and opening the tube, a white precipitate was separated and recrystallized from dilute ethanol, 1.4 g., m.p. ~270° dec. Johns,[13] who prepared this compound from 2-ethylmercapto-4-chloropyrimidine, reported a similar melting point, while Brown[25] reported ~275–278° dec. for this compound prepared from 2-mercapto-4-methylaminopyrimidine.

4-Methylamino-5-amino-2(1H)-pyrimidinone. 4-Methylamino-5-nitro-2(1*H*)pyrimidinone (obtained by nitration of the above compound according to Johns[13]) was suspended in water with half its weight of palladium-charcoal and shaken with hydrogen (1 atm.) until the theoretical uptake of the gas was observed. After filtration from catalyst and concentration of the filtrate to near dryness, precipitation of product occurred (45% yield), m.p. decomposition with prior browning at 220°. Johns[13] reported 225° (dec. eff.) and Brown[25] gave above 220° dec. The compound gave a positive phosphomolybdate test.

2-Oxy-9-methylpurine. The above methylamino pyrimidine (0.45 g.) was refluxed in 5 ml. of diethoxymethyl acetate for 2 hr. after which the mixture was cooled, filtered, and the tan precipitate recrystallized from 3–5 ml. of hot water to which 1 drop of concentrated ammonium hydroxide had been added. Upon cooling, 0.25 g. of needles was obtained. m.p. darkening at ~250°, melting with decomposition to a red liquid at 305–306° (Johns[13] reported browning at ~290°, melting with decomposition and effervescence at ~310°). The product gave a negative test with phosphomolybdate. For spectral properties see Fig. 3.

1-Methyl-2-oxypurine. One gram of 1-methyl-5-aminocytosine was heated with 20 ml. of diethoxymethyl acetate for 1 hr. at 120–130°. The dark amber solution was concentrated to dryness *in vacuo* and the residue dissolved in hot water. After cooling and filtration, the precipitate (0.6 g.) was recrystallized from hot water (with charcoal) to afford a white crystalline product. The melting point was indeterminate, as found previously by Johns,[12] decomposing slowly over 280°. For spectral properties, see Fig. 2. The compound gave a negative phosphomolybdate test.

5-Aminocytosine. Reduction of 5-nitrocytosine (1.5 g.) was carried out in a manner similar to that employed for 4-methylamino-5-nitro-2(1*H*)pyrimidinone (*vide supra*). After separation from catalyst, the filtrate was concentrated to about 30 ml. Thin prisms separated from the cooled solution. After recrystallization from 75% ethanol, (including treatment with charcoal), fine needles were obtained, 0.9 g., m.p., turned brown at ~200° with no definite decomposition point. A similar product was obtained by the procedure of Johns.[12] A phosphomolybdate test[10] was positive.

5-Oxy-1-v-triazolo(d)pyrimidine (2-oxy-8-azapurine). 5-Aminocytosine (1.1 g.) was dissolved in 7 ml. of 2*N* hydrochloric acid and treated with 0.01 mole of sodium nitrite. A white precipitate formed almost immediately. The precipitate was triturated several times with water and filtered. The precipitate was then washed with water, alcohol, ether, and dried; melting point, turned brown at ~240° and exploded at ~256°. Bergmann *et al.*[20] reported darkening at about 250° with no decomposition even at 300°

Anal. Calcd. for $C_4H_3N_5O$: C, 35.03; H, 2.20; N, 51.09. Found: C, 34.89; H, 2.33; N, 50.87.

The product was anhydrous while that reported previously[20] had an analysis corresponding to a monohydrate.

Spectrophotometric studies. Measurements were made with a Cary recording spectrophotometer, model 11, using techniques and buffers previously described.[4, 26] The apparent pk_a values are accurate to within 0.05 *p*H units unless specified otherwise and were determined spectrophotometerically by methods utilized previously.[4, 27]

Key to figures. All the spectra listed were run in aqueous solutions at *p*H values (or normality of hydrochloric acid solutions) indicated on the curves. 0.01*N* sodium hydroxide was taken as *p*H 12.0. The italicized letters refer to isobestic points.[28]

Acknowledgment. The authors are indebted to Miss Marjorie Capehart for technical assistance and to Dr. G. B. Brown for helpful discussions and continued interest.

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[CONTRIBUTION FROM THE DEPARTMENT OF MEDICINE, HARVARD MEDICAL SCHOOL, AND THE MASSACHUSETTS GENERAL HOSPITAL]

2-Amino-2-deoxy-D-idose (D-Idosamine) and 2-Amino-2-deoxy-D-talose (D-Talosamine)[1]

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Ammonolysis of methyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside in the presence of sodium methoxide and subsequent *N*-acetylation afforded methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (VI) and methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-idopyranoside. Hydrolysis of VI followed by acetylation gave 2-acetamido-3,4-di-*O*-acetyl-1,6-anhydro-2-deoxy-β-D-idopyranose identical to the compound synthesized from D-xylose. Mesylation of VI, followed by Walden inversion at C_3 and hydrolysis gave D-talosamine hydrochloride, identical to the compound synthesized from D-lyxose.

The isolation of D-talosamine from hydrolyzates of chondroitin sulfate[3] and its synthesis from D-lyxose[4] have been reported recently. The synthesis of D-talosamine described in this paper had been completed at the time of the above publications, and its report seems of interest because a different stereospecific route has been used. It is also a further example of the method used for the synthesis of D-allosamine[5] and D-gulosamine.[6]

In 1943, W. H. Myers and G. J. Robertson[7] reported briefly the action of ammonia on methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-gulopyrano-

side (or talopyranoside) prepared from D-galactose. Unfortunately the synthesis and the characterization of the anhydro sugar were not reported. The ammonolysis, followed by total acetylation, gave two compounds, one in a 55% yield, with m.p. 188° and $[\alpha]_D$ + 43.4° in chloroform, and the other in an 8% yield, with m.p. 260° and $[\alpha]_D$ + 70.3° in chloroform.

In the following years, pure methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-guloside (I) and pure methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-taloside (III) were prepared by Reichstein and his associates, starting from methyl 4,6-*O*-benzylidene-2,3-di-*O*-*p*-tolylsulfonyl-α-D-galactopyranoside (II).[8,9] In the first publication,[8] the yields reported were 70% of I and 16% of a secondary product derived from I, methyl 4,6-*O*-benzylidene-2-*O*-methyl-α-D-idopyranoside (V), indicating a nearly total scission of the C—S bond in the tosyl group located at C_2, before scission of the C—S bond at C_3 would take place. In the second publication,[9] the yields obtained were quite different, 37% of I, 26% of III and 30% of an unidentified product, indicating a similar resistance of both tosyl groups to hydrolytic splitting. The yields of I and III obtained in this laboratory were always similar to those reported by Gyr and Reichstein.[9]

Ammonolysis of the pure 2,3-anhydro derivatives I and III followed by *N*-acetylation gave in nearly quantitative yield methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (VI) and methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-idopyranoside (XI) respectively. *O*-Acetylation of VI afforded the 3-*O*-acetyl derivative VII, m.p. 192–193°, $[\alpha]_D^{26}$ + 48° in chloroform, identical with Myers and Robertson's main product, whereas *O*-acetylation of XI gave the 2-*O*-acetyl derivative XII, m.p. 286–287°, $[\alpha]_D^{27}$ + 86° in chloroform, the product representing the major fraction of Myers and Robertson's second product. It is evident that the starting material used by Myers and Robertson was a mixture of both I and III.[10]

In order to decrease the number of manipulations and also in view of the good properties of crystallization of the acetamido derivatives, the direct ammonolysis of the ditosylate II was attempted. When a methanolic solution of ammonia was used alone, the ammonolysis was unsuccessful, but when two moles of sodium methoxide were added, the reaction proceeded smoothly. After *N*-acetylation of the resulting mixture of compounds, methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (VI) was obtained directly by crystallization. The mother liquors were then acetylated in order to isolate the slightly soluble methyl 3-acetamido-2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-α-D-idopyranoside (XII). Work-up of the remaining mother liquors by chromatography and fractional crystallization increased the total yield of 2-amino derivatives VI and VII to 45% and of the 3-amino derivative XII to 26%. A secondary product, isolated in a 5% yield, was shown to be methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-idopyranoside (IV).[9] It was evidently derived from the 2,3-anhydro-talopyranoside derivative III, whereas Sorkin and Reichstein's secondary product V had been derived from the 2,3-anhydro-gulopyranoside derivative I. Thus, it is possible to estimate, in the present synthesis, the yield of the intermediate anhydroderivatives at 45% for the guloside derivative I and at 32% for the taloside derivative III.

As 2-amino-2-deoxy-D-idose (D-idosamine) had been recently obtained by synthesis from D-xylose, besides 2-amino-2-deoxy-D-gulose (D-gulosamine),[11] it was interesting to correlate the properties of the product obtained in the present stereospecific synthesis with those of the product obtained from D-xylose. Hydrolysis of VI with 60% acetic acid gave a sirupy glycoside XIII, characterized by its crystalline 3,4,6-tri-*O*-acetyl derivative XIV. In order to show that the glycoside XIII had not been hydrolyzed to D-idosamine or its 1,6-anhydro derivative, XIII obtained from XIV was condensed with benzaldehyde to give back VI in a 74% yield. Hydrolysis of the glycosidic linkage of XIII with simultaneous formation of the 1,6-anhydro ring did not proceed as smoothly as with the 3-amino derivative,[12] because of the proximity of the amino group to the site of reaction. Results were obtained only when the concentration of the hydrochloric acid was increased to 6*N*. Subsequent acetylation afforded the characteristic 2-acetamido-3,4-di-*O*-acetyl-1,6-anhdyro-

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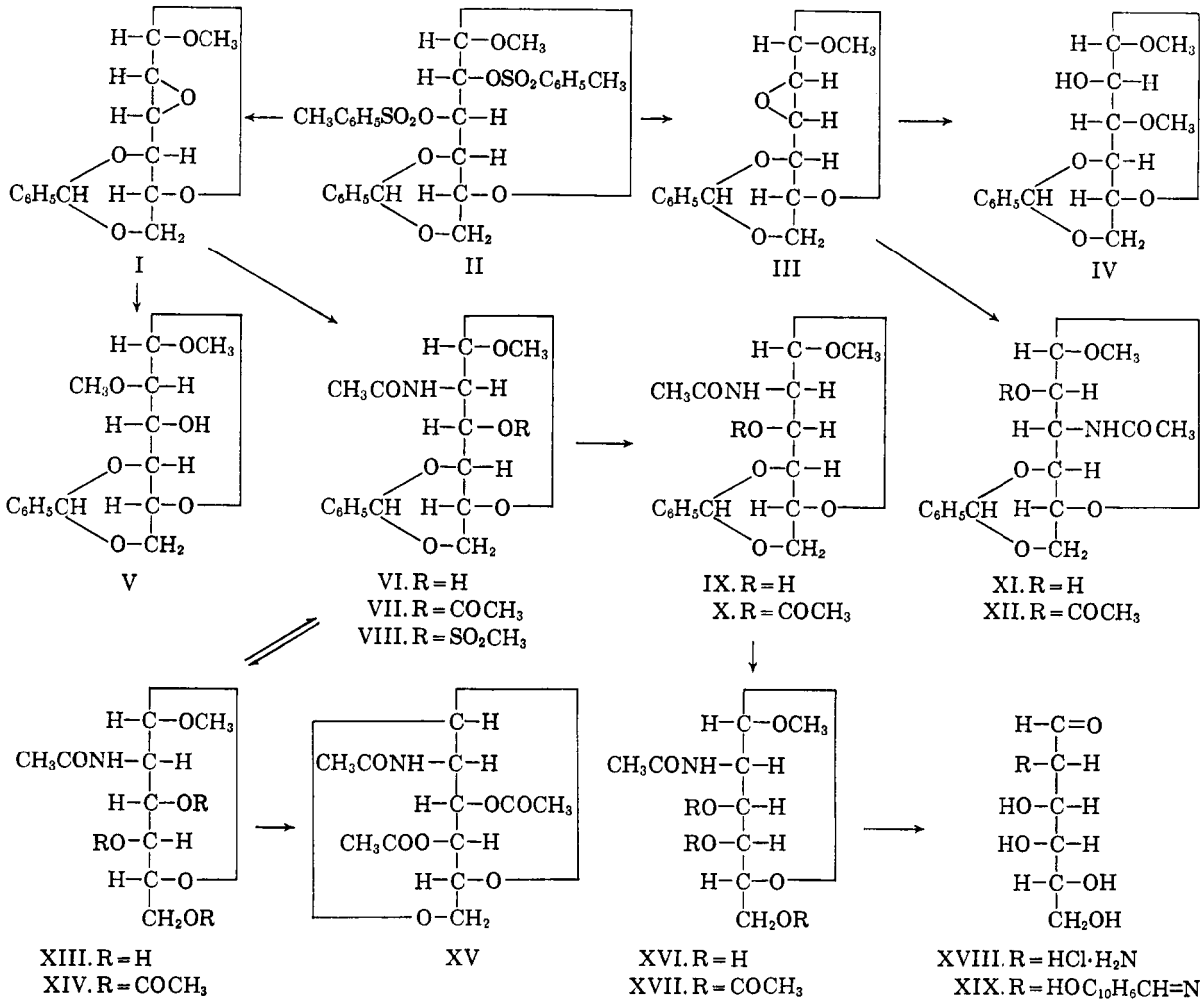

2-deoxy-β-D-idopyranose (XV), possessing properties similar to those of the compound prepared from D-xylose.[11]

2-Amino-2-deoxy-D-talose hydrochloride (D-talosamine hydrochloride) (XVIII) was obtained through Walden inversion of the 3-mesylate VIII by heating in Methyl Cellosolve in presence of sodium acetate[6,13] to give the talose derivative IX. This inversion proceeded smoothly, giving yields nearly as high as those obtained in the inversion of methyl 3 - acetamido - 4,6 - *O* - benzylidene - 3 - deoxy-2-*O*-methylsulfonyl-α-D-idopyranoside.[12] The corresponding compound possessing the hydroxyl groups at C_2 and C_3 in equatorial position, methyl 2 - acetamido - 4,6 - *O* - benzylidene - 2 - deoxy-3-*O*-methylsulfonyl-α-D-galactopyranoside, did not react,[6] which shows the strong influence of the conformation on the Walden inversion.

Scission of the benzylidene residue gave the sirupy taloside XVI, characterized by a crystalline triacetate XVII, and hydrolysis of XVI afforded the crystalline D-talosamine hydrochloride (XVIII), further characterized by a crystalline Schiff's base XIX with 2-hydroxynaphthaldehyde.[14] Identity of the D-talosamine hydrochloride thus obtained with the D-talosamine hydrochloride obtained from D-lyxose was established by paper chromatography and by their identical physical properties.

EXPERIMENTAL

Melting points were taken on a hot stage, equipped with a microscope, and correspond to "corrected melting point." Rotations were determined in semimicro or micro (for amounts smaller than 3 mg.) tubes with lengths of 100 or 200 mm., using a Rudolph Photoelectric Polarimeter Attachment, Model 200; the chloroform used was A.R. grade and contained approximately 0.75% of ethanol. Chromatograms were made with the flowing method on silicic acid; "Silica Gel Davison", from the Davison Co., Baltimore 3, Md. (grade 950; 60–200 mesh) was used without pretreatment. When deactivation by contact with moist air occurred, reactivation was obtained by heating to 170–200° (Manufacturer's instructions). The sequence of eluants was hexane, benzene or chloroform, ether, ethyl acetate, acetone, and methanol individually or in binary mixtures. The proportion of weight of substance to be adsorbed to weight of adsorbent was 1 to 50–100; the proportion of

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weight of substance in g. to volume of fraction of eluant in ml. was 1 to 100. The ratio of diameter to length of the column was 1 to 20. Evaporations were carried out *in vacuo*, with an outside bath temperature kept below 45°. Amounts of volatile solvent smaller than 20 ml. were evaporated by blowing dry nitrogen. Microanalyses by Dr. K. Ritter, Basel, and Dr. M. Manser, Zurich, Switzerland.

Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-idopyranoside (VI) *from* I. A suspension of 1.0 g. of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-gulopyranoside (I)[8] in 120 ml. of methanol saturated with ammonia at 0° was heated in sealed tubes at 100° for 40 hr. After cooling the solvent was evaporated, the residue was dissolved in 25 ml. of methanol, and 2.5 ml. of acetic anhydride was added. After a few hours the solvents were evaporated, the last traces being removed by codistillation with absolute toluene. The residue was recrystallized from a mixture of acetone and ether to give 1.14 g. (93%) of fine needles, m.p. 201–202°; $[\alpha]_D^{26}$ − 18 ± 1° (in chloroform, *c* 1.08).

Anal. Calcd. for $C_{15}H_{21}O_6N$: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.32; H, 6.65; N, 4.21.

Acetylation of 50 mg. of VI with acetic anhydride and absolute pyridine in the usual manner gave, after recrystallization from a mixture of acetone, ether, and pentane, 55 mg. (95%) of long silky needles of the *3-O-acetyl* derivative (VII), m.p. 192–193°; $[\alpha]_D^{26}$ + 48 ± 1° (in chloroform, *c* 0.66).[15]

Anal. Calcd. for $C_{18}H_{23}O_7N$: C, 59.18; H, 6.33. Found: C, 59.18; H, 6.27.

Methyl 3-acetamido-4,6-O-benzylidene-3-deoxy-α-D-idopyranoside (XI) *from* III. One hundred milligrams of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-talopyranoside (III)[9] and 15 ml. of methanol saturated with ammonia at 0° were heated in a sealed tube at 100° for 40 hr. After removal of the solvents and acetylation with 0.2 ml. of acetic anhydride, as described above, the crystalline residue was recrystallized from methanol to give 105 mg. (86%) of long needles, m.p. 230–231°; $[\alpha]_D^{22}$ + 51 ± 2° (in chloroform, *c* 0.97).

Anal. Calcd. for $C_{15}H_{21}O_6N$: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.32; H, 6.59; N, 4.26.

Acetylation of 60 mg. of XI with 0.3 ml. of acetic anhydride and 0.5 ml. of anhydrous pyridine in the usual manner, gave, after recrystallization from a mixture of chloroform and ether, 63 mg. (90%) of the *2-O-acetyl* derivative (XII), as rectangular prisms, m.p. 286–287° (sublimation above 260°); $[\alpha]_D^{27}$ + 86° ± 2° (in chloroform, *c* 0.91).[16]

Anal. Calcd. for $C_{18}H_{23}O_7N$: C, 59.18; H, 6.33. Found: C, 59.22; H, 6.38.

Ammonolysis of methyl 4,6-O-benzylidene-2,3-di-O-p-tolylsulfonyl-α-D-galactopyranoside (II). A solution containing 4.72 g. of II[8] in 120 ml. of methanol and 16.0 ml. (2 moles) of a 1*N* solution of sodium methoxide was saturated at 0° with ammonia. After heating in sealed tubes at 100° for 48 hr., the solvents were removed by distillation and the dry residue was dissolved in 100 ml. of methanol. After adding 10 ml. of acetic anhydride the solution was left overnight at room temperature, then boiled for a few minutes, and evaporated to dryness. The residue was extracted with chloroform and water and the organic solvent layer was washed with water and dried over sodium sulfate. After evaporation, a residue weighing 2.46 g. was obtained. It was dissolved in benzene and chromatographed on silicic acid. Elution with a mixture of benzene and ether 1:1 gave the starting material, melting after recrystallization at 175–177° (0.07 g.; 1.5%).

Pure ether eluted 0.28 g. of crystalline material. Recrystallization from a mixture of acetone, ether, and pentane afforded 0.24 g. (6%), m.p. 132–135°; $[\alpha]_D^{25}$ + 68 ± 1° (in chloroform, *c* 1.59).

Anal. Calcd. for $C_{15}H_{20}O_6$: C, 60.80; H, 6.80; OCH_3, 20.94. Found: C, 60.76; H, 6.81; OCH_3, 20.80.

On the basis of its mode of formation and properties, the structure of methyl 4,6-*O*-benzylidene-3-*O*-methyl-α-D-idopyranoside (IV)[17] was attributed to this compound. A mixture of ether and ethyl acetate 2:1 eluted crystalline fractions which gave after recrystallization from a mixture of acetone and ether 0.49 g. (19%) of methyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-idopyranoside (VI), m.p. 197–199°. The mother liquors of VI and the following crystalline fractions (1.44 g.) were acetylated by addition of 18 ml. of anhydrous pyridine and 5 ml. of acetic anhydride. After 1 day the mixture was evaporated and the last traces of solvent were removed by codistillation with toluene. The crystalline residue was dissolved in a mixture of chloroform and methanol 1:1, filtered through Darco G-60 and Celite, and the chloroform evaporated. The residual sirup kept at 0° gave 0.70 g. (24%) of methyl 3-acetamido-2-*O*-acetyl-4,6-*O*-benzylidene-3-deoxy-α-D-idopyranoside (XII), m.p. 290–291°.

The mother liquors were chromatographed on silicic acid. Elution with a mixture of ether and ethyl acetate 2:1 gave first methyl 2-acetamido-3-*O*-acetyl-2-deoxy-4,6-*O*-benzylidene-α-D-idopyranoside (VII), followed by methyl 3-acetamido-2-*O*-acetyl-3-deoxy-4,6-*O*-benzylidene-α-D-idopyranoside (XII). Recrystallization of these compounds yielded 0.73 g. (26%) of pure VII and 0.05 g. (2%) of pure XII, raising the total yields of 2-acetamido derivatives to 45% and of 3-acetamido derivative to 26%.

Hydrolysis of XII with sodium methylate in the usual manner gave methyl 3-acetamido-4,6-*O*-benzylidene-3-deoxy-α-D-idopyranoside (XI) in a 97% yield after recrystallization, m.p. 228–229°, $[\alpha]_D^{22}$ + 47 ± 2° (in chloroform, *c* 0.95).

Methyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-idopyranoside (XIV). A solution of 0.68 g. of VI in 6 ml. of glacial acetic acid was heated on a steam bath and 4 ml. of water was added. After heating 1 hr. the solution was diluted with water, evaporated and the residue was dried by additions of dry toluene, followed by distillation. The residue (0.55 g.) was then dried at 60° in high vacuum and acetylated with 2 ml. of dry pyridine and 1.2 ml. of acetic anhydride. After standing overnight at room temperature absolute ethanol was added to decompose the excess of anhydride. The solution was evaporated to dryness and the sirupy residue was dissolved in chloroform and chromatographed on silicic acid. Ethyl acetate eluted 0.52 g. (78%) of crystalline fractions. They recrystallized from ether in square plates or from a mixture of ether and pentane in prismatic needles to afford 0.32 g. (47%) of XIV, m.p. 104–105°, $[\alpha]_D^{28}$ + 61 ± 2° (in chloroform, *c* 1.01).

Anal. Calcd. for $C_{15}H_{23}O_9N$: C, 49.86; H, 6.42. Found: C, 49.91; H, 6.47.

The mother liquors had $[\alpha]_D^{26}$ + 39° (in chloroform, *c* 3.90) and still contained a large proportion of XIV, as shown by their transformation after alkaline hydrolysis into VI (see below) with a 50% yield.

Alkaline hydrolysis of XIV with sodium methylate at 0° in the usual manner, followed by removal of the sodium ions with Dowex 50, afforded in quantitative yield a sirupy *methyl 2-acetamido-2-deoxy-α-D-idopyranoside* (XIII). It was purified by dissolution in chloroform and chromatography on silicic acid. The fractions eluted with acetone were colorless, $[\alpha]_D^{29}$ + 14 ± 2° (in methanol, *c* 1.48).

Anal. Calcd. for $C_9H_{17}O_6N$: C, 45.95; H, 7.29, N, 5.96. Found: C, 45.92; H, 7.36; N, 5.90.

A mixture of 104 mg. of XIII, 0.6 ml. of freshly distilled benzaldehyde, and 150 mg. of freshly fused zinc chloride was shaken for 15 hr. The solution was precipitated by addi-

(15) Myers and Robertson[7] reported m.p. 188°; $[\alpha]_D$ + 43.4° in chloroform.

(16) Myers and Robertson[7] reported m.p. 260° and $[\alpha]_D$ +70.3° in chloroform.

(17) Gyr and Reichstein[8] reported m.p. 133–134° and $[\alpha]_D^{18}$ + 66.2 ± 1.5° (in chloroform, *c* 1.814).

tion of water and the mixture extracted with hexane. The precipitate was filtered (107 mg., 74%), washed with water and hexane, and dried. Recrystallization from a mixture of acetone, ether, and pentane gave needles, m.p. 191–196°, $[\alpha]_D^{26}$ −14 ± 2° (in chloroform, *c* 0.84). In admixture with VI described above, no depression of the m.p. was observed.

2-Acetamido-3,4-di-O-acetyl-1,6-anhydro-2-deoxy-β-D-idopyranose (XV). A solution of 57 mg. of XIV was refluxed with 1 ml. of 6*N* hydrochloric acid for 3 hr. After addition of absolute ethanol, the solution was evaporated to dryness. The sirupy residue (39 mg.) was acetylated with 0.7 ml. of dry pyridine and 0.5 ml. of acetic anhydride. After standing overnight at room temperature methanol was added and the solution was evaporated. The residue was dissolved in chloroform and chromatographed on silicic acid. Elution with ethyl acetate gave 38 mg. of crystalline fractions. Recrystallization from a mixture of acetone and ether gave 25 mg. (56%) of prisms, m.p. 127–129°, $[\alpha]_D^{25}$ −39 ± 2° (in chloroform, *c* 0.85).[18] In admixture with authentic material,[11] the melting point was not depressed.

Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-3-O-methylsulfonyl-α-D-idopyranoside (VIII). To a solution of 0.93 g. of VI in 10 ml. of pyridine cooled at −20° was added 1.0 ml. of methanesulfonyl chloride. The solution was left for 2 days at 0°, after which the excess chloride was decomposed by addition of ice. After extracting with chloroform the solvent layer was washed three times with ice cold 2*N* sulfuric acid, three times with saturated sodium bicarbonate solution, then with water, and dried over sodium sulfate. After evaporation the residue was dissolved in methanol and the solution was filtered through Celite and Darco G-60 to give, after concentration, 1.04 g. (90%) of long silky needles, m.p. 180–181° with slight dec., $[\alpha]_D^{26}$ + 65 ± 2° (in chloroform, *c* 0.69).

Anal. Calcd. for $C_{17}H_{23}O_8NS$: C, 50.86; H, 5.77; S, 7.99. Found: C, 50.69; H, 5.75; S, 7.91.

Methyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-talopyranoside (IX). A solution of 1.32 g. of VIII and 1.3 g. of sodium acetate trihydrate in 60 ml. of Methyl Cellosolve containing 5% of water was refluxed for 2 days. The solvent was evaporated and the residue extracted with chloroform and water. After three washings of the organic layer with water and drying over sodium sulfate, the solvent was evaporated. The residue was dissolved in benzene and chromatographed on silicic acid. Elution with a mixture of ether and ethyl acetate in the proportion 2:1, gave 0.241 g. (17%) of crude starting material. Elution with the same solvents in the proportion 1:1 gave crystalline fractions. Recrystallization from a mixture of acetone and ether gave 0.77 g. (72%, or 89% after deduction of the recovered starting material) of shiny platelets, m.p. 193–195°, $[\alpha]_D^{27}$ + 45 ± 1° (in chloroform, *c* 1.27).

Anal. Calcd. for $C_{16}H_{21}O_6N$: C, 59.43; H, 6.55. Found: C, 59.35, H, 6.54.

Acetylation with acetic anhydride and dry pyridine in the usual manner gave the *3-O-acetyl* derivative X in the form of prismatic needles, m.p. 165–167°, $[\alpha]_D^{26}$ + 123 ± 2° (in chloroform, *c* 1.02).

Anal. Calcd. for $C_{18}H_{23}O_7N$: C, 59.17; H, 6.34. Found: C, 59.13; H, 6.35.

Methyl 2-acetamido-3,4,6-tri-O-acetyl-2-deoxy-α-D-talopyranoside (XVII). Seven hundred milligrams of IX was treated with 60% acetic acid and the residue was acetylated as described above for the preparation of XIV. In the chromatography on silicic acid, crystalline fractions were eluted with ethyl acetate. Recrystallization from a mixture of ether and pentane gave 575 mg. (71%) of rectangular prisms, m.p. 102–103°, $[\alpha]_D^{23}$ + 61 ± 1° (in chloroform, *c* 1.54).

Anal. Calcd. for $C_{15}H_{23}O_9N$: C, 49.86; H, 6.42. Found: C, 49.86; H, 6.42.

Alkaline hydrolysis of XVII with barium methylate at 0° in the usual manner, followed by removal of the barium ions with Dowex 50, gave the sirupy *methyl 2-acetamido-2-deoxy-α-D-talopyranoside* (XVI) in quantitative yield. Purification was obtained by chromatography on silicic acid, the product being eluted by acetone as a colorless sirup, $[\alpha]_D^{26}$ + 7 ± 1° (in methanol, *c* 1.16).

Anal. Calcd. for $C_9H_{17}O_6N$: C, 45.95; H, 7.29. Found: C, 46.02; H, 7.30.

2-Amino-2-deoxy-D-talose hydrochloride (*D-talosamine hydrochloride*) XVIII. A solution of 144 mg. of XVI in 2 ml. of 2*N* hydrochloric acid was heated on the water bath for 2 hr. After evaporation, the last traces of hydrochloric acid, water and acetic acid were removed by codistillation with absolute ethanol and toluene, and the residual sirup was placed in a desiccator over soda lime and calcium chloride. After a few days crystals appeared in the sirup. They were isolated by washing with a mixture of acetone and ethyl acetate 3:7 in a yield of 86% (110 mg.). Recrystallization from a mixture of acetone and absolute ethanol gave hexagonal prisms, m.p. 150–151° dec.

Anal. Calcd. for $C_6H_{14}O_5NCl$: C, 33.26; H, 6.48; Cl, 16.44. Found: C, 33.30; H, 6.56; Cl, 16.54.

The product was compared with that obtained from D-lyxose[4] by paper chromatography on Whatman No. 1 and No. 54 papers using a descending system and the mixture of solvents pyridine, ethyl acetate, water and acetic acid, in proportions, 5:5:3:1.[19] The following $R_{Glucosamine}$ of the hydrochloride derivatives were observed: D-talosamine (present work) 1.07; D-talosamine (from D-lyxose) 1.06; D-gulosamine[6] 1.04; D-galactosamine 0.89.

2-Deoxy-2-(2'-hydroxynaphthylidenamino)-β-D-talose (XIX). To a solution of 33 mg. of XVIII and 20 mg. of sodium acetate trihydrate in 0.8 ml. of water was added a solution of 70 mg. of 2-hydroxynaphthaldehyde in 7 ml. of methanol. The solution was left in the dark at room temperature for 4 hr., then evaporated *in vacuo* below 20°. The residue was dissolved in benzene and chromatographed on silicic acid. Crystalline fractions were eluted with acetone and were recrystallized from a mixture of methanol and acetone to give 34 mg. (62%) of small yellow prisms, m.p. 160–161° dec. The substance showed mutarotation, from $[\alpha]_{5461}^{28}$ − 77 (after 8 min.) to $[\alpha]_{5461}^{29}$ − 62 ± 5° (after 2 and 120 hr., in methanol, *c* 0.20).

Anal. Calcd. for $C_{17}H_{19}O_6N$: C, 61.26; H, 5.75. Found: C, 60.91; H, 6.46.

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(18) Kuhn and Bister[11] reported m.p. 127° and $[\alpha]_D^{22}$ −39 ± 1° (in chloroform, *c* 1.12).

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