proton multiplet, H-1,2,3,4), 5.71, 6.00 (two protons, H-6, H-6'), 6.20 (one-proton multiplet, H-5), 7.95, 7.98, 8.01 (three-, six-, and three-proton singlets, OAc), 8.62 (nine-proton singlet, CMe_3).

Nmr Data for 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl Ethylxanthate (9).—Substance **9**, prepared by the method of Schneider, *et al.*,[14] gave nmr data (60 MHz, chloroform-*d*): τ 4.42–5.05 (four-proton multiplet, H-1,2,3,4), 5.33 (two-proton quartet, J = 7 Hz, CH_2 of ethyl), ~5.83 (two-proton multiplet, H-6,6'), 6.29 (one-proton multiplet, H-5), 7.95, 7.98, 8.00 (three-, six-, and three-proton singlets, OAc), 8.59 (three-proton triplet, CH_3 of ethyl).

Nmr Data for 4,6-Di-*O*-acetyl-1-S-acetyl-2,3-dideoxy-1-thio-α-D-*erythro*-hex-2-enopyranose (11).—D-Glucal triacetate was treated with thiolacetic acid and sulfuric acid[41] according to the procedure of Tejima, *et al.*[16] to give **11**, mp 102–105° (lit.[16] mp 104–105°). In chloroform-*d*, the 60-MHz spectrum of **11** gave τ 3.70 (one-proton multiplet, W_h = 4.8 Hz, H-1), 4.08 [two-proton singlet with satellites, $J_{2,3}$ = ~10 Hz, H-2, 3 (lit.[16] τ 4.10 singlet)], 4.59 (one-proton quartet, $J_{4,5}$ = 9 Hz, H-4), 5.68 (one-proton quartet, $J_{5,6}$ = 5 Hz, $J_{6,6'}$ = 12.5 Hz, H-6), 5.90 (one-proton quartet, $J_{5,6'}$ = 2.5 Hz, H-6'), 6.10 (one-proton multiplet, width = 16.5 Hz, H-5), 7.58 (three-proton singlet, SAc), 7.90, 7.93 (three-proton singlets, OAc). Large values of $J_{4,5}$, indicative of the axial–quasi axial disposition of H-4 and H-5, have been observed[42] for related 2,3-unsaturated pyranose derivatives.

(41) This experiment was performed by J. S. Jewell and P. Durette.

(42) R. J. Ferrier, W. G. Overend, and G. H. Sankey, *J. Chem. Soc.*, 2380 (1965).

The spectrum of **11** in acetone-d_6 was measured at 100 and at 220 MHz (Figure 8) and gave the following data: τ 3.78 (one-proton triplet, width 6.6 Hz, H-1), 4.01 (one-proton doublet of narrow quartets, $J_{2,3}$ = 10.3 Hz, width of quartets 4.7 Hz, H-2), 4.15 (one-proton doublet of narrow multiplets, H-2), 4.68 (one-proton doublet of narrow multiplets, $J_{4,5}$ = 9.3 Hz, width of multiplets 4.5 Hz, H-4), 5.77 (one-proton quartet, $J_{5,6}$ = 5.0 Hz, $J_{6,6'}$ = 11.7 Hz, H-6), 5.92 (one-proton quartet, $J_{5,6'}$ = 2.8 Hz, H-6'), 6.12 (one-proton multiplet, width 17.0 Hz, H-5). Addition of benzene-d_6 to the solution caused the H-2 and H-3 signals to collapse to a singlet, and H-5 signal to shift to higher field. At the same time the H-1 signal collapsed to W_h = 4.5 Hz and the H-4 signal collapsed to a doublet of narrow doublets, $J_{1,4}$ = ~2 Hz.

Registry No.—**1**, 6739-54-4; **2**, 13639-47-9; **3**, 13639-48-0; **4**, 13639-49-1; **5**, 13639-50-4; **6**, 6806-56-0; **7**, 6612-63-1; **8**, 6767-60-8; **9**, 13639-54-8; **10**, 13639-55-9; **11**, 4631-35-0; 2-(2,3,4-tri-*O*-acetyl-β-D-ribopyranosyl)-2-thiopseudourea hydrobromide, 13639-57-1; 2-(2,3,4-tri-*O*-acetyl-α-L-arabinopyranosyl)-2-thiopseudourea hydrobromide, 13639-58-2.

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Amino Derivatives of Starches. Amination of 6-*O*-Tritylamylose

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Amylose aminated at the secondary hydroxyl groups was prepared by (a) tritylation, *p*-tolylsulfonylation, reaction with sodium azide, reduction, and detritylation, or by (b) the same method except for replacement of sodium azide with hydrazine. The product of route a, DS 0.45, was *N*-acetylated and hydrolyzed to give mainly 3-amino-1,6-anhydro-3-deoxy-D-altrose. The product of route b, DS 0.8, gave on hydrolysis in low yield 3-amino-1,6-anhydro-3-deoxy-D-altrose and 2-amino-2-deoxy-D-glucose. Apparently both amination routes proceed through the 2,3-D-*manno*-epoxide derivative, the modified units of product (a) having mainly the D-*altro* configuration. Attempts to apply the Guthrie amination reaction (successive periodate oxidation, controlled reaction with phenylhydrazine, and reduction) failed at the reduction stage with both starch and 6-*O*-tritylamylose, although evidence was obtained that the phenylazo group was present in the latter.

Amylose has been aminated to a degree of substitution (DS) of 1.4 by successive *p*-tolylsulfonylation, hydrazinolysis, and reduction.[1] The product obtained contained 3,6-anhydro units and subsequent model studies[2-4] showed that the main modified unit present very probably possessed the 3,6-diamino-3,6-dideoxy-D-altrose structure.[2,3] We then decided to block C-6 hydroxyl participation by the use of 6-*O*-tritylamylose[5,6] and to replace the secondary *p*-tolylsulfonyloxy group by reaction with azide ion rather than by reaction with the more basic hydrazine molecule. Accordingly, 6-*O*-tritylamylose was *p*-tolylsulfonylated to a DS of 0.8. It has been pointed out previously[1] that evidence exists to show that this product had been sulfonated mainly, if not exclusively, at the C-2 hydroxyl group. This amylose derivative was then treated with sodium azide, under the conditions used previously[7] for monosaccharide derivatives, to produce a product, with the trityl group intact, containing an azide function (DS 0.45). The azide entity was transformed readily to the amino group by reduction with lithium aluminum hydride[8] and the product was detritylated with methanolic hydrochloric acid.[5,6] The final, aminated amylose (DS 0.45) was purified by dialysis and was isolated by lyophilization as a white, nonhygroscopic powder of high dextrorotation that was readily soluble in water and dimethyl sulfoxide. The *N*-acetyl derivative was prepared and showed similar properties.

The amino sugar fraction of the acid hydrolysate of the *N*-acetylaminated amylose showed two components by paper chromatography in an approximate 5:1 ratio. The main component crystallized and was identified as 3-amino-1,6-anhydro-3-deoxy-D-altropy-

(1) M. L. Wolfrom, M. I. Taha, and D. Horton, *J. Org. Chem.*, **28**, 3553 (1963).

(2) M. L. Wolfrom, P. Chakravarty, and D. Horton, *ibid.*, **30**, 2728 (1965).

(3) M. L. Wolfrom, Y.-L. Hung, and D. Horton, *ibid.*, **30**, 3394 (1965).

(4) M. L. Wolfrom, Y.-L. Hung, P. Chakravarty, G. U. Yuen, and D. Horton, *ibid.*, **31**, 2227 (1966); M. L. Wolfrom, P. Chakravarty, and D. Horton, *ibid.*, **31**, 2502 (1966).

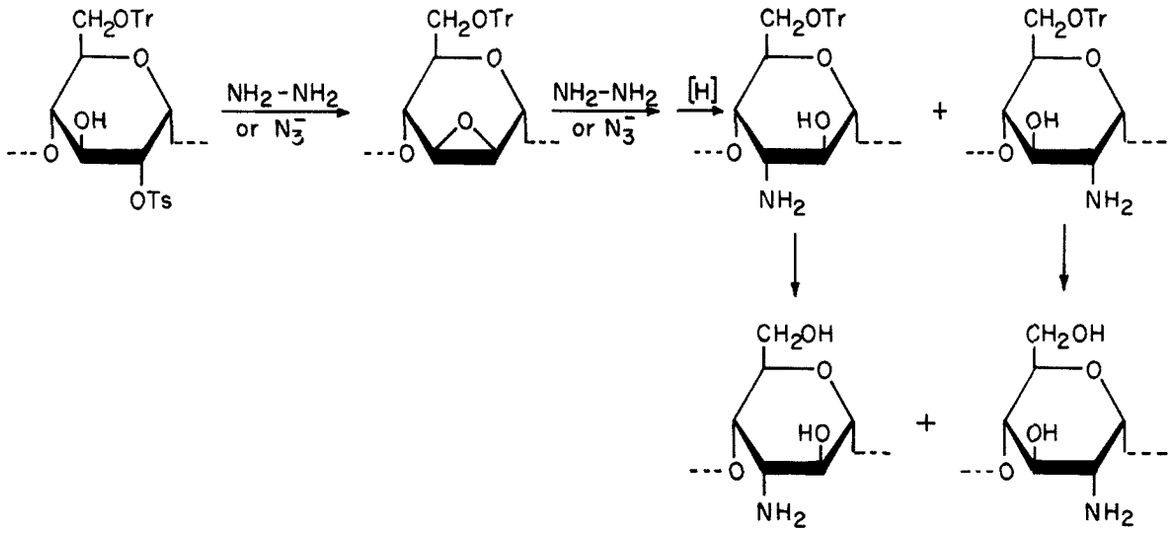
(5) R. L. Whistler and S. Hirase, *ibid.*, **26**, 4600 (1961).

(6) W. M. Hearon, G. D. Hiatt, and C. R. Fordyce, *J. Am. Chem. Soc.*, **65**, 2449 (1943).

(7) M. L. Wolfrom, J. Bernsmann, and D. Horton, *J. Org. Chem.*, **27**, 4505 (1962).

(8) R. L. Whistler and D. G. Medcalf, *Arch. Biochem. Biophys.*, **104**, 150 (1964).

SCHEME I



ranose hydrochloride.[9] As it is known that D-altrose readily undergoes 1,6-anhydro formation, under acidic conditions,[10] the 3-amino-1,6-anhydro-3-deoxy-D-altropyranose hydrochloride obtained was considered to have been formed from 3-amino-3-deoxy-D-altrose hydrochloride during the acid treatment. The minor component was not obtained crystalline by the procedure used. Thus, replacement of the interior *p*-tolylsulfonyloxy group(s) had proceeded mainly through 2,3-D-*manno*-epoxide formation[2] even in the azide replacement.

Amination of the 6-*O*-tritylamylose was effected by reaction with azide rather than by reaction with the more basic hydrazine molecule originally used with the nontritylated amylose. Accordingly, the 2(3)-*O*-*p*-tolylsulfonyl-6-*O*-tritylamylose (*p*-tolylsulfonyloxy DS 0.8) was subjected to a prolonged reaction with hydrazine in methoxyethanol. Catalytic reduction of the product by hydrogen in the presence of palladium–charcoal[11] resulted in a complete reduction of the hydrazino groups and partial removal of the trityl groups. Total detritylation of the product was achieved on treatment with methanolic hydrogen chloride,[5] yielding an aminated amylose with DS 0.8. The so-aminated 6-*O*-tritylamylose was hydrolyzed by acid without previous detritylation; there was isolated, in low yield, both 3-amino-1,6-anhydro-D-altrose hydrochloride and 2-amino-2-deoxy-D-glucose hydrochloride. The nature of the procedure employed for the isolation makes the amounts and relative proportions of these crystalline products unmeaningful. Both substances are those predictable[12] from the opening of the 2,3-D-*manno*-epoxide ring although the one with the D-altro configuration would be the expectedly favored product. Model experiments[2] with methyl 2,6-di-*O*-methylsulfonyl-α-D-glucopyranoside have also led to products possessing the D-altro configuration when this glycoside derivative was brought into reaction with either hydrazine or sodium azide (see Scheme I).

Finally, an attempt was made to prepare an aminated amylose in which one of the secondary hydroxyl groups had been replaced by the amino group with retention of the D-glucose unit configuration. To this end the remarkable reaction established by Guthrie and Johnson[13] was applied. These investigators had shown that methyl 4,6-*O*-benzylidene-α-D-glucopyranoside could be converted with phenylhydrazine into the corresponding 3-deoxy-3-phenylazo derivative in high yield, and that this derivative, on reduction, yielded the corresponding methyl glycoside derivative of 3-amino-3-deoxy-D-glucose. Accordingly, commercial periodate-oxidized starch was treated with phenylhydrazine and a yellow-orange product was obtained in high yield. Such a product had been described by Barry and coworkers,[14] who had then subjected it to further treatment and obtained glyoxal bis(phenylhydrazone). Attempts to reduce this apparent phenylazo derivative to the amino group were unsuccessful. It was then considered that an undesirable C-6 hydroxyl participation might be occurring to hinder the reduction and, accordingly, the reaction was repeated with 6-*O*-tritylamylose.[5] This derivative would be analogous to the methyl 4,6-*O*-benzylidene-α-D-glucopyranoside of Guthrie and Johnson[13] in that both the C-4 and C-6 positions were blocked. Considerable difficulty was encountered in the glycol cleavage of 6-*O*-tritylamylose, owing to its insolubility, but this end was finally achieved (~80%) with lead tetraacetate in dioxane solution. The resultant, oxidized 6-*O*-tritylamylose was brought into reaction with phenylhydrazine and there was obtained a yellow phenylazo derivative of the proper analysis and infrared absorption spectral characteristics. Repeated attempts to reduce this material, or its detritylated derivative, with several catalysts did not lead to a definitive, ninhydrin-positive product. It is probable that the polymeric nature of the phenylazo derivative hinders the desired course of this reaction. Furthermore, the exact structure of the polymeric dialdehyde from the periodate oxidation of amylose cannot be considered as definitively established and, therefore, the phenylhydrazine reaction product

(9) P. A. Levene and G. M. Meyer, *J. Biol. Chem.*, **55**, 221 (1923); L. F. Wiggins, *J. Chem. Soc.*, 18 (1947).

(10) N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **57**, 1716 (1935); 961 (1940).

(11) P. E. Verkade, W. D. Cohen, and A. K. Vroege, *Rec. Trav. Chim.*, **59**, 1123 (1940).

(12) W. N. Haworth, W. H. G. Lake, and S. Peat, *J. Chem. Soc.*, 271 (1939); W. O. Cutler and S. Peat, *ibid.*, 782 (1939).

(13) R. D. Guthrie and L. F. Johnson, *ibid.*, 4166 (1961).

(14) V. C. Barry, *Nature*, 152, 537 (1943); V. C. Barry and P. W. D. Mitchell, *J. Chem. Soc.*, 4020 (1954).

may not possess quite the structure expected. The conditions of Guthrie and Johnson[13] are different from those employed by Barry and co-workers[14] in the Barry degradation,[14] which leads to chain scission with the production of glyoxal bis(phenyhydrazone).

Experimental Section

2(3)-*O*-*p*-Tolylsulfonyl-6-*O*-tritylamylose.—6-*O*-Tritylamylose[5,15] (50 g) was dissolved in dry pyridine (500 ml) and shaken with *p*-toluenesulfonyl chloride (96 g, 4 equiv) for 12 hr. The mixture was poured into ice and methanol and agitated in a Waring Blendor. The resulting white powder was washed successively with water, methanol, and ether and then dried: yield 53 g (80.8%), $[\alpha]^{20}D$ +67° (*c* 1.1, dimethyl sulfoxide).

Anal. Calcd for $[C_6H_{8.25}O_{4.2}(C_{19}H_{15})_{0.95}(OSO_2C_7H_7)_{0.8}]_n$: C, 68.46; H, 5.56; S, 5.06; trityl, 45.9. Found: C, 68.24; H, 5.57; S, 5.05; trityl, 44.5.

Treatment of 2(3)-*O*-*p*-Tolylsulfonyl-6-*O*-tritylamylose with Sodium Azide.—2(3)-*O*-*p*-Tolysulfonyl-6-*O*-triphenylmethylamylose (20 g, DS of *p*-tolylsulfonyl group 0.8) was dissolved in *N*,*N*-dimethylformamide (600 ml). The solution was heated at 125° in an oil bath, and water (32 ml), urea (2 g), and sodium azide (16 g) were added. Heating was continued for 72 hr under reflux at 125° and in a stream of nitrogen. After cooling in ice and water, the resultant slightly brown, supernatant liquid was poured into ice and water (2.5 l.) and stirred. The precipitate was collected by centrifugation, suspended in water, and dialyzed against distilled water for 3 days. After centrifugation, the white precipitate was dried over calcium chloride under reduced pressure to yield 16 g (97%): λ_{max}^{KBr} 2.81 (OH), 4.69 (N_3, strong), 6.23, 6.72, 6.92, 14.28 (aryl) μ.

Anal. Calcd for $[C_6H_7O_2(OH)_{1.5}(N_3)_{0.45}(OSO_2C_7H_7)_{0.1}(OC_{19}H_{15})_{0.95}]_n$: C, 70.95; H, 5.60; N, 4.52; S, 0.76; triphenylmethyl, 55.2. Found: C, 70.41; H, 5.69; N, 4.36; S, 0.86; triphenylmethyl, 55.0.

Preparation of an Aminated Amylose by Reduction and Detritylation of the Above Azide.—The above azide (DS of azido group 0.45, 13.3 g) was dissolved in dried tetrahydrofuran (300 ml) and to this solution was added carefully, with shaking, a suspension of lithium aluminum hydride (4.5 g) in tetrahydrofuran (230 ml). The mixture was stirred for 18 hr at room temperature and was then refluxed for 2 hr in a water bath under protection from moisture. After cooling at 0°, water was carefully added to hydrolyze the excess lithium aluminum hydride and the solution was then diluted with an equal volume of water. To the cooled mixture was added cold 1 *N* hydrochloric acid (1 l.) with stirring. The resultant white precipitate was collected by centrifugation, washed with water and then with a mixture of methanol–ether (1:2, v/v), and dried: yield 9.7 g. This product did not show any absorption of azido group by infrared spectroscopy.

The reduced product (9.7 g) was suspended in methanol (200 ml) containing concentrated hydrochloric acid (2 ml) and shaken for 6 hr at room temperature. The insoluble material was filtered, washed with methanol and ether, and dried. The product was finely powdered and was treated again for 5 hr with fresh methanol (100 ml) containing concentrated hydrochloric acid (1 ml), filtered, washed, and dried: yield 3.8 g. This completely detritylated product was dissolved in saturated sodium bicarbonate solution (200 ml), dialyzed against distilled water fo 3 days, and filtered; the filtrate was lyophilized to yield 2.0 g of a fluffy, white, hygroscopic powder, $[\alpha]^{25}D$ +183° (*c* 1.37, dimethyl sulfoxide). This product was readily soluble in water and dimethyl sulfoxide and was sparingly soluble in *N*,*N*-dimethylformamide.

Anal. Calcd for $[C_6H_7O_2(OH)_{2.55}(NH_2)_{0.45}]_n$: C, 44.55; H, 6.47; N, 3.90. Found: C, 44.47; H, 6.42; N, 3.84; S, 0.54.

***N*-Acetylaminated Amylose.**—The above aminated amylose (DS of amino group 0.40, 2.0 g) was dissolved in water (30 ml), acetic anhydride (15 ml) was added with stirring, and the reaction mixture was stirred for 18 hr at room temperature. After diluting with water (200 ml), the mixture was dialyzed against distilled water for 3 days and lyophilized to give a white, nonhygroscopic powder in a yield of 1.6 g (72%), $[\alpha]^{20}D$ +181° (*c* 1, dimethyl sulfoxide). This product was soluble in water and dimethyl sulfoxide.

Anal. Calcd for $[C_6H_7O_2(OH)_{2.6}(NHCOCH_3)_{0.4}]_n$: N, 3.19; $COCH_3$, 9.64. Found: N, 3.17; $COCH_3$, 10.10.

Acid Hydrolysis of *N*-Acetylaminated Amylose.—The above *N*-acetylaminated amylose (DS of acetamido group 0.4, 1.4 g) was dissolved in water (140 ml) and hydrochloric acid (210 ml) was added to bring the acidity to 1.2 *N*. The solution was heated for 5 hr under reflux in a boiling water bath. After cooling, the resultant slightly brown solution was treated with a small amount of activated carbon and filtered. The filtrate was neutralized with Amberlite IRA-410 (HCO_3^- form), filtered, and washed with water. The filtrate and washings were combined and concentrated to 50 ml under reduced pressure at 50°. The resultant solution was passed through a column of Dowex 50 (H^+ form, 20 ml by volume) and the column was washed with water. The amino compounds adsorbed on the column were eluted with 0.5 *N* hydrochloric acid, and the eluent (150 ml, reducing to Fehling reagent) was collected and evaporated under reduced pressure at 50°. Excess hydrochloric acid was removed by the addition and evaporation of ethanol. After the third addition of ethanol, the resultant syrup was dried, under reduced pressure, over calcium chloride to yield 0.4 g. This syrup was dissolved in a small amount of water, spotted on two sheets of paper (Whatman No. 3MM, 46 × 57 cm), and developed by the descending method for 4 days with 1-butanol–ethanol–water (4:1:1, v/v). After air drying, the paper revealed two ninhydrin-positive bands in the monosaccharide region. Each band was excised and eluted with water, and the eluate was evaporated to dryness under reduced pressure at 50°. From the faster migrating band, a crystalline material appeared, which was washed with ethanol and acetone, and dried: yield 123 mg, mp 218° dec (coloration at 190°), $[\alpha]^{20}D$ −178.5° (*c* 1.07, water), Fehling reduction negative. These data are in agreement with the constants (216° dec, $[\alpha]D$ −172° (water)) reported[9] for 3-amino-1,6-anhydro-3-deoxy-D-altropyranose hydrochloride.

Anal. Calcd for $C_6H_{11}O_4N$:HCl: C, 36.46; H, 6.08; N, 7.09; Cl, 17.98. Found: C, 35.71; H, 6.35; N, 7.21; Cl, 18.29.

The material in the slower migrating band was obtained as a colorless syrup (119 mg). By visual comparison, the amount of this material was about one-fifth that of the total amount of the faster moving component. No crystalline product was obtainable from the syrup.

Treatment of 2(3)-*O*-*p*-Tolylsulfonyl-6-*O*-tritylamylose with Hydrazine and Reduction of the Product.—The 2(3)-*O*-*p*-tolylsulfonyl-6-*O*-tritylamylose (DS of sulfonate 0.8, 40 g) was dissolved in methoxyethanol (150 ml), using heat, then mixed with hydrazine[16] (400 ml) and heated for 6 hr under reflux in an atmosphere of nitrogen. If the solid which had separated did not dissolve, more methoxyethanol was added through the condenser until a clear solution was obtained. The heating was continued for 7 days and the hydrazine was removed azeotropically by codistillation with methoxyethanol under reduced pressure. The final syrup was dissolved in methoxyethanol (100 ml) and treated with palladium–charcoal catalyst (10 g of 10% catalyst) in the presence of hydrogen (500 psi) for 24 hr at 65–70°. The catalyst was removed by centrifugation and the supernatant solution was poured into water (1 l.). The sulfur-free, white powder which separated was collected by filtration, washed successively with water, ethanol, and ether, and then dried: yield 10.3 g (44.2%), $[\alpha]^{20}D$ +80° (*c* 0.8, dimethyl sulfoxide).

Anal. Calcd for $[C_6H_{8.65}O_{4.2}(NH_2)_{0.8}(C_{19}H_{15})_{0.55}]_n$: C, 67.07; H, 6.28; N, 3.81; trityl, 45.4. Found: C, 66.84; H, 6.24; N, 3.77; trityl, 43.7.

Acid Hydrolysis of the Aminated 6-*O*-Tritylamylose.—A suspension of the above product (4.5 g) in 1.6 *N* hydrochloric acid (520 ml) was heated for 10 hr on a boiling water bath, decolorized with active carbon, and filtered, and the filtrate was extracted with ether to remove triphenylmethanol. The aqueous layer was then neutralized with Amberlite IRA 411 (HCO_3^-, 800 ml) and concentrated to 20 ml. The slightly yellow solution was passed through a column of Dowex 50 W-X4 (40 ml) and the column was washed with water. The amino sugar fraction was eluted from the column with 0.5 *N* hydrochloric acid (500 ml) and the eluent was evaporated. Hydrochloric acid was removed by addition and evaporation with ethanol. The residual yellow syrup was dissolved in 2 ml of methanol and chromatographed on paper (Whatman 3MM, two 46 × 57 cm sheets) by the descending

(15) Prepared from Superlose (Stein-Hall, New York, N. Y.), an unmodified amylose.

(16) Matheson Coleman and Bell, anhydrous, 97%+.

method with development (4 days) by 1-butanol–ethanol–water (4:1:1 v/v). Two ninhydrin-positive bands were located, excised, and eluted with water. The resultant syrup from the faster moving band was crystallized from methanol to yield 16 mg, mp and mmp 219° dec (coloration at 190°). X-Ray powder diffraction pattern[17] was identical with that of an authentic specimen of 3-amino-1,6-anhydro-3-deoxy-D-altropyranose:[9] 7.75 m, 5.76 vs (1), 4.98 m, 4.85 vs (1), 4.23 m, 4.00 w, 3.82 s (3), 3.56 s (2), 3.43 m, 3.30 w, 3.05 s, 3.01 s, 2.89 w, 2.76 m, 2.61 m, 2.57 m, 2.48 m, 2.40 w, 2.36 w, 2.31 m, 2.05 m, 1.89 w.

The syrup from the more slowly migrating band gave crystals, 22 mg, identified by X-ray powder diffraction pattern[18] as 2-amino-2-deoxy-D-glucose hydrochloride.

Aminated Amylose.—The above aminated (by hydrazine) 6-*O*-tritylamylose (5 g) was suspended in methanol (100 ml) containing concentrated hydrochloric acid (1 ml) and was shaken for 8 hr at room temperature. The solid material was filtered, washed with methanol, and dissolved in water. The aqueous solution was poured into a saturated aqueous solution of sodium hydrogen carbonate (100 ml) and dialyzed against distilled water for 3 days. Lyophilization yielded a pale cream powder: yield 1.6 g (58.8%), $[\alpha]^{20}D$ +132° (*c* 1.36, dimethyl sulfoxide).

Anal. Calcd for $[C_6H_{9.2}O_{4.2}(NH_2)_{0.8}]_n$: N, 6.90. Found: N, 6.88.

Attempted Reduction of the Reaction Product of Periodate-Oxidized Starch with Phenylhydrazine.—To a hot solution of "dialdehyde starch" (5 g, Sumstar-S, assay 95%, Miles Chemical Division, Sumner Chemicals, Elkhart, Ind.) in water (600 ml) was added rapidly a solution of phenylhydrazine hydrochloride (5 g) in water (100 ml). The yellow-orange precipitate[14] that formed was filtered and dried: yield 4.3 g.

Anal. Calcd for $(C_{12}H_{14}N_2O_4)_n$: N, 11.5. Found: N, 12.1.

Hydrogenation of the above product at 100° with 800 psi of hydrogen and a Raney nickel catalyst gave a light yellow solid of slightly lower nitrogen content which was not the expected amino derivative.

Lead Tetraacetate Oxidation of 6-*O*-Triphenylmethylamylose.—6-*O*-Triphenylmethylamylose[5,6] (DS 1.02, 45.3 g) was dissolved in 1800 ml of purified dioxane. To the solution was added 99.0 g of lead tetraacetate (dried in a vacuum desiccator over phosphorus pentaoxide and solid potassium hydroxide for 24 hr)[19] in one-third portions over a period of 1 hr under mechanical stirring. The reaction was allowed to proceed at room temperature. A simultaneous blank experiment was performed. At intervals, lead tetraacetate consumption was determined by iodimetry. An aliquot of the reaction mixture was added to an excess of aqueous potassium iodide in the presence of sodium acetate[20] and the iodine liberated was then titrated with standard thiosulfate. The results follow (time, moles of oxidant per hexose unit): 1 hr, 0.50; 5 hr, 0.69; 17 hr, 0.75; 20 hr, 0.74. At the reaction time of 20 hr, ethylene glycol was added to the mixture to destroy the remaining oxidant. The precipitated lead diacetate was filtered with suction and washed with a small amount of dioxane. The filtrate and washings were combined, added to two volumes of water, and stirred in a blender. The resulting precipitate was collected on a funnel and was again returned to water in the blender. The washing process was repeated as above. Finally, the product was washed with methanol and dried under reduced pressure: yield 41.5 g. In the infrared spectrum, the product showed a strong absorption at 1725 cm^{-1} (aldehyde carbonyl) and the absorption for hydroxyl group.

Anal. Calcd for $[OCH(CHO)CHCH_2O(C_6H_5)_3OCH(CHO)]_n$: C, 74.61; H, 5.51. Found: C, 73.88; H, 5.73.

3-Deoxy-3-phenylazo-6-*O*-triphenylmethylamylose.—The above oxidized 6-*O*-triphenylmethylamylose (29.5 g) was dissolved in warm pyridine (370 ml), and water (37 ml) and phenylhydrazine (30 ml) were added. The mixture was then stirred mechanically at room temperature for 2 days, then lightly boiled under reflux for 2 hr. After cooling, the solution was evaporated to half-volume under reduced pressure and poured into a large amount of methanol stirred in a blender. The resultant precipitate was collected on a funnel and again added to fresh methanol in the blender. After agitation, the product was filtered and washed thoroughly with methanol. The yellow product was then dried under reduced pressure: yield 28.5 g. The product had the absorption expected for OH or NH groups, and absorptions at 1610 (C=N region[21]) and at 1520 cm^{-1} (Ar—N=N—R[22]).

Anal. Calcd for $[C_6H_7O_2(OH)_{1.23}(N_2C_6H_5)_{0.75}(OC_{19}H_{15})_{1.02}]_n$: C, 75.49; H, 5.78; N, 4.41; trityl, 52.20. Found: C, 75.02; H, 6.26; N, 4.76; trityl, 52.24.

Various attempts to reduce this material, with or without trityl removal, by hydrogen (600 psi) with a palladium (110°) or Raney nickel (150°) catalyst did not lead to a definitive ninhydrin-positive product.

Registry No.—3-Amino-1,6-anhydro-3-deoxy-D-altropyranose hydrochloride, 13942-78-4.

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(17) Interplanar spacings in angstroms for Cu Kα radiation; relative intensities were estimated visually; s, strong; m, moderate; w, weak; v, very. The strongest lines are numbered (1, strongest); equal numbers represent lines of approximately equal intensity.

(18) I. Werner, *Mikrochim. Acta*, **39**, 133 (1952).

(19) C. E. Ballou, *Methods Carbohydrate Chem.*, **2**, 282 (1963).

(20) A. S. Perlin, *ibid.*, **1**, 427 (1962).

(21) R. D. Guthrie and J. Honeyman, *J. Chem. Soc.*, 2441 (1959).

(22) G. J. F. Chittenden and R. D. Guthrie, *ibid.*, 1045 (1964).