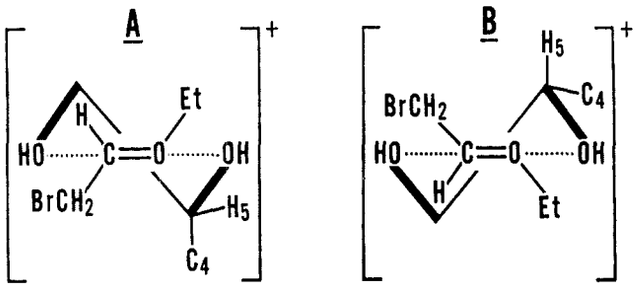

Figure 4.—Schematic line structure depicting transoid oxonium ion from BEA and compound 1; A is favored form. C_1–C_3 not shown nor are all hydrogens.

crystalline, was hydrolyzed, extracted with ether, and treated with *p*-toluenesulfonyl chloride in pyridine to yield a crystalline 3,4,5,6-tetra-*O*-methyl-1,2-di-*O*-*p*-tolylsulfonyl-D-mannitol, mp 98–100°.

Experimental Section

Tlc was carried out on silica gel G[8] with air-equilibrated plates of 0.25-mm thickness and the solvent systems as specified. The spots were detected by spraying with 5% ethanolic sulfuric acid and heating until charred. Linear horizontal paper chromatography was performed on Schleicher & Schuell 2043b with a solvent system *n*-BuOH–*i*-PrOH–H_2O, 3:1:1 (v/v). The spots were detected by either the periodate–permanganate spray of Lemieux and Bauer[9] or the $AgNO_3$–NaOH dipping reagent of Smith.[10] Ir spectra of samples were determined with a Perkin-Elmer Model 621 spectrophotometer, usually as KBr pellets. Nmr spectra were obtained with a Varian Model A-60 or Model HA-100 spectrometer. Chemical shifts were compared against internal tetramethylsilane or sodium 3-(trimethylsilyl)-1-propanesulfonate. Uv spectra were measured with a Cary Model 14 spectrophotometer. The melting points of samples in capillary tubes were measured on a Mel-Temp apparatus or a Mettler FP-1.

***cis,trans*-1,2-*O*-Bromoethylidene-D-mannitol (1).**—To a solution of 300 ml of concentrated hydrochloric acid and 300 ml of water was added 60 g of D-mannitol and 32 g of BEA. The heterogenous solution was mechanically shaken until homogenous, usually in less than 15 min. After standing 4–16 hr the reaction mixture was poured onto 2 l. of chopped ice and neutralized with 30% sodium hydroxide to pH 7.0 ± 0.1.

The neutralized solution was divided in half and processed as follows. Concentration under aspirator vacuum (bath temperature <60°) gave a thick slush, which was triturated with five 200-ml portions of boiling 2-propanol. Removing 2-propanol by evaporation yielded a tan solid which was dissolved in a minimum of hot water and blended with Avicel until a free flowing powder resulted. After 16-hr air drying, this powder was placed atop an Avicel chromatographic column (7 × 31 cm d × h, ~350 g), which had been prepared in a methyl ethyl ketone–water azeotropic solvent, and the column was developed with the same solvent. The first 400 ml of eluate was discarded; the next 4-l. portion was collected and concentrated under aspirator vacuum to a semicrystalline mass, which, on examination by paper and tlc[11] chromatography, was noted to be monoacetal with a trace of diacetal. By dissolving the mass in 200 ml of hot water, cooling to room temperature, and extracting immediately with three 50-ml portions of chloroform, the trace impurity was removed from the aqueous solution. Concentrating this solution to dryness gave a crystalline mass that was dissolved in a boiling mixture of 100 ml of 2-propanol and 5 ml of water, followed shortly by 200 ml of warm ethyl acetate. After the treated solution was cooled to room temperature and stored at 0–5° for 16 hr, the crystals that formed were separated by filtration to give 6.57 g of *cis,trans* 1: mp 151–153°; $[\alpha]^{24}D$ +2.3° (*c* 1.08, H_2O); nmr data (center values) triplets δ 5.15, 5.27 ($J \sim 4$ Hz), doublets 3.51, 3.53 ($J \sim 8$ Hz); λ_{max}^{KBr} 3320 (OH); R_f 0.60. In four runs 3.1, 3.4, 3.3, and 3.1 molar equiv of sodium metaperiodate were reduced[12] in ~15–30 min with no additional reduction over 22 hr. Further crystallization did not change the melting point.

Anal. Calcd for $C_8H_{15}BrO_6$: C, 33.46; H, 5.26; Br, 27.83. Found: C, 33.44; H, 5.46; Br, 27.87.

On further elution of the Avicel column with 2 l. of 50% ethanol, D-mannitol (21 g) was recovered.

***cis,trans*-3,4,5,6-Tetra-*O*-acetyl-1,2-*O*-bromoethylidene-D-mannitol (1-Ac_4).**—Compound 1 (1.115 g) was dissolved in 25 ml anhydrous pyridine, the solution was cooled to −5°, acetic anhydride (20 ml) was added, and the reaction mixture was stored at 0–5° for 24 hr. After storage the mixture was poured on 400 ml of chopped ice; this chilling caused an oil to separate that on storage at 0–5° transformed over a 48-hr period to a granular solid. After separating this solid by filtering on a funnel and washing with water (25–50 ml), it was air dried for 16 hr and recrystallized from a mixture of 6 ml of ethanol and 12 ml of hexane. After 3 days at 0–5° the crystals were separated and air dried: 1.347 g; mp 76–78°; $[\alpha]^{27}D$ +26° (*c* 1.99, $CHCl_3$); λ_{max}^{KBr} 1750 (C=O); multiple ascent tlc revealed two overlapping spots with benzene–*t*-BuOH 50:1 (v/v); nmr shows four acetyl methyl groups. Two recrystallizations from 2-propanol, followed by vacuum pumping for 24 hr at room temperature, gave an analytical sample.

Anal. Calcd for $C_{16}H_{23}BrO_{10}$: C, 42.21; H, 5.09; Br, 17.55. Found: C, 42.50; H, 5.10; Br, 17.76.

1,2-*O*-Ethylidene-D-mannitol.—Compound 1 (15.17 g) was dissolved in 250 ml of 95% ethanol, containing 20 ml of water. A solution of soidum hydroxide (3 g) in 50 ml of 95% ethanol and 10 ml of water was blended with the initial solution, before adding 5.0 g of 5% Pd–C. The final mixture was immediately hydrogenolyzed at room temperature, 51.5 psi → 46.5 psi in ~15 min (4.5 psi theory), when the hydrogenolysis was halted. Filtration through a bed of Celite 535 removed the catalyst. After dilution with 300 ml of water, the filtrate was neutralized with 0.1 *N* hydrochloric acid to pH 7.1 ± 0.05. Evaporation gave a crystalline mass, which was triturated with three 75-ml portions of boiling isopropanol. Removal of the 2-propanol resulted in a white solid; it was recrystallized from a mixture of 40 ml of 2-propanol and 20 ml of ethyl acetate. Separating the crystals by filtration gave 7.36 g of the title compound, mp 130–140°; concentrating the filtrate gave 5.5 g of compound. An additional recrystallization from 2-propanol (6 ml/g) gave an analytically pure sample: mp 151–153°; $[\alpha]^{24}D$ +2.6° (*c* 0.567, H_2O); R_f 0.54; δ 1.34, 1.37 (CH_3), 5.05, 5.16 (CH).

Anal. Calcd for $C_8H_{16}O_6$: C, 46.15; H, 7.74. Found: C, 46.28; H, 7.88.

3,4,5,6-Tetra-*O*-methyl-1,2-*O*-*p*-tolylsulfonyl-D-mannitol.—Sodium hydride (6.5 g, 55% oil dispersion) was washed with three 100-ml portions of anhydrous ether and finally covered with 100 ml of anhydrous ether. Dimethyl sulfate (8 ml) and 1,2-*O*-ethylidene-D-mannitol (1.98 g) were mixed with the sodium hydride suspension, and the mixture was stirred for 3 days at room temperature. Ethanol was added to destroy excess hydride. After this solution was diluted with water (~100 ml), the ether layer was separated and the aqueous portion extracted with two 50-ml portions of ether. After the combined ether extracts were dried, concentration left 1.92 g of syrup (3,4,5,6-tetra-*O*-methyl-1,2-*O*-ethylidene-D-mannitol) which resisted crystallization. This syrup was dissolved in 50 ml of methanol, 4 drops of concentrated hydrochloric acid was added, and the mixture was allowed to stand 16 hr at room temperature, when it was diluted with 50 ml of water and neutralized with 0.01 *N* NaOH to pH 7.0 ± 0.1. The neutralized solution was transferred with water to a continuous ether extract for 16 hr. Removal of the ether left a syrup that resisted crystallization. To 382 mg of this syrup, dissolved in 5 ml of anhydrous pyridine, was added 1.0 g of *p*-toluenesulfonyl chloride and the mixture stored at 0–5° for 3 days. After the dropwise addition of water (~3 ml), the mixture was diluted with water (50 ml total) to yield a thick syrup. On standing at 0–5° for 6 days this syrup solidified; the solid was broken up, separated by filtration, washed on the funnel with ice water (~10 ml), air dried, and recrystallized from 5 ml of 95% ethanol to give 252 mg of crystalline title compound: mp

(8) The mention of firm names or trade products does not imply that they are endorsed by the U. S. Department of Agriculture over similar or unmentioned products.

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98–100°; $[\alpha]^{22}D$ +48.8° (*c* 0.041, 95% EtOH); λ_{max}^{KBr} 2840 (OCH_3), 1373, 1180 (SO_3) cm^{-1}; λ_{max} in 95% ethanol δ 262 (ϵ 1200) 273 (1000), 2.45 ($ArCH_3$), 3.38 (OCH_3).

Anal. Calcd for $C_{24}H_{34}O_{10}S_2$: C, 52.73; H, 6.27; S, 11.73. Found: C, 52.67; H, 6.09; S, 11.42.

Registry No.—1, 21903-06-0; 1-Ac_4, 21903-07-1; 1,2-*O*-ethylidene-D-mannitol, 21903-08-2; 3,4,5,6-tetra-*O*-methyl-1,2-di-*O*-*p*-tolylsulfonyl-D-mannitol, 21903-09-3.

Acknowledgments.—The author wishes to thank Clara McGrew, Bonita Heaton, and Karen A. Jones for the microchemical analyses and W. A. Boyd for the nmr data.

An Anomalous Stereochemical Course and a Color Phenomenon in the Addition of Anthranilic Acid to a Sugar Nitro Olefin. The Synthesis of 2,3-Diamino-2,3-dideoxy-D-mannose[1,2]

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Most additions of nucleophiles to the nitro olefin **1**, methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside, give products having a 2,3-diequatorial orientation of substituents (D-*gluco* configuration), but the 2,3-axial–equatorial orientation (D-*manno* configuration) may arise with anthranilic acid as addend. While this addend, when employed in a 2:1 molar ratio in the presence of a catalytic amount of potassium hydroxide, furnished methyl 4,6-*O*-benzylidene-2-(2-carboxyanilino)-2,3-dideoxy-3-nitro-β-D-glucopyranoside (**2**) in 83% yield, it gave the D-*manno* isomer (**9**) of **2** in 56% yield as the sole, isolated product when the ratio of reactants was 1:1 and the catalyst was omitted. Addition to **1** of methyl anthranilate afforded only the methyl ester (**3**) of **2** and not the methyl ester (**10**) of **9**. However, either ester was obtained from its parent acid with diazomethane. The crystalline D-*manno* acid (**9**) and ester (**10**) are yellow, but are colorless in solution. Compound **2** was converted by several steps into methyl 2,3-diacetamido-2,3-dideoxy-β-D-glucopyranoside (**8**), and compound **9** was similarly converted into new, β-glycosidic derivatives of 2,3-diamino-2,3-dideoxy-D-mannose and finally into the reducing diamino sugar dihydrochloride (**14**).

Certain compounds of anthranilic acid with sugars exist in nature as bacterial metabolites. Thus, 1-(2-carboxyphenyl)amino-1-deoxy-D-ribulose has been detected in cultures of *Aerobacter aerogenes*[3] and *Escherichia coli*,[4] and 1-(2-carboxyphenyl)amino-1-deoxy-D-fructose is produced by *Salmonella typhimurium*[5] and *Neurospora crassa*.[6] These compounds, which are considered to be intermediates in the bacterial biosynthesis of tryptophan, have also been synthesized chemically.[7] To our knowledge, no sugars that carry an *o*-carboxyphenylamino group at a carbon atom other than C-1 have been described. It was therefore decided to synthesize such compounds and, at the same time, to test the scope of the synthesis of 2,3-diamino sugars recently worked out in this laboratory.[8,9] The synthesis is based on amination of 2,3-unsaturated 3-nitro glycosides followed by hydrogenation to the diamino stage.

The Addition of Anthranilic Acid.—Methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside (**1**), a versatile acceptor for nucleophilic addends including ammonia[8] and aliphatic amines[10] among others,[10,11] was refluxed with a 2–3 molar excess of anthranilic acid in benzene solution in the presence of a catalytic amount of potassium hydroxide. A colorless, crystalline addition product (**2**) was isolated in 83% yield (Scheme I). When an excess of anthranilic acid was maintained but the catalyst omitted, the yield of **2** was only 41%; however, an isomeric product was isolated in 22% yield, as characteristic lemon-yellow crystals. The separable amount of yellow isomer rose to 56% and the colorless isomer could no longer be isolated[12] when equimolar proportions of **1** and anthranilic acid were employed in the absence of potassium hydroxide catalyst.

The two isomers gave infrared (ir) spectra that were generally similar but differed considerably in detail (see Experimental Section). They had nearly identical melting points but widely different specific rotations. The presence of a free carboxyl group in each was demonstrated by the production of methyl esters by diazomethane. The esters differed strongly in their rotations and melting points, and the ester arising from the yellow isomer formed yellow crystals, too, whereas the other ester was colorless like its acid. It will be shown that the colorless acid was methyl 4,6-*O*-benzylidene-2-(2-carboxyanilino)-2,3-dideoxy-3-nitro-β-D-glucopyranoside (**2**) and that the yellow acid was methyl 4,6-*O*-benzylidene-2-(2-carboxyanilino)-2,3-dideoxy-3-nitro-β-D-mannopyranoside (**9**).

Considering the results of numerous additions of nucleophiles to **1** already reported,[8,10,11] compound **2** was the expected product. Almost all of the various addition products previously obtained from **1** had possessed the D-*gluco* configuration. A single exception[8] was a minor isomer, of then undetermined con-

(1) (a) Part XIV in a series on the reactions of nitro sugars. (b) For part XIII, see H. H. Baer and F. Rajabalee, *Can. J. Chem.*, **47**, 4086 (1969).

(2) This work was done as part of a Ph.D thesis submitted by F. K. to the University of Ottawa, 1968. It was presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

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(12) Whether or not a minor proportion of **2** was present cannot be stated with certainty since fractional crystallization of the mother liquor proved to be difficult.