R_f and color as 1,4-naphthoquinone monoxime (V) but a small amount of a brownish material was slightly separated from II on silica gel. When V was superimposed onto a spot of II, almost all of II was identical with V in R_f and color. Alumina gave less data, since the R_f values were low. The ultraviolet spectra of II and V in base gave a λ_{max} of 413 mμ.

2-Nitroso-1-naphthol (IV).—To a 500-ml erlenmeyer flask was added 10 g (0.07 mole) of 1-naphthol and 50 ml of glacial acetic acid. Complete solution was not necessary. Solid $NaNO_2$ (7.0 g, 0.10 mole) was gradually added with swirling. The solid gradually dissolved. Heat and some gases were evolved. A dark colored, thick mixture formed. After 5 min ice and water were added until no further solid precipitated. The mixture was filtered, washed with water, and pressed dry. The solid was stirred in a beaker to remove the last traces of acetic acid. The filtered, air-dried, yellow product weighed 12.0 g (99.4% yield), mp 142–146° dec (lit.[3] 145–150, 152–156, and 162° dec). The controversy on the melting points is summarized.[3] The tlc of IV (as prepared here) showed two yellow spots on silica gel which corresponded to the major product IV (R_f 0.32) and V (R_f 0.51). There was a small amount of material near the origin as well. No unreacted 1-naphthol was found. A copper chelate was formed by IV. About 10 mg of IV was purified on an alumina column with 1:4 acetone and benzene: mp 150° dec. 1,2-Naphthoquinone and $NH_2OH \cdot HCl$ also gave pure IV, mp 150° dec. [When this nitrosation procedure was used to prepare 1-nitroso-2-naphthol,[4] a brown solid was formed: crude yield, 99%; mp 95° (lit.[14] mp 97° crude, 99% yield, and 106° recrystallized). Tlc (silica gel) yielded a major and a very minor spot. A basic aqueous solution formed a chopper chelate.]

1,4-Naphthoquinone Monoxime Acetate.—In a 125-ml erlenmeyer flask, 1,4-naphthoquinone monoxime (1.0 g) was dissolved in a slight excess of aqueous KOH (0.43 g, 30 ml) to yield a deep red solution. Excess (2 ml) acetic anhydride was added and the flask was shaken. An immediate reaction took place and a red solid precipitated. The shaking was continued for 5 min. The precipitate was filtered, washed with water, and air dried; yield was 1.0 g (crude), mp 125–126°.

Recrystallization from hot aqueous ethanol with charcoal gave yellow needles, mp 130.4–131.5°. *Anal.* Calcd for $C_{12}H_9NO_3$: C, 66.97; H, 4.22; N, 6.51. Found: C, 66.94; H, 4.29; N, 6.13. The infrared spectrum showed two carbonyl absorption bands (1783 and 1658 cm^{-1}). Bands were also visible at 1597 (aromatic and C=C), 1193 (CO), and 937 (NO) cm^{-1}. The nmr and infrared spectra are consistent with the proposed structure. These data do not conform to the structure given in the literature[5b] (mp 132.5°). Under the acidic Beckmann conditions,[5b] the same compound was formed as identified by melting point (130.5–131.5°) and by infrared spectral analysis.

1,4-Naphthoquinone Monoxime (V).—Hydroxylamine hydrochloride (7.0 g, 0.1 mole) was refluxed with 2 drops of concentrated HCl solution and 15.8 g (0.1 mole) of 1,4-naphthoquinone in 25 ml of 95% ethanol for 10 min. This solution was cooled and diluted with water. A brown solid formed (Va). Part of the solid was dissolved in aqueous KOH, filtered, and precipitated with concentrated HCl to give a gray solid (Vb). The total crude yield was 15.0 g (86.7%), mp 197° dec (lit.[5] 198–199° dec). There was no difference in the R_f values (0.52) or color of Va and Vb on silica gel. They both exhibit absorption bands at 3140–2750 (OH), 1625 (CO), 1585 (C=C), 1550 (C=N), 970 (N—O), and 846 (two adjacent H) cm^{-1}.

1-Naphthyl acetate (VI) was prepared in 5 min by shaking 10.2 g (0.1 mole) of acetic anhydride with 14.4 g (0.1 mole) of 1-naphthol dissolved in an equivalent amount of aqueous NaOH. The yield was 90%, mp 46–48° (lit.[15] mp 49°).

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Amino Derivatives of Starches. 2-Amino-3,6-anhydro-2-deoxy-D-mannose[1]

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Treatment of phenyl 2-acetamido-2-deoxy-6-*O*-(*p*-tolylsulfonyl)-α-D-mannopyranoside (**1a**) with base gives phenyl 2-acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (**3a**), converted by acid hydrolysis into a crystalline 2-amino-3,6-anhydro-2-deoxy-D-mannose hydrochloride (**4**), a reference compound required in structural studies on aminated starch derivatives. Chemical and physical evidence indicated that **4** possessed a furanoid ring system.

In the previous paper in this series[2] it was shown that methyl 3,6-anhydro-2-*O*-(*p*-tolylsulfonyl)-α-D-glucopyranoside is very resistant to amination by displacement of the C-2 substituent with hydrazine. It was inferred, and verified by experiment, that 3,6-anhydro-2-*O*-(*p*-tolylsulfonyl)-D-glucopyranose units in a polysaccharide show a similar lack of reactivity toward hydrazine. Consequently, units of 2-amino-3,6-anhydro-2-deoxy-D-mannose are not probable constituents of an aminated amylose prepared[3] by hydrazinolysis followed by reduction of a 2(?),6-di-*O*-(*p*-tolylsulfonyl)-amylose. Reference compounds have been synthesized for possible[4] and probable[5] reactions in the amination process. In this paper the synthesis is described of the last of these proposed[4] reference compounds, 2-amino-3,6-anhydro-2-deoxy-D-mannose.

Treatment of phenyl 2-acetamido-2-deoxy-6-*O*-(*p*-tolylsulfonyl)-α-D-mannopyranoside[4] (**1a**) with aqueous ethanolic sodium hydroxide at room temperature, or with ethanolic sodium acetate at reflux, gave the crystalline phenyl 2-acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (**3a**) in good yield; acetylation gave the crystalline 4-acetate (**3b**). Acid hydrolysis of the anhydro glycoside (**3a**) gave, in high yield, a crystalline, chromatographically homogeneous 2-amino-3,6-anhydro-2-deoxy-D-mannose hydrochloride (**4**). This substance reduced Fehling solution, but did not recolorize Schiff reagent, indicating that it was not an aldehyde or aldehydrol form, even though it exhibited no detectable mutarotation.

(1) Supported by Contract No. 12-14-100-5760(71) (OSURF Project 1301) from the U. S. Department of Agriculture, Northern Utilization Research and Development Division, Peoria, Ill. The opinions expressed in this article are those of the authors, and not necessarily those of the supporting agency.

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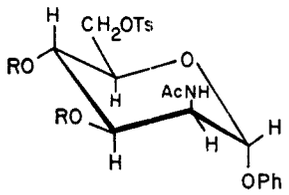
Substance **4** undoubtedly has the furanoid ring structure, since equilibration between ring forms occurs under the acid hydrolytic conditions. The *cis*-fused [3.3.0] system in the furanoid form has negligible strain compared with the [3.2.1] system in the pyranoid from. Furanoid ring systems are known to be the stable structures in 3,6-anhydro-D-glucose[6-8] and 3,6-anhydro-D-mannose;[9] 3,6-anhydro-D-galactose exists in the acyclic form[7] since a furanoid form would necessitate a highly strained *trans* fusion of five-membered rings.

Mercaptolysis of the anhydro glycoside **3a** gave a chromatographically homogeneous syrup which on acetylation gave syrupy 2-acetamido-4,5-di-*O*-acetyl-3,6-anhydro-2-deoxy-D-mannose diethyl dithioacetal. The latter was chromatographically homogeneous, and its nmr spectrum indicated the presence of two ethyl groups, three acetyl groups, and an NH group.

Attempts to cleave the 3,6-anhydro ring of the anhydro glycoside **3a** with boron trichloride[10] led to the anhydro amino sugar **4** as the only chromatographically detectable amino sugar.

Structures assigned in this work are supported by physical data, and details of spectral correlations are given in the Experimental Section. Inversion of the pyranoid ring conformation in the transformation of **1a** into **3a** is clearly demonstrated by the change in the observed splitting of the H-1 signal in the derived acetates **1b** and **3b**. In **1b** and the analogous phenyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-mannopyranoside[4] (**2**), the splitting (~2 cps) is indicative of the *gauche* relationship of H-1 and H-2 (diequatorial in this case). In the acetate **3b** of the anhydro glycoside **3a**, this splitting is increased to 7.5 cps, indicative of the diaxial (antiparallel) arrangement of H-1 and H-2. Spectroscopic data exclude a possible 2,6-epimine structure for the anhydro glycoside, since **3a** and **3b** both exhibit N–H absorptions in the infrared[11] and an NH signal in the nmr spectrum. The latter assignment was verified by deuterium exchange, which also effected decoupling of the NH proton from H-2 and permitted assignment of the H-2 signal.



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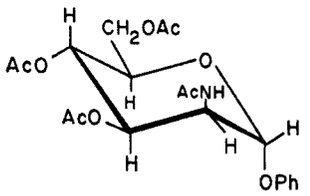
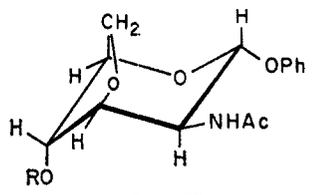
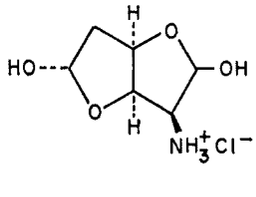
b, R = Ac



2



3a, R = H
b, R = Ac



4

The nmr spectrum of the anhydro amino sugar **4**, in deuterium oxide, shows at lowest field a pair of doublets, total integral one proton, at τ 4.30 and 4.42, in the intensity ratio 3:1; the splittings were 5.4 and 4.2 cps, respectively. These signals are assigned to H-1 of the anomeric furanose forms, since chemical evidence rules out the aldehydrol form, and the pyranose form would have been expected to give splittings of 2–3 cps (equatorial H-1) and 7–8 cps (axial H-1). The furanose ring probably adopts a twist conformation[12] having C-2 displaced below and C-3 above the plane of C-1, C-4, and O-4. The crystalline anhydro amino sugar appears to be a single anomer; in dimethyl sulfoxide solution its nmr spectrum gave only one signal in the range τ 2.0–5.25, a one-proton doublet, τ 4.58 ($J_{1,2}$ = 4 cps) which may be assigned to H-1. Mutarotation of **4** in water may be very rapid, and it is possible that the NH_3^+ group is able to catalyze mutarotation very effectively by intramolecular protonation of the ring oxygen, so long as the solvent used can act as a proton acceptor during a subsequent step. It is noteworthy that 3,6-anhydro-D-mannose[9] and 2-amino-2-deoxy-β-D-mannose hydrochloride[13] do not exhibit observed mutarotation in water.

Acetylation of **4** with acetic anhydride in pyridine gave a syrup whose nmr spectrum indicated it to be a triacetyl derivative, preponderantly of one anomeric form, presumably that of the crystalline precursor.

Experimental Section[14]

Nmr Data. A. For Phenyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-mannopyranoside[4] (2).—The nmr spectrum in deuteriochloroform gave the following data: τ 8.00, 7.99, 7.98, 7.94 (three-proton singlets, acetyls); 5.67–6.15 (three-proton multiplet, H-5,6,6′); 5.20 (one-proton octet, changes to quartet when sample is deuterated, $J_{2,3}$ = 4.5 cps, H-2); 4.83 (one-proton triplet, $J_{4,5}$ = 10 cps, H-4); 4.54 (one-proton doublet, $J_{1,2}$ = 2 cps, H-1); 4.44 (one-proton quartet, $J_{3,4}$ = 10 cps, H-3); 3.73 (one-proton broadened doublet, $J_{2,NH}$ = 9.5 cps, shifts with change in concentration, and disappears on deuteration, NH); 2.87 (five-proton multiplet, Ph).

B. For Phenyl 2-Acetamido-3,4-di-*O*-acetyl-2-deoxy-6-*O*-(*p*-tolylsulfonyl)-α-D-mannopyranoside[4] (1b).—The nmr spectrum in deuteriochloroform gave the following data: τ 8.03, 7.99, 7.93 (three-proton singlets, acetyls); 7.56 (three-proton singlet, CH_3 of Ts); 5.60–6.10 (three-proton multiplet, H-

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5,6,6′); 5.20 (one-proton octet, changes on deuteration, H-2); 4.35–4.85 (three-proton multiplet, $J_{1,2}$ = ~2 cps, H-1,3,4); 3.63 (one-proton broadened doublet, shifts with change in concentration, and disappears on deuteration, NH); 2.87 (five-proton multiplet, Ph), 2.68 (two-proton doublet, $J_{2',3'}$ = 8 cps, H-3′,5′ of Ts); 2.22 (two-proton doublet, $J_{2',3'}$ = 8 cps, H-2′,6′ of Ts).

Phenyl 2-Acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (3a). Procedure A.—Phenyl 2-acetamido-2-deoxy-6-*O*-(*p*-tolylsulfonyl)-α-D-mannopyranoside[4] (**1a**, 1.0 g) in ethanol (10 ml) was treated with 1 *N* aqueous sodium hydroxide (5 ml), the mixture was kept for 24 hr at room temperature, and then solid carbon dioxide was added to neutralize the solution. The solid was filtered, the filtrate and washings were evaporated, and the residue was extracted with acetone. The extract was decolorized with activated carbon, and evaporated to a syrup, which was crystallized from chloroform to yield 0.45 g (77%): mp 160–161°; $[\alpha]^{22}D$ +42.5° (*c* 1.3, methanol); λ_{max}^{KBr} 3.00 (OH), 3.06 (NH), 6.09, 6.50 (NHAc), 6.30, 6.72 (aryl C=C), 13.00, 14.40 μ (substituted benzene), no absorption at 8.50 μ (sulfonate); X-ray powder diffraction data: 10.16 m, 6.81 s (1), 5.54 m, 5.18 m, 4.53 s (3), 4.25 s (2), 3.87 m, 3.72 w, 3.57 w, 3.39 m.

Anal. Calcd for $C_{14}H_{17}NO_5$: C, 60.22; H, 6.13; N, 5.02. Found: C, 60.09; H, 6.14; N, 5.02.

Procedure B.—A solution of **1a** (1.0 g) and anhydrous sodium acetate (0.5 g) in absolute ethanol (50 ml) was refluxed for 36 hr, and then evaporated. The residue was extracted with acetone, and evaporation of the extract gave a colorless syrup which was crystallized from chloroform to yield 0.40 g (65%); physical constants were identical with those reported for **3a** prepared by procedure A.

Phenyl 2-Acetamido-4-*O*-acetyl-3,6-anhydro-2-deoxy-α-D-mannopyranoside (3b).—Phenyl 2-acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (**3a**, 0.27 g) was treated with pyridine (1 ml) and acetic anhydride (1 ml) for 18 hr at room temperature. The solution was poured into ice and water (25 ml) and extracted with chloroform (three 10-ml portions). The extract was washed with aqueous sodium bicarbonate, dried over magnesium sulfate, and evaporated, and the resultant syrup was crystallized from ethanol–ether to yield 0.26 g (85%): mp 146°; $[\alpha]^{23}D$ −14° (*c* 1, chloroform); λ_{max}^{KBr} 3.10 (NH), 5.70 (OAc), 6.04, 6.46 (NHAc), 6.30, 6.70 (aryl C=C), 13.00, 14.40 μ (substituted benzene); nmr data (deuteriochloroform): τ 8.02, 7.83 (three-proton singlets, NAc, OAc); τ 5.63–5.91 (three-proton multiplet, H-5,6,6′); 5.22–5.60 (two-proton multiplet, changes on deuteration, H-2,4); 5.02 (one-proton quartet, *J* = 6.0 and 2.5 cps, H-3); 4.70 (one-proton doublet, $J_{1,2}$ = 7.5 cps, H-1); 3.83 (one-proton broadened doublet, $J_{2,NH}$ = 9.5 cps, disappears on deuteration, NH); 2.83 (one-proton multiplet, Ph); X-ray powder diffraction data: 10.40 m, 8.50 s (3), 7.63 m, 6.07 w, 5.47 w, 5.15 s (1), 4.55 m, 4.33 s (2), 4.23 w, 4.06 vw, 3.93 m, 3.72 w, 3.55 m.

Anal. Calcd for $C_{16}H_{19}NO_8$: C, 59.80; H, 5.95; N, 4.36. Found: C, 60.04; H, 5.95; N, 4.66.

2-Amino-3,6-anhydro-2-deoxy-D-mannose Hydrochloride (4).—Phenyl 2-acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (**3a**, 150 mg) was heated with 6 *N* hydrochloric acid (5 ml) for 1 hr at 95°. The solution was cooled and filtered, and the filtrate was extracted with ether to remove phenol. The brown solution was evaporated and the residue, codistilled several times with 1-propanol, gave a crystalline residue. The product was recrystallized from water–1-propanol to yield 86 mg (81%), decomposing without melting over the range 135–240°: $[\alpha]^{20}D$ +57° (*c* 1, water) with no observed mutarotation; R_{GN}[15] 1.03; λ_{max}^{KBr} 3.0–3.5 (OH, NH_3^+), 6.20, 6.67 μ (NH_3^+); nmr data (deuterium oxide): τ 4.30 and 4.42 (doublets, relative intensities 3:1, total integral one proton, $J_{1,2}$ = 5.4 and 4.2 cps, respectively, H-1 of anomers); 5.03–5.42, 5.49–5.72 (four protons, multiplets, H-2,3,4,5); 5.92–6.33 (two-proton multiplet, H-6,6′); in methyl sulfoxide-d_6, 1.65 (three-proton broad singlet, disappears on deuteration, NH_3^+); 4.58 (one-proton doublet, $J_{1,2}$ = 4 cps, H-1 of single anomer; changes on deuteration to 1-proton multiplet, H-1 of anomers); X-ray powder diffraction data: 7.63 w, 6.07 s (2,2), 5.54 vw, 5.28 s (2,2), 4.82 s (2,2), 4.31 vw, 4.04 s (1), 3.83 w, 3.65 w, 3.41 vw, 3.29 m, 2.99 w, 2.91 m, 2.77 m, 2.51 s (3).

Anal. Calcd for $C_6H_{12}ClNO_4$: C, 36.47; H, 6.12; Cl, 17.95; N, 7.09. Found: C, 36.72; H, 6.24; Cl, 17.72; N, 7.29.

2-Acetamido-3,6-anhydro-2-deoxy-D-mannose Diethyl Dithioacetal.—Phenyl 2-acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (**1a**, 1.0 g) was stirred with ethanethiol (20 ml) and concentrated hydrochloric acid (10 ml) for 24 hr at 0°. The mixture was diluted with methanol (250 ml), neutralized with lead carbonate, filtered, and the filtrate and washings were concentrated to a syrup: yield 1.02 g (92%), homogeneous by thin layer chromatography (1:4 methanol–benzene); λ_{max}^{film} 3.05 (OH, NH), 6.10, 6.50 μ (NHAc).

2-Acetamido-4,5-di-*O*-acetyl-3,6-anhydro-2-deoxy-D-mannose Diethyl Dithioacetal.—2-Acetamido-3,6-anhydro-2-deoxy-D-mannose diethyl dithioacetal (0.5 g) was treated with pyridine (5 ml) and acetic anhydride (5 ml) for 18 hr at room temperature. The mixture was poured into ice and water (50 ml) and the solution was extracted with three 20-ml portions of chloroform. The extract was washed with aqueous sodium bicarbonate, water, and then dried (magnesium sulfate) and evaporated. The residue was freed from pyridine by codistillation with benzene to give a syrup, yielding 0.60 g (92%) which was homogeneous by thin layer chromatography (4:1 benzene–methanol): λ_{max}^{film} 3.10 (NH), 5.80 (OAc), 6.05, 6.50 μ (NHAc); nmr data: τ 8.73 (six-proton triplet, CH_3 of ethyl groups); 7.40 (four-proton quartet, CH_2 of ethyl groups); 8.08, 8.05, 7.86 (three-proton singlets, acetyls); 3.97 (one-proton doublet, *J* = 9.6 cps, NH).

Anal. Calcd for $C_{16}H_{27}NO_6S_2$: C, 48.83; H, 6.91; N, 3.56. Found: C, 48.27 (mean of four determinations); H, 6.79 (mean of four determinations); N, 3.53.

Acetylation of 2-Amino-3,6-anhydro-2-deoxy-D-mannose Hydrochloride.—2-Amino-3,6-anhydro-2-deoxy-D-mannose hydrochloride (**4**, 100 mg) was treated with pyridine (2 ml) and acetic anhydride (2 ml) for 18 hr at room temperature. The mixture was poured into ice and water (20 ml) and extracted with three 10-ml portions of chloroform. The extract was washed with water, dried (magnesium sulfate), and evaporated, and the residue was freed from pyridine by codistillation with benzene, to give a clear syrup, yield 102 mg (70%), homogeneous by thin layer chromatography (4:3 ethyl acetate–benzene): λ_{max}^{film} 3.10 (NH), 5.76 (OAc), 6.05, 6.48 μ (NHAc); nmr data (deuteriochloroform): τ 7.85, 7.90, 7.96 (three-proton singlets, acetyls); 6.03 (two-proton multiplet, H-6,6′); τ 4.60–5.55 (four-proton multiplet, H-2,3,4,5); 3.85 and 3.70 (doublets, total integral one proton, relative intensity 10:1, $J_{1,2}$ = 3.0 and 4.5 cps, respectively, H-1 of anomers); 3.42 (one-proton broad multiplet, NH).

Treatment of Phenyl 2-Acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (3a) with Boron Trichloride.—Phenyl 2-acetamido-3,6-anhydro-2-deoxy-α-D-mannopyranoside (**3a**, 10 mg) was suspended in dry dichloromethane (2 ml), the mixture was cooled to −78°, and boron trichloride (5 g) at −78° was added. The mixture was kept for 4 hr at −78° with exclusion of moisture (calcium chloride tube), and then overnight at room temperature. The flask was evacuated to remove the solvent. The residue was codistilled five times with 3-ml portions of methanol. The residue was heated with 6 *N* hydrochloric acid (1 ml) for 1 hr, the solution was diluted with water (5 ml), filtered, and extracted with ether (5 ml), and the aqueous solution was codistilled several times with 1-propanol to remove acid. The residue was examined by paper chromatography in the Fischer–Nebel solvent system,[15] with 2-amino-2-deoxy-D-mannose hydrochloride and 2-amino-3,6-anhydro-2-deoxy-D-mannose hydrochloride as reference standards. A single ninhydrin-positive zone was observed, corresponding to 2-amino-3,6-anhydro-2-deoxy-D-mannose.

Acknowledgment.—The authors thank Mr. J. D. Wander and Mr. J. B. Hughes for nmr spectral measurements, and Dr. S. Hanessian (Parke-Davis & Co., Ann Arbor, Michigan) for measuring spectra of compounds *2* and **3b**.

(15) Mobility relative to 2-amino-2-deoxy-D-glucose, by descending chromatography on Whatman No. 1 paper, 5:5:3:1 pyridine–ethyl acetate–water–acetic acid, according to F. G. Fischer and H. J. Nebel, *Z. Physiol. Chem.*, **302**, 10 (1955), with indication by ninhydrin.