TABLE III

CHEMICAL SHIFTS OF ACETYL METHYL PROTONS

Compd.	Configuration	Chemical shifts, τ (integral, protons) — Axial OAc	Equatorial and primary (OAc and NHAc)
Acetylated Aldopyranosyl Bromides			
I	α-D-*xylo*		7.89 (3), 7.92 (6)
II	β-D-*arabino*	7.86 (3)	7.91 (3), 7.98 (3)
III	α-D-*lyxo*	7.83 (3)	7.90 (3), 7.95 (3)
IV	β-D-*ribo*	7.85 (6)	7.98 (3)
V[a]	α-D-*gluco*		7.91 (6), 7.97 (3), 7.99 (3)
VI	α-D-*galacto*	7.86 (3)	7.91 (3), 7.97 (3), 8.01 (3)
VII	α-D-*manno*	7.83 (3)	7.91 (3), 7.92 (3), 8.00 (3)
Acetylated 2-Amino-2-deoxyaldopyranosyl Halides			
VIII[b]	α-D-*gluco*		7.92 (3), 7.96 (6), 7.99 (3)
IX[c]	α-D-*gluco*		7.77 (3), 7.91 (3), 7.94 (3)
X[d]	α-D-*gluco*		7.89 (3), 7.93 (3), 8.15 (3)
Acetylated Aldopyranoses			
XI	α-D-*lyxo*	7.87 (3), 7.90 (3)	7.95 (3), 7.98 (3)
XII	β-D-*manno*	7.80 (3)	7.90 (6), 7.95 (3), 8.00 (3)

[a] Data supersede values given in ref. 2b. [b] *N*-Acetyl 1-chloride. [c] Hydrobromide 1-bromide. [d] *N*-(2,4-Dinitrophenyl) 1-bromide.

acetyl-α-D-galactopyranosyl bromide (VI), m.p. 84–86° (lit.[35] m.p. 84–85°). Crystalline 1,2,3,4-tetra-*O*-acetyl-β-D-ribopyranose was converted by the method of Levene and Tipson[36] into tri-*O*-acetyl-β-D-ribopyranosyl bromide (IV), m.p. 94° (lit.[36] m.p. 96°). Crystalline 1,2,3,4-tetra-*O*-acetyl-α-D-lyxopyranose (XI) was converted by the method of Levene and Wolfrom[16] into sirupy tri-*O*-acetyl-α-D-lyxopyranosyl bromide (III), $[\alpha]^{28}D$ +95° (*c* 2, chloroform); the solution of XI in hydrogen bromide–acetic acid was kept for 1 hr. at 25° rather than the 20 min. specified by Levene and Wolfrom. Crystalline 1,2,3,4,6-penta-*O*-acetyl-β-D-mannopyranose (XII), m.p. 113–114°, was converted by the method of Levene and Tipson[37] into tetra-*O*-acetyl-α-D-mannopyranosyl bromide (VII), sirup, $[\alpha]^{21}D$ +125° (*c* 0.7, chloroform) [lit.[37] $[\alpha]D$ +123° (chloroform)].

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2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranosyl Chloride[38] **(VIII).**—This compound was prepared directly[39] from 2-acetamido-2-deoxy-D-glucose and had m.p. 125–127° (lit.[39] m.p. 127–128°). The n.m.r. spectrum showed, in addition to the signals listed in Tables I–III, a 1-proton doublet at τ 3.28 (*J* = 9.5 c.p.s., NH proton). This signal disappeared, without observed change in the rest of the spectrum except near τ 5.5 (H-2), when the prepared sample (in $CDCl_3$) was shaken with 0.05 ml. of deuterium oxide for 40 min. at room temperature.

3,4,6-Tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl Bromide Hydrobromide[40] **(IX).**—This compound, prepared by an adaptation[41] of the original[40] procedure, had m.p. 149° (lit.[40] m.p. 149–150°). In addition to the data listed in Tables I–III, the n.m.r. spectrum showed a broad 3-proton multiplet at τ 1.38 ($-NH_3^+$).

3,4,6-Tri-*O*-acetyl-2-deoxy-2-(2,4-dinitroanilino)-α-D-glucopyranosyl Bromide[42] **(X).**—This compound, prepared by the procedure of Horton and Wolfrom,[43] had m.p. 160° (lit.[42] m.p. 160–162°). In addition to the data listed in Tables I–III, the n.m.r. spectrum showed the following signals due to the 2 substituent[8]: τ 2.85 (1-proton doublet, *J* = 9.3 c.p.s., NH), 1.71 (1-proton quartet, $J_{5',6'}$ = 9.0 c.p.s., $J_{3',5'}$ = 3.0 c.p.s., H-5′), 1.23 (1-proton doublet, $J_{5',6'}$ = 9.0 c.p.s., H-6′), and 0.90 (1-proton doublet, $J_{3',5'}$ = 3.0 c.p.s., H-3′). The τ 2.85 signal did not undergo deuterium exchange under the conditions used for compound VIII, even after 12 hr.

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Amino Derivatives of Starches. Derivatives of 3,6-Diamino-3,6-dideoxy-D-altrose[1,2]

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Hydrazinolysis of methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside (I), followed by reduction, gives methyl 3,6-diamino-3,6-dideoxy-α-D-altropyranoside, isolable in high yield as the *N,N′*-diacetyl (IV) or *N,N′*-(2,4-dinitrophenyl) (III) derivatives. The structure and stereochemistry of the product were proved by a sequence of degradation reactions and by comparison of the products with derivatives of known α-amino acids. 3,6-Diacetamido-3,6-dideoxy-D-altrose was prepared by way of 3,6-diacetamido-3,6-dideoxy-D-altrose diethyl dithioacetal (XIII).

A program in this laboratory is concerned with the synthesis and structural characterization of aminated polysaccharides derived from starches. An aminated amylose has been prepared[3] from a di-*O*-*p*-tolylsulfonyl derivative of a slightly derivatized amylose, by hydrazinolysis and reduction. Possible reactions of a 2,6-disulfonate ester of amylose, when treated with hydrazine or azide ion and subsequently reduced, have been discussed in the preceding paper in this series. Direct displacement of the sulfonate ester groups would lead to a 2,6-diamino-2,6-dideoxy-D-mannose residue, although more probable routes in the hydrazinolysis reaction would involve either 2,3-epoxide formation with subsequent nitrogen attack at C-3, or 3,6-anhydro ring formation, with or without further displacement at C-2. We have conducted studies on the amination of simple systems to provide models for the reaction in the polysaccharide system and to furnish reference compounds for fragmentation studies on the aminated polysaccharides. 2,6-Diamino-2,6-dideoxy-D-mannose has already been synthesized[4] as such a

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(2) Reported in part in Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 3D.

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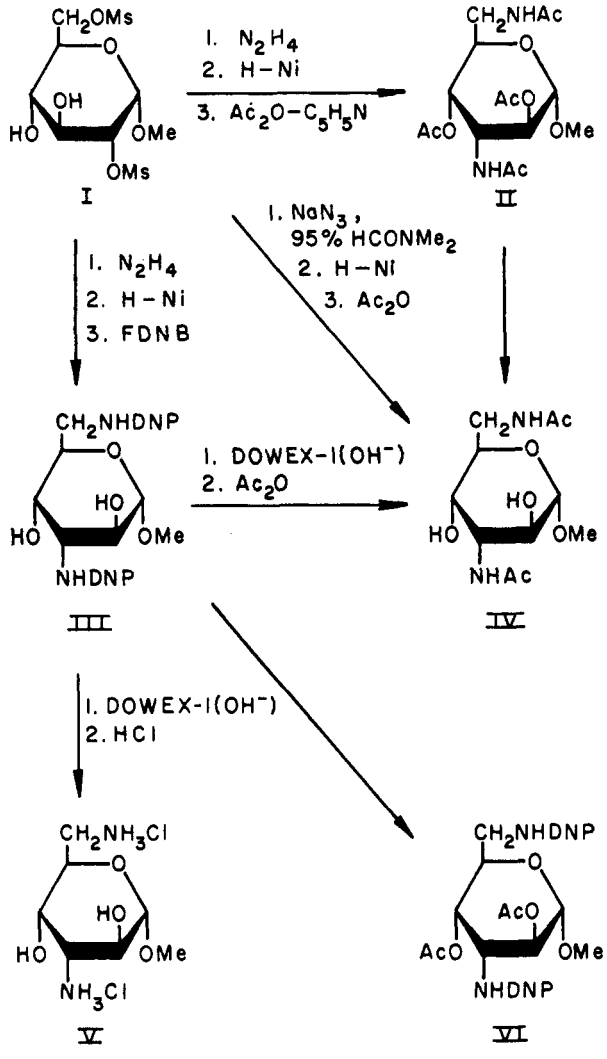
SCHEME I



DNP = 2,4-dinitrophenyl

FDNB = 1-fluoro-2,4-dinitrobenzene

reference compound. The present work reports a study on the reaction of methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside (I) (and the di-*p*-toluenesulfonate analog) with hydrazine and with azide ion, as a model for the reaction leading to the aminated amylose reported previously.[3] Reduction of the hydrazinolysis product is shown to give methyl 3,6-diamino-3,6-dideoxy-α-D-altropyranoside in high yield, indicating that 3,6-diamino-3,6-dideoxy-D-altrose residues are probably a major component of aminated amylose.[3] The 3,6-diamino-3,6-dideoxy-D-altrose derivatives reported herein represent examples of a novel class of diamino sugars.[5] There is considerable current interest in synthesis of diamino sugars, since 2,6-diamino-2,6-dideoxyhexose moieties are found in a number of antibiotics.[6]

Hydrazinolysis of methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside[7] (I), followed by reduction and acetylation gave in high yield a methyl 3,6-diacetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-D-hexopyranoside (II), which on *O*-deacetylation gave a crystalline methyl 3,6-diacetamido-3,6-dideoxy-α-D-hexopyranoside (IV) (see Scheme I). Assignment of one of the acetamido groups to C-3 was based on the fact that IV did not undergo periodate oxidation. The diaminohexose glycoside could also be isolated from the reduced hydrazinolysate as its crystalline *N,N'*-bis(2,4-dinitrophenyl) derivative III from which the amino group could be regenerated and the product isolated as dihydrochloride V or diacetamido derivative IV. The dimethanesulfonate I was employed in this work because the corresponding 2,6-di-*p*-toluenesulfonate[8] has not been obtained crystalline. Since the amylose amination had been effected[3] through the *p*-toluenesulfonated polysaccharide, it was desirable to demonstrate that the sirupy methyl 2,6-di-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside gave the diamino sugar derivative II in approximately the same yield, and this was done.

Azide replacement of sulfonate ester groups is a facile reaction at the primary C-6 position,[9] but forcing conditions[10] are required for replacement at secondary positions. Treatment of I with sodium azide in aqueous acetone solution under long reflux,[9] followed by reduction, caused replacement of only one of the methylsulfonyloxy groups, presumably that on C-6, by an amino group, and the product was isolated as its hydrochloride XV. Under forcing conditions[10] considerable darkening occurred, but it was possible to isolate the diamino sugar in low yield (6%) as the *N,N'*-diacetyl derivative IV.

Since one acetamido group in II may reasonably be assigned to C-6, and the other to C-3, it is evident that an intermediate epoxide is involved in the reaction, which undergoes attack by hydrazine at C-3. This intermediate could be the 2,3-epoxide having the D-*manno* configuration, formed by rearside attack on C-2 by the oxygen atom at C-3, or it could conceivably be the 3,4-epoxide having the D-*altro* configuration, formed by epoxide migration[11] from the D-*manno* 2,3-epoxide. The 3,6-diamino sugar derivative formed from the former intermediate would have the D-*altro* configuration, that from the latter would have the D-*manno* configuration. There is abundant evidence from ammonolysis studies on methyl 2-chloro-2-deoxy-β-D-glucopyranoside[12] and methyl 2-*O*-*p*-tolylsulfonyl-β-D-glucopyranoside[13] that the 3-amino sugar having the D-*altro* configuration is the major product in this type of system. The principle of diaxial scission of epoxides cannot be used for configurational predictions in this case since compound I does not have a fused-ring system to lock its conformation. The following sequence of degradations (Scheme II) was undertaken to assign total structure to II and to determine the configuration at C-2 and C-3; the results prove that II and its derivatives have the D-*altro* configuration.

(5) Concurrently with our preliminary report,[2] the synthesis of another 3,6-diamino-3,6-dideoxyhexose, having the D-*ido* configuration, was reported: S. Hanessian and T. H. Haskell, Abstracts of Papers, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964, p. 2D.

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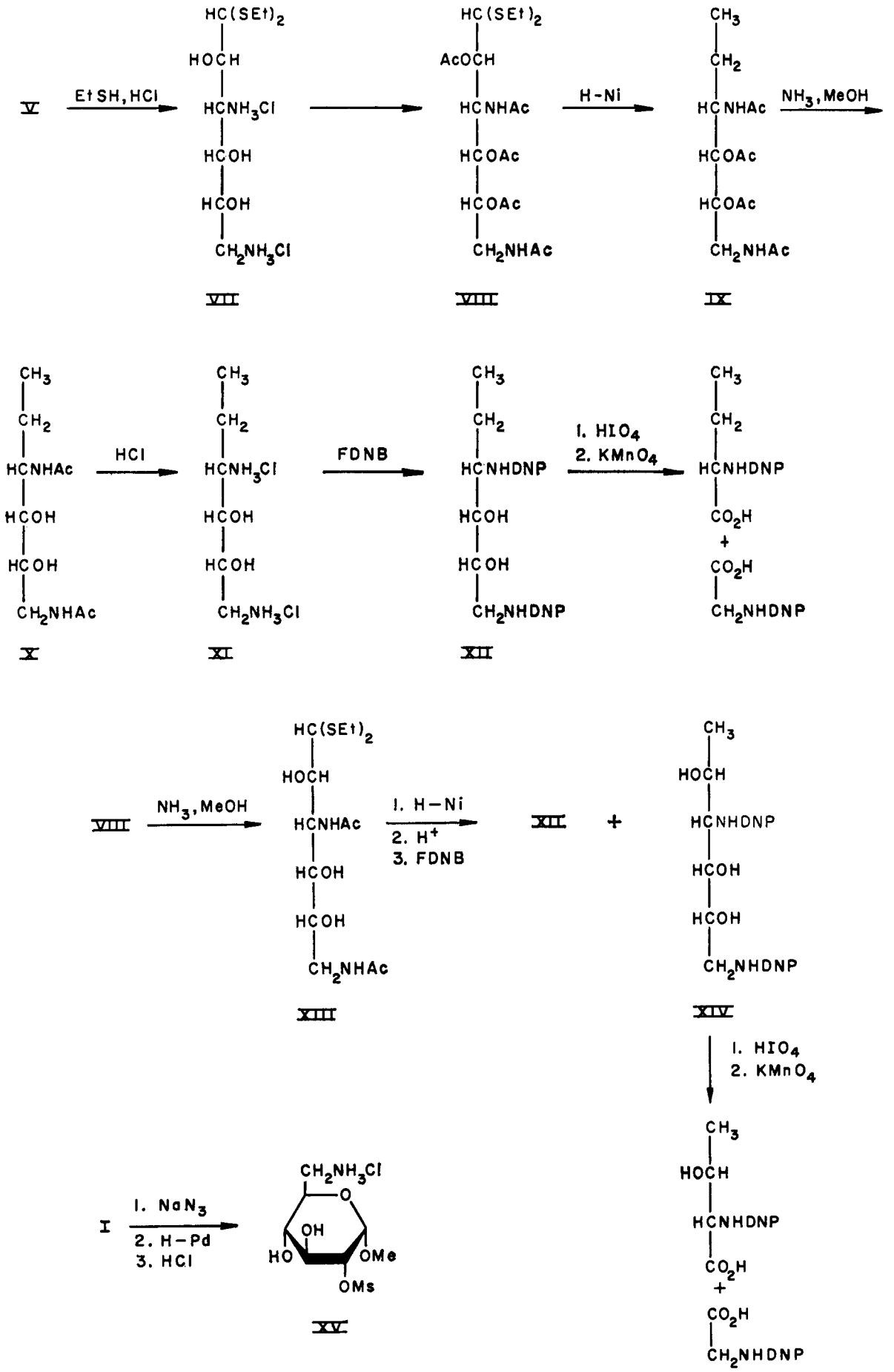
SCHEME II


V
EtSH, HCl
VII
VIII
H-Ni
IX
NH3, MeOH
X
HCl
XI
FDNB
XII
1. HIO4
2. KMnO4
CO2H
+
CO2H
VIII
NH3, MeOH
XIII
1. H-Ni
2. H+
3. FDNB
XII
+
XIV
1. HIO4
2. KMnO4
I
1. NaN3
2. H-Pd
3. HCl
XV
OH
HO
OMe
OMs

Substance V was converted by mercaptolysis into the acyclic diethyl dithioacetal dihydrochloride VII which on complete acetylation to VIII and *O*-deacetylation yielded the diacetamidodideoxy derivative XIII of the dithioacetal. Removal of the thioacetal groups from XIII gave crystalline 3,6-diacetamido-3,6-dideoxy-D-altrose. Compound XIII was reductively desulfurized[14] and the product was isolated as its *N*,*N*'-bis(2,4-dinitrophenyl) derivative XIV. Periodate cleavage of the latter, followed by permanganate oxidation[15] produced the *N*-(2,4-dinitrophenyl) derivatives of the known amino acids glycine and L-threonine, which were firmly characterized on a crystalline basis. This rigorously establishes the configuration of C-2 and C-3 in V and allocates the D-*altro* configuration to it. Other possible epoxide scission products are excluded by this evidence.

When the fully acetylated diethyl dithioacetal VIII of the diamino aldose was subjected to reductive desulfurization[14] there was obtained as the isolated product a substance (IX) whose analysis indicated that two of its carbon atoms had been reduced to the hydrocarbon stage. A small proportion of the *O*-deacetylated analog of IX also accompanied the reductive desulfurization of the derivative XIII. The n.m.r. spectrum of IX showed the presence of an ethyl group, indicating that reduction at C-2 as well as at C-1 had occurred. The structure of IX was proved by *O*-deacetylation to X, hydrolysis to the dihydrochloride XI, conversion into the 3,6-bis(2,4-dinitrophenyl) derivative XII, and periodate cleavage of the glycol group in XII with subsequent oxidation of the aldehydes formed. The *N*-(2,4-dinitrophenyl) derivatives of glycine and L-α-aminobutyric acid were isolated; new constants for the latter are recorded. These data prove that the desulfurization product (IX) is 3,6-diacetamido-4,5-di-*O*-acetyl-1,2,3,6-tetradeoxy-D-*ribo*-hexitol. The loss of the 2-acetoxy group during desulfurization of VIII is closely analogous to the loss of a 2-benzoyloxy group in the Raney nickel desulfurization of 3-benzamido-2,4-di-*O*-benzoyl-3,6-dideoxy-D-mannose diethyl dithioacetal observed by Wintersteiner and co-workers[16] during structural studies on mycosamine. These authors proposed that the reaction involves attack by sulfur on C-2 to displace the 2-acyloxy group, with formation of an episulfonium ion intermediate, which undergoes desulfurization to give the 1,2-dideoxyalditol. The difference in the behavior of VIII and XIII on desulfurization can be attributed to the fact that the acetoxy group is a better leaving group than the hydroxyl group.

Experimental Section

Methyl 3,6-Dideoxy-3,6-bis(2,4-dinitroanilino)-α-D-altropyranoside (III).—Methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside[7,17] (I, 50 g.) was refluxed with anhydrous hydrazine[18] (500 ml.) under nitrogen for 2 days. Excess hydrazine was removed by distillation under reduced pressure and the resultant sirup was dissolved in water (250 ml.) and treated with Raney nickel[19] (36 g.) for 2 days. After removal of the catalyst, the solvent was removed under reduced pressure to give a glass, yield 50 g. Paper chromatography with the Fischer–Nebel[20] solvent system revealed a single ninhydrin-positive zone, R_f 0.77. The glassy product was dissolved in 1 l. of acetone–water (1:4, v./v.) and shaken mechanically with sodium carbonate (25 g.) and 1-fluoro-2,4-dinitrobenzene (28.6 ml.) for 24 hr. The yellow solid which formed was collected by filtration, homogenized in a Waring Blendor, and washed with water, yield 54 g. (72%). Crystallization from acetone–water gave a yellow compound with low recovery: m.p. 226–227°; $[\alpha]^{22}D$ +55° (*c* 1, acetone); λ_{max}^{KBr} 2.90 (OH), 3.00 (NH), 6.18, 6.30, 6.70 (aryl C=C), 6.58 (NH,NO_2), 7.46 (NO_2), 12.10, 13.40 μ (substituted benzene); X-ray powder diffraction data[21] 12.63 vw, 9.94 w, 8.67 w, 7.67 vw, 7.25 vw, 6.81 vw, 6.33 vw, 5.01 s (2), 4.80 s (3), 4.13 s (1), 3.82 m, 3.48 w, 3.34 w, 3.15 w, 3.01 w.

Anal. Calcd. for $C_{19}H_{20}N_6O_{12}$: C, 43.54; H, 3.85; N, 16.04. Found: C, 43.86; H, 4.07; N, 16.07.

Methyl 2,4-Di-*O*-acetyl-3,6-dideoxy-3,6-bis(2,4-dinitroanilino)-α-D-altropyranoside (VI).—Methyl 3,6-dideoxy-3,6-bis-(2,4-dinitroanilino)-α-D-altropyranoside (III, 200 mg.) was treated with acetic anhydride (0.5 ml.) and pyridine (0.5 ml.) for 24 hr. at room temperature. The reaction mixture was poured into ice and water and the precipitated yellow solid was collected, yield 200 mg. Recrystallization from ethyl acetate gave pure material: m.p. 243–244°; $[\alpha]^{18}D$ +96° (*c* 0.6, acetone); λ_{max}^{KBr} 3.00 (NH), 5.73 (OAc), 6.18, 6.30 (aryl C=C), 6.50 (NH,NO_2), 7.50 (NO_2), 12.10, 13.40 μ (substituted benzene); X-ray powder diffraction data[21] 12.28 w, 9.51 w, 8.93 w, 8.40 s (2), 7.14 vw, 6.61 vw, 5.75 m, 4.90 w, 4.72 w, 4.29 w, 4.13 s (1), 3.79 w, 3.59 w, 3.39 w, 3.29 s (3).

Anal. Calcd. for $C_{23}H_{24}N_6O_{14}$: C, 45.40; H, 3.98; N, 13.81. Found: C, 45.20; H, 4.02; N, 13.68.

Methyl 3,6-Diamino-3,6-dideoxy-α-D-altropyranoside Dihydrochloride (V).—Crude methyl 3,6-dideoxy-3,6-bis(2,4-dinitroanilino)-α-D-altropyranoside (III, 20 g.) was dissolved in acetone (700 ml.), and water (300 ml.) was added. The yellow solution was passed slowly through a column (45 × 5 cm.) of Dowex-1 (OH^-) ion-exchange resin,[22] which had been prewashed with acetone–water (7:3 v./v.) solvent. The column was washed until free from amino sugar (negative ninhydrin reaction), and the combined effluent and washings were concentrated. Concentrated hydrochloric acid (8 ml.) was added to a methanolic solution of the resultant sirup and the excess hydrochloric acid was removed by codistillation with 1-propanol. A solid formed which was crystallized from methanol–1-propanol as large prisms: yield 7.45 g. (76%); m.p. 178° dec.; $[\alpha]^{20}D$ +87° (*c* 2.0, water); λ_{max}^{KBr} 2.90 (OH), 3.30, 3.65, 4.90, 6.23 μ (NH_3^+); X-ray powder diffraction data[21] 8.93 m, 7.08 s (3), 6.71 w, 6.19 m, 5.61 m, 5.47 w, 4.90 w, 4.44 m, 4.13 m, 3.87 m, 3.63 s (1), 3.40 m, 3.24 m, 3.16 vw, 3.08 vw, 3.00 s (2).

Anal. Calcd. for $C_7H_{18}Cl_2N_2O_4$: C, 31.33; H, 6.84; Cl, 26.74; N, 10.56. Found: C, 31.09; H, 6.87; Cl, 26.56; N, 10.51.

Methyl 3,6-Diacetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-D-altropyranoside (II). A. From Methyl 2,6-Di-*O*-(methylsulfonyl)-α-D-glucopyranoside (I).—Methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside (I, 10 g.) was treated with hydrazine and the hydrazino compound (not isolated) was reduced with Raney nickel as described above for the synthesis of III. The resultant dried, glassy product (10 g.) was shaken with pyridine (30 ml.) and acetic anhydride (30 ml.) for 24 hr. at room temperature. Ice and water were added to the mixture, and after 1 hr. the solution was extracted with chloroform. The chloroform extract was dried (magnesium sulfate), the filtrate and washings were concentrated, codistilled repeatedly with toluene to remove pyridine, and the residue was crystallized from 1-propanol and ligroin by seeding with an authentic sample from B (below) and cooling, yield 6.1 g. (51%), m.p. 72–74°. Recrystallization

(14) M. L. Wolfrom and J. V. Karabinos, *J. Am. Chem. Soc.*, **66**, 909 (1944).

(15) M. L. Wolfrom, R. U. Lemieux, and S. M. Olin, *ibid.*, **71**, 2870 (1949).

(16) M. von Saltza, J. D. Dutcher, J. Reid, and O. Wintersteiner, *J. Org. Chem.*, **28**, 999 (1963).

(17) The authors thank Dr. D. H. Ball for a crystal nucleus of this compound.

(18) Technical hydrazine, anhydrous 95+%, Olin Mathieson Chemical Corp., New York 22, N. Y.

(19) Raney nickel catalyst no. 28, The Raney Catalyst Division of the W. R. Grace Co., Inc., Chattanooga, Tenn. The Raney nickel was washed to near neutrality with water before use.

(20) F. G. Fischer and H. J. Nebel, *Z. Phyisol. Chem.*, **302**, 10 (1955).

(21) Interplanar spacing, in Å., Cu Kα radiation. Relative intensity, estimated visually: s, strong; m, moderate; w, weak; v, very. First three strongest lines are numbered (1, strongest); double numbers indicate approximately equal intensities.

(22) Obtained from Dowex-1 (Cl^-), 8% cross linked, dry mesh 50–100.

from the same solvent with seeding gave pure material as a 1:1 solvate with 1-propanol: m.p. 74°; $[\alpha]^{22}D$ +44° (*c* 2, chloroform); λ_{max}^{KBr} 5.76 (OAc), 6.00, 6.40 μ (NHAc), X-ray powder diffraction data[21] 7.83 s (1), 7.03 vw, 6.46 m, 6.11 w, 5.68 w, 5.31 m (3), 4.85 m, 4.60 m, 4.33 vw, 4.11 w, 3.97 m, 3.66 s (2), 3.41 vw.

Anal. Calcd. for $C_{15}H_{24}N_2O_8 \cdot C_3H_8O$: C, 51.54; H, 7.59; N, 6.66. Found: C, 51.43; H, 7.95; N, 6.73.

B. From Methyl 3,6-Diamino-3,6-dideoxy-α-D-altropyranoside Dihydrochloride (V).—Methyl 3,6-diamino-3,6-dideoxy-α-D-altropyranoside dihydrochloride (V, 0.2 g.) was treated with pyridine (2 ml.) and acetic anhydride (2 ml.) for 24 hr. at room temperature. The product was isolated as in A, and crystallized from 1-propanol–ligroin, yield 0.2 g. (65%), m.p. 72–74°. This product was identical with that obtained in A above by mixture melting point and infrared spectrum.

C. From Methyl 2,6-Di-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside.—Methyl 2,6-di-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside[6,23] (1.05 g.) was treated with hydrazine and the hydrazino compound (not isolated) was reduced with Raney nickel as described above for the synthesis of III. The resultant glass was treated with pyridine (3 ml.) and acetic anhydride (3 ml.) for 24 hr. at room temperature. The product was isolated as in A and crystallized from the same solvent, yield 473 mg. (52% over-all), m.p. 74–75°, $[\alpha]^{22}D$ +44° (*c* 1.7, chloroform). This material was identical with that obtained in A above by mixture melting point, X-ray powder diffraction data, and by its infrared spectrum.

Methyl 3,6-Diacetamido-3,6-dideoxy-α-D-altropyranoside (IV). **A. From Methyl 3,6-Dideoxy-3,6-bis(2,4-dinitroanilino)-α-D-altropyranoside** (III).—The 2,4-dinitroanilino groups were removed from methyl 3,6-dideoxy-3,6-bis(2,4-dinitroanilino)-α-D-altropyranoside (III, 0.7 g.) with Dowex-1 (OH^-) as described above for the synthesis of V, and the final aqueous acetone solution was concentrated to low volume. Methanol (15 ml.) was added and the solution was stirred with acetic anhydride (1 ml.) for 90 min. at room temperature. Water (50 ml.) was added and, after 2 hr., excess acetic acid was removed by stirring with Dowex-1 (CO_3^{2-}) ion-exchange resin. The resin was filtered and washed with water. The filtrate and washings were combined, concentrated, and codistilled with 1-propanol to remove water. Crystallization of the residue from acetone gave a product, yield 0.306 g. (83%), m.p. 172–173°. Recrystallization from ethanol–acetone gave a pure product: m.p. 172–173°; $[\alpha]^{22}D$ +78° (*c* 1.0, methanol); λ_{max}^{KBr} 6.08, 6.4 μ (NHAc); X-ray powder diffraction data[21] 7.63 m, 6.76 m, 6.33 m, 5.83 m, 5.40 s (1), 4.87 w, 4.67 m, 4.40 s (1), 3.97 m, 3.85 vw, 3.56 w, 3.48 vw, 3.36 s (3), 3.15 vw, 3.09 s (2).

Anal. Calcd. for $C_{11}H_{20}N_2O_6$: C, 47.81; H, 7.30; N, 10.11. Found: C, 48.03; H, 7.26; N, 10.13.

When subjected to periodate oxidation, the substance consumed no oxidant.

B. From Methyl 3,6-Diacetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-D-altropyranoside (II).—Dry ammonia gas was passed for 1 hr. at 0° through a solution of methyl 3,6-diacetamido-2,4-di-*O*-acetyl-3,6-dideoxy-α-D-altropyranoside (II, 5 g.) in methanol (200 ml.). After 2 hr. at room temperature, the solvent was removed under reduced pressure and the resultant sirup was crystallized from acetone–ether, yield 3.25 g. (98%), m.p. 172–173°, $[\alpha]^{21}D$ +79° (*c* 1, methanol). The product was identical with that obtained in A above by X-ray powder diffraction data, infrared spectrum, and mixture melting point.

C. From Methyl 2,6-Di-*O*-(methylsulfonyl)-α-D-glucopyranoside (I) by Azide Replacement.—The procedure was essentially the one described by Wolfrom, Bernsmann, and Horton[10] except that a higher reaction temperature was used. Sodium azide (1 g.) was dissolved in water (12 ml.). To the solution were added urea (0.5 g.), *N*,*N*-dimethylformamide (250 ml.), and methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside (I, 5 g.). The homogeneous solution was heated at 150° for 36 hr. under nitrogen. Solvent was removed from the dark solution by distillation under reduced pressure. The black residue was then codistilled with toluene and extracted with acetone. The acetone extract was decolorized with carbon. The sirupy diazido sugar (not isolated) was treated with Raney nickel (12 g.) in ethanol (50 ml.) for 2 days. Raney nickel was removed by filtration. The sirup (1.96 g.) obtained gave a positive ninhydrin test. Acetic anhydride (4 ml.) was added to a methanol solution (20 ml.) of this sirup. After 90 min., excess acetic anhydride was hydrolyzed and the acetic acid was neutralized with Dowex-1 (CO_3^{2-}) ion-exchange resin as described above for the synthesis of IV from III. After removal of solvent, the sirup was crystallized from acetone, yield 250 mg. (6.4% over-all), m.p. 170°, $[\alpha]^{22}D$ +79° (*c* 1, methanol). Comparison of this material with methyl 3,6-diacetamido-3,6-dideoxy-α-D-altropyranoside (IV) [m.p. 173°, $[\alpha]^{21}D$ +79° (*c* 1, methanol)], prepared by hydrazinolysis from (I), by infrared spectrum, X-ray powder diffraction data, and mixture melting point, confirmed their identity.

Aliquots (30 ml.) were withdrawn at selected time intervals from another run under the above reaction conditions. Solvent was removed by distillation under reduced pressure and the residue was extracted with acetone. Investigation of the sirup, by thin layer chromatography (silica gel) with ethyl acetate as developer, showed that one methylsulfonyloxy group was completely replaced in 3 hr., and that the second was replaced only gradually, with complete replacement being achieved after 36 hr. of heating. However, after 6 hr. of heating the reaction mixture had become black in color. The R_f values of the starting material (I), monoazido, and diazido derivatives were 0.52, 0.72, and 0.88, respectively.

Methyl 6-Amino-6-deoxy-2-*O*-(methylsulfonyl)-α-D-glucopyranoside Hydrochloride (XV).—The general procedure of Cramer and co-workers[9,24] was used. A solution of methyl 2,6-di-*O*-(methylsulfonyl)-α-D-glucopyranoside (I, 4.5 g.) in acetone (60 ml.), to which a solution of sodium azide (6.76 g.) in water (40 ml.) had been added, was refluxed for 4 days, and the solvent was removed under reduced pressure. The residue was extracted with acetone, and the extract was concentrated to a sirup. Thin layer chromatography (silica gel) of this sirup with ethyl acetate as developer showed a single spot, the monoazido derivative, R_f 0.52. A solution of this sirup in ethanol (80 ml.) was hydrogenated over 5% palladium on charcoal (0.5 g.) for 18 hr. at 3-atm. pressure. The catalyst was removed by filtration, the filtrate was concentrated and acidified with concentrated hydrochloric acid, and the excess hydrochloric acid was removed by codistillation with 1-propanol. The sugar hydrochloride was decolorized by boiling with carbon in methanol, and crystallized from methanol–ether, yield 3.14 g. (79%), m.p. 201° dec. Recrystallization from the same solvent gave pure material: m.p. 202° dec.; $[\alpha]^{20}D$ +96° (*c* 1.66, water); X-ray powder diffraction data[21] 7.02 s (2), 6.23 m, 5.68 vw, 5.40 vw, 5.03 m, 4.74 m, 4.17 s (1), 3.63 s (2), 3.45 m, 3.26 m, 3.06 m.

Anal. Calcd. for $C_8H_{18}ClNO_7S$: C, 31.22; H, 5.90; Cl, 11.52; N, 4.55; S, 10.42. Found: C, 31.60; H, 6.16; Cl, 11.20; N, 4.85; S, 10.16.

3,6-Diamino-3,6-dideoxy-D-altrose Diethyl Dithioacetal Dihydrochloride (VII).—A solution of methyl 3,6-diamino-3,6-dideoxy-α-D-altropyranoside dihydrochloride (V, 6 g.) in concentrated hydrochloric acid (30 ml.) was shaken mechanically with ethanethiol (30 ml.) for 2 days at room temperature. Excess methanol was added, the mixture was neutralized with lead carbonate and filtered, and the filtrate was concentrated to a sirup under reduced pressure. This sirup was dissolved in hot ethanol. Air evaporation of solvent deposited a white solid which was collected and washed with 2-propanol, yield 4.5 g. (56%), m.p. 184° dec. Crystallization from ethanol gave pure product: m.p. 186° dec.; $[\alpha]^{21}D$ +31° (*c* 2.3, water); λ_{max}^{KBr} 3.03 (OH), 3.28, 3.44, 5.14, 6.24 (NH_3^+), 7.73 μ (SEt); X-ray powder diffraction data[21] 14.03 m, 9.83 m, 7.14 s (3), 6.56 w, 6.19 m, 5.31 m, 4.82 s (1), 4.60 w, 4.15 w, 3.85 s (2,2), 3.62 s (2,2), 3.45 vw, 3.30 w, 3.03 vw, 2.88 vw, 3.75 m, 2.60 w, 2.50 w.

Anal. Calcd. for $C_{10}H_{26}Cl_2N_2O_3S_2$: C, 33.61; H, 7.33; Cl, 19.84; N, 7.84; S, 17.95. Found: C, 33.60; H, 7.51; Cl, 19.95; N, 7.96; S, 17.34.

Aliquots (0.5 ml.) in another run with methyl 3,6-diamino-3,6-dideoxy-α-D-altropyranoside (V, 0.275 g.), concentrated hydrochloric acid (2.75 ml.), and ethanethiol (2.75 ml.) were withdrawn at selected time intervals and neutralized as described above. Paper chromatography of the sirup with a 40:10:49:1 butanol–ethanol–water–concentrated ammonia solvent system indicated (by ninhydrin) that the dithioacetal (R_f 0.76) and another substance or mixture, R_f 0.41 (presumably thioglycosides), began to form after 1 hr. The starting material (R_f 0.28) was present in only a trace amount after 48 hr.; the major

(23) Methyl 2,6-di-*O*-*p*-tolylsulfonyl-α-D-glucopyranoside was obtained as a sirup by chromatography of the crude product on a silica gel column eluted with 2% methanol in chloroform.

(24) F. Cramer, H. Otterbach, and H. Springmann, *Ber.*, **92**, 384 (1959).

component was the dithioacetal and the minor one was the other (presumably thioglycosides).

3,6-Diacetamido-2,4,5-tri-*O*-acetyl-3,6-dideoxy-D-altrose Diethyl Dithioacetal (VIII).—Crude 3,6-diamino-3,6-dideoxy-D-altrose diethyl dithioacetal dihydrochloride (VII, 4 g.) was acetylated with acetic anhydride and pyridine as described above for the synthesis of II, and the product was isolated in the same manner. The resultant sirup was dissolved in a small volume of ethanol and crystallized by adding ether: yield 4.8 g. (87%); m.p. 161–162°; $[\alpha]^{21}D$ +45° (*c* 1.0, chloroform); λ_{max}^{KBr} 5.76 (OAc), 6.04, 6.40 μ (NHAc); X-ray powder diffraction data[21] 12.45 m, 10.05 m, 8.93 m, 7.97 vs (1), 7.03 m, 6.37 s (2), 5.75 vw, 5.37 m, 5.10 m, 4.77 m, 4.58 m, 3.93 s (3), 3.72 m, 3.34 m, 2.98 m.

Anal. Calcd. for $C_{20}H_{34}N_2O_8S_2$: C, 48.56; H, 6.93; N, 5.66; S, 12.97. Found: C, 48.77; H, 7.10; N, 5.64; S, 13.08.

3,6-Diacetamido-4,5-di-*O*-acetyl-1,2,3,6-tetradeoxy-D-*ribo*-hexitol (IX).—A solution of 3,6-diacetamido-2,4,5-tri-*O*-acetyl-3,6-dideoxy-D-altrose diethyl dithioacetal (VIII, 3 g.) in absolute ethanol (150 ml.) was boiled with neutral Raney nickel (30 g.) for 6 hr. The nickel was filtered and washed with methanol. The filtrate was concentrated and the sirup was crystallized from ethanol–petroleum ether (b.p. 36–60°), yield 1.40 g. (73%), m.p. 190–193°. Recrystallization from ethanol gave pure material: m.p. 194–195°; $[\alpha]^{21}D$ −25° (*c* 1.05, methanol); λ_{max}^{KBr} 5.81 (OAc), 6.1 μ (NAc); n.m.r. data[25] τ 9.11 (triplet, 3 protons, 1-CH_3, $J_{1,2}$ = 6.5 c.p.s.), 8.79 (multiplet, 2 protons, 2-CH_2), 8.01, 7.91 (singlets, 3 protons each), 7.96 (singlet, 6 protons, 3,6-NAc, 4,5-OAc), 3.17 (broad multiplet, 2 protons, disappearing after deuteration, 3,6-NH); X-ray powder diffraction data[21] 6.86 s (1), 6.11 m, 5.16 s (2), 4.82 m, 4.55 m, 3.95 s (3,3), 3.80 s, 3.55 w, 3.44 w, 3.31 s (3,3), 3.06 m.

Anal. Calcd. for $C_{14}H_{24}N_2O_6$: C, 53.15; H, 7.65; N, 8.86; CH_3CO, 54.50. Found: C, 52.90; H, 7.60; N, 8.86; CH_3CO, 54.31.

3,6-Diacetamido-1,2,3,6-tetradeoxy-D-*ribo*-hexitol (X).—3,6-Diacetamido-4,5-di-*O*-acetyl-1,2,3,6-tetradeoxy-D-*ribo*-hexitol (IX, 0.9 g.) was *O*-deacetylated with methanolic ammonia as described above for the synthesis of compound IV. The product, a white solid, was isolated in the same manner. It was recrystallized from ethanol–acetone–ether, yield 0.6 g. (91%), m.p. 148–149°. Recrystallization effected in the same manner gave pure material: m.p. 150–151°; $[\alpha]^{21}D$ −29° (*c* 1, water); λ_{max}^{KBr} 3.00 (OH), 6.08, 6.49 μ (NHAc); X-ray powder diffraction data[21] 11.48 s (1), 6.15 m, 5.12 s (2), 4.10 m, 3.97 m, 3.74 m, 3.55 m, 3.35 w, 3.12 w.

Anal. Calcd. for $C_{10}H_{20}N_2O_4$: C, 51.70; H, 8.68; N, 12.06. Found: C, 51.75; H, 8.91; N, 11.97.

3,6-Diamino-1,2,3,6-tetradeoxy-D-*ribo*-hexitol Dihydrochloride (XI).—3,6-Diacetamido-1,2,3,6-tetradeoxy-D-*ribo*-hexitol (X, 250 mg.) was heated with 2 *N* hydrochloric acid on a steam bath for 2 hr. The solution was concentrated and codistilled with 1-propanol to remove excess hydrochloric acid. The white, crystalline product formed was suspended in acetone and collected by filtration, yield 0.223 g. (94%), m.p. 249–250°. Recrystallization from methanol gave pure material: m.p. 256°; $[\alpha]^{20}D$ 0 ± 2° (*c* 0.94, water); λ_{max}^{KBr} 3.0 (OH), 3.35, 5.05, 6.20 μ (NH_3^+); X-ray powder diffraction data[21] 6.86 s (3,3), 5.19 m, 4.85 s (3,3), 4.15 vw, 3.90 s (2), 3.56 s (1), 3.28 vw, 3.00 m, 2.71 w, 2.56 w, 2.46 w, 2.32 vw, 2.25 vw, 2.19 vw.

Anal. Calcd. for $C_6H_{18}Cl_2N_2O_2$: C, 32.59; H, 8.19; Cl, 32.07; N, 12.67. Found: C, 32.89; H, 8.35; Cl, 32.26; N, 12.98.

1,2,3,6-Tetradeoxy-3,6-bis(2,4-dinitroanilino)-D-*ribo*-hexitol (XII).—3,6-Diacetamido-1,2,3,6-tetradeoxy-D-*ribo*-hexitol dihydrochloride (XI, 0.4 g.) was dissolved in acetone–water (1:4, v./v.). The solution was shaken mechanically with sodium bicarbonate (0.66 g.) and 1-fluoro-2,4-dinitrobenzene (0.48 ml.) for 12 hr. An orange oil separated. Solvent was removed from the mixture by distillation under reduced pressure. The residue was triturated with benzene to remove excess 1-fluoro-2,4-dinitrobenzene and then extracted with acetone. The acetone extract was dried (magnesium sulfate) and the yellow filtrate was evaporated to a sirup which crystallized from methanol, yield 0.63 g. (72%), m.p. 189–190°. Recrystallization from methanol gave pure material: m.p. 190°; $[\alpha]^{28}D$ +132° (*c* 1.46, acetone); λ_{max}^{KBr} 2.9 (OH), 3.0 (NH), 6.18, 6.30, 6.60 (aryl C=C), 6.52 (NH,NO_2), 7.50 (NO_2), 12.1, 13.4 μ (substituted benzene); X-ray powder diffraction data[21] 10.28 s (2), 9.31 m, 7.03 m, 5.28 vw, 5.04 s (1), 4.80 m, 4.35 w, 3.92 w, 3.69 m, 3.54 w, 3.39 w, 3.19 s, 3.07 s (3).

Anal. Calcd. for $C_{18}H_{20}N_6O_{10}$: C, 45.00; H, 4.20; N, 17.50. Found: C, 45.10; H, 4.40; N, 17.80.

3,6-Diacetamido-3,6-dideoxy-D-altrose Diethyl Dithioacetal (XIII).—3,6-Diacetamido-2,4,5-tri-*O*-acetyl-3,6-dideoxy-D-altrose diethyl dithioacetal (VIII) was *O*-deacetylated with methanolic ammonia as described above for the synthesis of IV and the product was isolated in the same manner. The resultant sirup was crystallized from ethyl acetate: yield 1.4 g. (95%); m.p. 101–102°; $[\alpha]^{21}D$ +22° (*c* 1, methanol); λ_{max}^{KBr} 3.0 (OH), 6.05, 6.40 μ (NHAc); X-ray powder diffraction data[21] 11.05 s (3), 8.67 s (1), 7.03 m, 6.56 vw, 5.99 m, 5.75 s (2), 5.37 w, 5.28 w, 5.07 m, 4.62 m, 4.33 m, 4.15 w, 4.00 m, 3.06 s, 3.55 w, 3.35 s, 3.25 w, 3.10 w, 3.05 vw, 3.01 w, 2.75 m, 2.63 vw, 2.49 m.

Anal. Calcd. for $C_{14}H_{28}N_2O_5S_2$: C, 45.62; H, 7.66; N, 7.60; S, 17.40. Found: C, 45.48; H, 7.68; N, 7.83; S, 17.29.

3,6-Diacetamido-3,6-dideoxy-D-altrose.—The desulfurization procedure of Defaye[26] was followed. 3,6-Diacetamido-3,6-dideoxy-D-altrose diethyl dithioacetal (XIII, 1.10 g.) was dissolved in water (16.8 ml.) and ether (24 ml.) was added. To this vigorously stirred solution a solution of bromine (660 mg.) in ether (14.4 ml.) containing water (0.48 ml.) was added slowly. After the addition was complete, the acidic solution was neutralized by stirring with Amberlite IR-45 (OH^- form) ion-exchange resin. After removal of the resin the solvent was removed under reduced pressure to yield a sirup. This sirup was dissolved in hot ethanol and acetone was added to turbidity. Air evaporation of solvent deposited a white solid which was collected and washed with acetone, yield 710 mg. (90%). Crystallization was effected in the same manner to give a pure material: m.p. 178°; $[\alpha]^{19}D$ +13 ± 2° (*c* 1.4, water), +38 ± 2° (*c* 1.5, methanol). No mutarotation was observed after acid (1 drop of concentrated hydrochloric acid) or base (3 drops of concentrated ammonium hydroxide) was added. The substance showed a positive Benedict test; X-ray powder diffraction data[21] 11.79 s, 10.65 s (2), 8.42 m, 7.63 vw, 4.98 m, 4.72 w, 4.51 s (3), 4.25 s (1), 4.10 w, 3.62 m, 3.36 m, 3.21 vw, 3.09 w, 2.90 w, 2.75 w, 2.70 w, 2.58 m, 2.52 m.

Anal. Calcd. for $C_{10}H_{18}N_2O_6$: C, 45.80; H, 6.92; N, 10.68. Found: C, 45.44; H, 7.00; N, 10.35.

The ring structure and anomeric configuration of this product are under further investigation.

1,3,6-Trideoxy-3,6-bis(2,4-dinitroanilino)-D-altritol (XIV).—3,6-Diacetamido-3,6-dideoxy-D-altrose diethyl dithioacetal (XIII, 1 g.) was reductively desulfurized with Raney nickel as described above for the synthesis of IX, and the product, a sirup, was isolated in the same manner. The acetamido groups were hydrolyzed as described above for the synthesis of XI, the sirupy product was decolorized with carbon in boiling methanol, and then shaken with sodium bicarbonate (1.14 g.) and 1-fluoro-2,4-dinitrobenzene (0.84 ml.) in 20 ml. of acetone–water (1:4 v./v.) for 12 hr. The solvent was removed from the yellow mixture under reduced pressure, and the residue was extracted with acetone. The acetone extract was dried (magnesium sulfate) and filtered. The yellow sirup, obtained after solvent removal, showed two major components by thin layer chromatography (silica gel) with 1:1 ethyl acetate–benzene developer. Separation was effected on thick-coated silica gel plates (0.75 mm.). The faster moving yellow zone was eluted with acetone to give a sirup which was crystallized from methanol, yield 0.13 g., m.p. 189–190°, identical with authentic 1,2,3,6-tetradeoxy-3,6-bis(2,4-dinitroanilino)-D-*ribo*-hexitol (XII) by mixture melting point and infrared spectral comparison. The material in the slower moving zone was similarly collected and the resultant sirup was crystallized from methanol: yield 0.51 g. (39% from XIII); m.p. 192–193°; $[\alpha]^{20}D$ +146° (*c* 1.92, acetone); λ_{max}^{KBr} 2.85 (OH), 3.00 (NH), 6.34, 6.80 (aryl C=C), 6.52 (NH,NO_2), 12.10, 13.14 μ (substituted benzene); X-ray powder diffraction data[21] 10.78 m, 7.97 w, 6.76 m, 5.44 m, 5.01 m, 4.82 w, 4.19 w, 3.97 w, 3.60 m (3), 3.36 m (2), 3.11 s (1).

Anal. Calcd. for $C_{18}H_{20}N_6O_{11}$: C, 43.55; H, 4.06; N, 16.93. Found: C, 43.90; H, 4.43; N, 16.94.

Oxidative Degradation of 1,2,3,6-Tetradeoxy-3,6-bis(2,4-dinitroanilino)-D-*ribo*-hexitol (XII).—1,2,3,6-Tetradeoxy-3,6-bis-

(25) Spectra were determined with a Varian A-60 n.m.r. spectrometer (Varian Associates, Palo Alto, Calif.), with deuteriochloroform as the solvent and tetramethylsilane as the internal standard. Deuteration was performed by shaking the prepared sample for 15 min. with 1 drop of deuterium oxide

(26) J. Defaye, *Bull. soc. chim. France*, 2686 (1964).

(2,4-dinitroanilino)-D-*ribo*-hexitol (XII, 351 mg., 0.731 mmole) was dissolved in hot methanol (45 ml.). The yellow solution was cooled to room temperature and periodic acid (0.3 *M*, 5 ml.) was added. The mixture was placed in the dark for 36 hr.; oxidant consumption 1.2 moles/mole of oxidant. The spectrophotometric procedure of Aspinall and Ferrier[27] was followed except that the oxidation was carried out in 90% methanol, and further dilution with methanol was employed for the spectrophotometric measurements.

The acidic solution was neutralized with barium carbonate, filtered, and washed with methanol. The yellow filtrate was evaporated and the residue was extracted with acetone. The acetone extract was dried (magnesium sulfate) and evaporated. The resultant sirup was dissolved in acetone (35 ml.) and to this was added 15 ml. of water. The yellow solution was heated with potassium permanganate (400 mg.) at 80° for 3.5 hr. The acetone was removed by evaporation under reduced pressure, water was added, and a stream of sulfur dioxide was passed through the aqueous suspension. A yellow solid separated from the aqueous solution and was removed by three extractions with ethyl acetate. Solvent was removed from the dried (magnesium sulfate) extract to give a yellow residue. Paper chromatography with pH 6 aqueous phosphate buffer[28] (1 *M* sodium dihydrogen phosphate in 0.5 *M* disodium hydrogen phosphate) showed one yellow spot (zone 1) corresponding to *N*-(2,4-dinitrophenyl)-L-α-aminobutyric acid and a slower one (zone 2) corresponding to *N*-(2,4-dinitrophenyl)glycine. Zone materials were isolated by excising them from chromatograms on Whatman No. 3MM paper and eluting with the above phosphate buffer. Each solution of yellow compound in the sodium phosphate buffer solution was acidified with hydrochloric acid and extracted three times with ethyl acetate. The dried (magnesium sulfate) ethyl acetate filtrate from zone 1 was evaporated to a sirup, yield 112 mg. (57% from XII). This was crystallized from 2-propanol–isopropyl ether, yield 40 mg., m.p. 167°, $[\alpha]^{19}D$ −36° (*c* 1, acetone). Comparison with an authentic specimen (see below) of *N*-(2,4-dinitrophenyl)-L-α-aminobutyric acid, m.p. 167°, $[\alpha]^{19}D$ −36° (*c* 1.2, acetone), by infrared spectrum, X-ray powder diffraction data, and undepressed mixture melting point, confirmed the identity.

The dried ethyl acetate filtrate from zone 2 was concentrated under reduced pressure to give 71 mg. of product (40% from XII). This was crystallized from acetone–ether–petroleum ether (b.p. 36–60°), yield 55 mg., m.p. 193°. The product was identical with an authentic sample (see below) of *N*-(2,4-dinitrophenyl)glycine (m.p. 202°) by infrared spectrum and X-ray powder diffraction data.

Oxidative Degradation of 1,3,6-Trideoxy-3,6-bis(2,4-dinitroanilino)-D-altritol (XIV).—1,3,6-Trideoxy-3,6-bis(2,4-dinitroanilino)-D-altritol (XIV, 333 mg., 0.673 mmole) was oxidized with periodic acid as described above for 1,2,3,6-tetradeoxy-3,6-bis(2,4-dinitroanilino)-D-*ribo*-hexitol (XII) except that more methanol (60 to 70 ml.) was used to achieve a homogeneous solution. The reaction mixture was processed as described above and subsequently oxidized by potassium permanganate (400 mg.) in 70% acetone–water (50 ml.) at 80° for 3.5 hr. to give a mixture of two acidic products. Separation of these acids on paper was effected by the same procedure described above. The dried ethyl acetate filtrate from the leading zone was concentrated to a sirup, yield 0.13 g. (69% from XIV). This was crystallized as long yellow needles from ether–petroleum ether (b.p. 36–60°), yield 100 mg., m.p. 144–145°, $[\alpha]^{20}D$ −48° (*c* 1, acetone), identical by comparison (mixture melting point, infrared spectrum, and X-ray powder diffraction data) with an authentic (see below) sample, m.p. 146°, $[\alpha]^{17}D$ −48° (*c* 1, acetone), of *N*-(2,4-dinitrophenyl)-L-threonine. The dried ethyl acetate extract from the slower moving zone was concentrated to give a semisolid product, yield 70 mg. (39% from XIV). This material was crystallized from acetone–ether–petroleum ether (b.p. 36–60°), yield 50 mg., m.p. 193°, identified as *N*-(2,4-dinitrophenyl)glycine by comparison with an authentic (see below) specimen (infrared spectrum, X-ray powder diffraction data, and mixture melting point).

Preparation of Authentic Samples of N-(2,4-Dinitrophenyl) Derivatives of Glycine, L-α-Aminobutyric Acid, and L-Threonine.—These derivatives were prepared from the known amino acids by the procedure of Rao and Sober[29] with some modifications. After acidification with hydrochloric acid, the crystalline solid, from glycine, separated and was recrystallized from acetone–petroleum ether (b.p. 36–60°): m.p. 202°; X-ray powder diffraction data[21] 9.61 m, 7.38 m, 6.41 w, 5.90 m, 5.13 w, 4.58 s (3,3), 4.37 m, 4.00 s (3,3), 3.72 s (1), 3.53 m, 3.28 s, 3.10 s (2), 2.94 w, 2.86 w, 2.71 m.

The acidified aqueous solution from L-α-aminobutyric acid was extracted three times with ethyl acetate and the dried extract was concentrated to a sirup which was crystallized from 2-propanol–isopropyl ether, m.p. 167°, $[\alpha]^{19}D$ −36° (*c* 1.2, acetone). This melting point is different from the one (133°) reported by Rao and Sober[29] and may denote polymorphism. Alderton[30] reported $[\alpha]^{26}D$ −38° (*c* 0.991, ethyl acetate) and X-ray powder diffraction data which were in agreement with those found by us.

The solution obtained from L-threonine on acidification with hydrochloric acid was extracted three times with ethyl acetate and the dried extract was concentrated to yield crystals. These crystals were dissolved in a small volume of acetone and ether was added. Addition of petroleum ether (b.p. 36–60°), gave light yellow needles: m.p. 146°; $[\alpha]^{17}D$ −48° (*c* 1, acetone); X-ray powder diffraction data[21] 9.41 w, 5.40 s, 5.10 s (1), 4.74 w, 5.35 m, 4.05 w, 3.95 s (2), 3.74 s (3), 3.58 w, 3.40 w, 3.07 s, 2.95 w, 2.88 w.

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