The product was homogeneous on paper chromatography and had R_{ad} 1.5. The nmr spectrum showed the purine ring protons as two singlets at τ 1.55 and 1.85. The H-1′ proton occurred as a doublet (J = 3 cps) at τ 4.26.

Registry No.—**3,** 13116-37-5; **4,** 13116-38-6; **5,** 13116-39-7; **6,** 13116-40-0; **8,** 13116-41-1; **9,** 13116-42-2; **10,** 13137-25-2; **11,** 13137-26-3; **13,** 13137-28-5; **14,** 13137-27-4; **15,** 13143-63-0; **16,** 13116-43-3; **18,** 13116-44-4; **18** picrate, 13116-45-5.

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Pyrrolidine Sugars. Synthesis of 9-(4-Acetamido-4-deoxy-β-D-xylofuranosyl)adenine and Other Derivatives of 4-Amino-4-deoxy-D-xylose[1]

ELMER J. REIST, LINDA V. FISHER, AND LEON GOODMAN

Life Sciences Research, Stanford Research Institute, Menlo Park, California

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Derivatives of 4-amino-4-deoxy-D-xylose have been prepared starting from methyl β-L-arabinopyranoside (**1**). Selective benzoylation of the equatorial hydroxyls of **1** gave methyl 2,3-di-*O*-benzoyl-β-L-arabinopyranoside (**2**). Tolylsulfonation of **2** followed by nucleophilic displacement of the tosylate by azide ion, then debenzoylation, and hydrogenation gave methyl 4-amino-4-deoxy-α-D-xylopyranoside (**8**). Acetylation of **8** followed by acetolysis gave 4-acetamido-1,2,3,5-tetra-*O*-acetyl-4-deoxy-D-xylofuranose (**14**) together with a trace amount of pyranose (**16**). Conversion of **14** to 9-(4-acetamido-4-deoxy-β-D-xylofuranosyl)adenine (**17**) was accomplished in the usual fashion. The nmr spectrum of **17** in D_2O exhibited the phenomenon of hindered internal rotation.

In recent years, there has been great interest in the preparation of derivatives of monosaccharides in which the ring oxygen has been substituted by some other heteroatom such as nitrogen or sulfur. Our interest in the preparation of fraudulent nucleosides as compounds of potential biological significance directed us to the synthesis of monosaccharides in which the sulfur or nitrogen atom was on C-4 in order that the resulting ring closed sugar would have the desired furanose configuration. The preparation of D-ribose analogs, the derivatives of 4-thio-D-ribose,[2] and 4-acetamido-D-ribose[3] has been reported previously. Subsequently, it was desired to prepare similar nucleoside derivatives with the configuration of D-xylose, since some biological activity has been reported for 9-(β-D-xylofuranosyl)adenine.[4]

Numerous reports have been published which describe the preparation of substituted 4-aminoxylose sugars, *e.g.*, 4-acetamido-4,5-dideoxy-D-xylose,[5] 4,5-diacetamido-4,5-dideoxy-L-xylose,[5,6] 4-acetamido-4-deoxy-L-xylose,[7] and sulfonylated 4-azido-4-deoxy-D-xylose.[8] None of the approaches described seemed applicable to our purposes, however; so an alternative route was investigated which proved successful for the preparation of derivatives of the desired 4-acetamido-4-deoxy-D-xylose. The results are described in this paper. A subsequent paper will describe the preparation of 4-thio-D-xylose.

The selective benzoylation of methyl α-D-galactopyranoside at the primary and secondary equatorial hydroxyls[9,10] proved to be an entré to derivatives of 4-amino-4-deoxy-D-glucose.[9] Since the configuration about the ring of the functional groups of D-glucose is the same as that of D-xylose, a similar approach seemed logical for the 4-amino-4-deoxy-D-xylose series. With this idea in mind, methyl β-L-arabinopyranoside[11] (**1**) was treated under controlled conditions with benzoyl chloride in pyridine to give a fair yield of a crystalline dibenzoate which was tentatively assigned the structure of the desired methyl 2,3-di-*O*-benzoyl-β-L-arabinopyranoside (**2**). This dibenzoate **2** could be treated with *p*-toluenesulfonyl chloride in pyridine or methanesulfonyl chloride in pyridine to give crystalline methyl 2,3-di-*O*-benzoyl-4-*O*-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (**3**) or methyl 2,3-di-*O*-benzoyl-4-*O*-methylsulfonyl-β-L-arabinopyranoside (**4**), respectively. That the sulfonate of **3** and **4** was indeed at C-4 was demonstrated when **4** was debenzoylated with excess methanolic sodium methoxide to give a high yield of methyl 4-*O*-methylsulfonyl-β-L-arabinopyranoside (**5**). If the methylsulfonate had been located on either C-2 or C-3, it would have been adjacent to a *trans* hydroxyl function and epoxide formation should have occurred. Only with a 4-sulfonate was epoxide formation not possible.

Methyl 2,3-di-*O*-benzoyl-4-*O*-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (**3**) was treated with sodium azide in *N*,*N*-dimethylformamide (DMF) to give crystalline methyl 4-azido-2,3-di-*O*-benzoyl-4-deoxy-α-D-xylopyranoside (**6**). Debenzoylation of **6** with methanolic sodium methoxide gave a good yield of crystalline methyl

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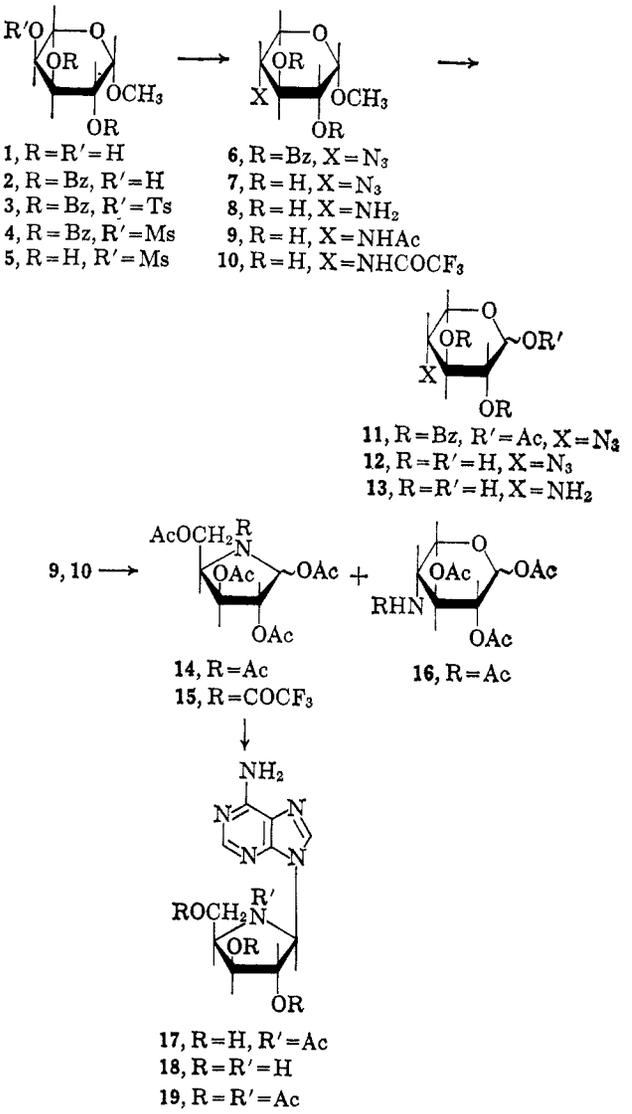
4-azido-4-deoxy-α-D-xylopyranoside (**7**). Methyl 4-amino-4-deoxy-α-D-xylopyranoside (**8**) was easily prepared from **7** by hydrogenation of the azide using 5% palladium on charcoal. In an effort to prepare the parent 4-amino-4-deoxy-D-xylose (**13**), the methyl glycoside (**8**) was hydrolyzed with 6 *N* aqueous hydrochloric acid. The product obtained was a dark syrup which consisted of at least two different reducing sugars as evidenced by paper chromatography; so an alternative approach was investigated. Treatment of methyl 4-azido-2,3-di-*O*-benzoyl-4-deoxy-α-D-xylopyranoside (**6**) under acetolysis conditions gave crude 1-*O*-acetyl-4-azido-2,3-di-*O*-benzoyl-4-deoxy-D-xylopyranose (**11**). Deacetylation of crude **11** at room temperature with methanolic sodium methoxide afforded a low yield of crystalline 4-azido-4-deoxy-D-xylose (**12**). Hydrogenation of **12** in the presence of hydrochloric acid gave a crystalline product, assumed to be 4-amino-4-deoxy-D-xylose (**13**) hydrochloride. This material could not be characterized satisfactorily and the analytical values did not correspond to any logical structure. Thus, the behavior of **13** was similar to that of 4-amino-4-deoxy-D-glucose[9] rather than that of 4-amino-4,6-dideoxy-D-glucose.[12]

A recent publication by Strachan and co-workers[13] described the preparation of *N*-trifluoroacetates of carbohydrates and the base-catalyzed removal of the *N*-trifluoroacetate under conditions which might be compatible with the chemistry of purine nucleosides. The *N*-trifluoroacetate blocking group appeared to present a possible approach to the preparation of 9-(4-amino-4-deoxy-β-D-xylofuranosyl)adenine (**18**). Treatment of methyl 4-amino-4-deoxy-α-D-xylopyranoside (**8**) with trifluoroacetic anhydride gave crystalline methyl 4-deoxy-4-trifluoroacetamido-α-D-xylopyranoside (**10**). Acetolysis of **10** gave a syrup which had spectral properties that were compatible with the furanose structure (**15**). All attempts to prepare a nucleoside from **15** were unsuccessful. Extensive decomposition occurred and, at best, only trace amounts of nucleosidelike material were formed.

Efforts were now devoted to synthesize 9-(4-acetamido-4-deoxy-β-D-xylofuranosyl)adenine (**17**). *N*-Acetylation of methyl 4-amino-4-deoxy-α-D-xylopyranoside (**8**) by the procedure of Dick and Jones[7] gave crystalline methyl 4-acetamido-4-deoxy-α-D-xylopyranoside (**9**). Acetolysis of **9** gave a mixture of products from which syrupy 4-acetamido-1,2,3,5-tetra-*O*-acetyl-4-deoxy-D-xylofuranose (**14**) was isolated. The nmr spectrum of **14** indicated that the α and β anomers occurred in approximately equal amounts. Small amounts of a syrup that had the necessary spectral characteristics for the pyranose (**16**) were isolated. The reaction of the acetylated furanose (**14**) with chloromercuri-6-benzamidopurine in the presence of titanium tetrachloride gave, after deacylation, a mixture of nucleosides. Ion-exchange chromatography of this mixture gave a 22% yield of 9-(4-acetamido-4-deoxy-β-D-xylofuranosyl)adenine (**17**). The nmr spectrum of **17** in D_2O exhibited the same double peaks owing to restricted rotation of the *N*-acetate that were observed for 4′-acetamidoadenosine.[3] Acetylation of **17** gave the triacetate (**19**). As in the case of the acetylated 4′-acetamidoadenosine, the nmr of **19** in deuteriochloroform showed no indication of the restricted rotation observed for **17** in D_2O (Scheme I).

SCHEME I



The contrast in behavior toward acetolysis conditions of methyl 4-acetamido-4-deoxy-α-D-xylopyranoside (**9**) and methyl 4-acetamido-4-deoxy-α-D-glucopyranoside[10] is noteworthy. Thus, while the acetolysis of **9** gives the furanose derivative (**14**) with the nitrogen in the ring almost entirely, the glucose analog of **9** gives only the pyranose derivative analogous to **16**.

Experimental Section[14]

Methyl 2,3-Di-*O*-benzoyl-β-L-arabinopyranoside (2).—A solution of 19.0 g (0.12 mole) of methyl β-L-arabinopyranoside (**1**) in 240 ml of pyridine was treated with 31.1 ml (0.27 mole) of benzoyl chloride in the manner described for the preparation of methyl

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(14) Melting points were determined with a Fisher–Johns apparatus and are corrected. Thin layer chromatograms were run on silica gel HF (E. Merck AG, Darmstadt). Spots were detected by visual examination under an ultraviolet lamp or by spraying with sulfuric acid, then developing at *ca.* 100° for a few minutes. The nmr spectra were run on the Varian A-60 or H-100 spectrometers. Organic solutions were dried over magnesium sulfate.

2,3,6-tri-*O*-benzoyl-α-D-galactopyranoside from methyl α-D-galactopyranoside.[9] The reaction mixture was poured into 400 ml of saturated aqueous sodium bicarbonate, then was extracted with three 200-ml portions of ether followed by three 100-ml portions of chloroform. After evaporation of the ether layer, digestion of the resulting oil with 300 ml of boiling cyclohexane caused crystallization to occur. Recrystallization from benzene–hexane gave 19.1 g (44%) of product, mp 140.5–143.0°. The analytical sample was recrystallized from diethyl ether and had mp 141.5–142.5°; $[\alpha]^{20}D$ +210° (*c* 1, chloroform); λ_{max}^{Nujol} 2.80 (OH), 5.75, 585 μ (C=O).

Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.5; H, 5.41. Found: C, 64.4; H, 5.32.

Evaporation of the chloroform layer gave 2.1 g (6%) of methyl 2-*O*-benzoyl-β-L-arabinopyranoside, mp 145–147°, which was identical with authentic 2-*O*-benzoate.[11]

Methyl 2,3-Di-*O*-benzoyl-4-*O*-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (3).—A mixture of 6.0 g (16 mmoles) of methyl 2,3-di-*O*-benzoyl-β-L-arabinopyranoside (**2**) and 6.2 g (32 mmoles) of *p*-toluenesulfonyl chloride in 60 ml of dry pyridine was heated at 50° under a nitrogen atmosphere with stirring for 15 hr. The reaction was cooled and poured slowly into 120 ml of cold water. The product crystallized and was removed by filtration. The precipitate was dissolved in chloroform, washed with water, dried, and evaporated to dryness *in vacuo*. The residue was crystallized from methanol to give 4.8 g (57%) of product: mp 162.5–164.0°; $[\alpha]^{21}D$ +173° (*c* 1, chloroform); λ_{max}^{Nujol} 5.78 (C=O), 8.44, 12.20 μ (OSO_2).

Anal. Calcd for $C_{27}H_{26}O_9S$: C, 61.6; H, 4.98; S, 6.09. Found: C, 61.5; H, 4.96; S, 5.95.

Methyl 2,3-Di-*O*-benzoyl-4-*O*-methylsulfonyl-β-L-arabinopyranoside (4).—To a mixture of 11.5 g (31 mmoles) of methyl 2,3-di-*O*-benzoyl-β-L-arabinopyranoside (**2**) in 60 ml of dry pyridine was added 7.72 ml (99 mmoles) of methanesulfonyl chloride dropwise with stirring. The reaction mixture was kept at room temperature for 18 hr, then the excess methylsulfonyl chloride was decomposed by the cautious addition of 3 ml of water, and the mixture was evaporated to dryness *in vacuo*. The residue was partitioned between 100 ml each of ether and saturated aqueous sodium bicarbonate solution. The ether layer was washed with water then was dried and evaporated to dryness *in vacuo* to give 16.9 g of crude product as an oil. Crystallization was induced by digestion of the oil with boiling cyclohexane and letting the two-phase system cool. The cooled cyclohexane was decanted and the residue was recrystallized from methanol to give 11.5 g (82%) of white product: mp 106.5–108.5°; $[\alpha]^{22}D$ +205° (*c* 1, chloroform); λ_{max}^{Nujol} 5.75 (C=O), 8.44 μ (OSO_2).

Anal. Calcd for $C_{21}H_{22}O_9S$: C, 56.0; H, 4.92; S, 7.12. Found: C, 56.2; H, 4.83; S, 7.07.

Methyl 4-*O*-Methylsulfonyl-β-L-arabinopyranoside (5).—A mixture of 8.0 g (17.8 mmoles) of methyl 2,3-di-*O*-benzoyl-β-L-arabinopyranoside (**4**) in 45 ml of methanol was stirred at room temperature with 4.5 ml of 1 *N* methanolic sodium methoxide for 16 hr. The reaction was neutralized with IRC 50 (H), then was filtered and evaporated to dryness *in vacuo*. The residue was partitioned between 50 ml each of chloroform and water. The aqueous phase was evaporated to dryness *in vacuo* to give 5.8 g of crude product as solid which was recrystallized from chloroform to give 4.0 g (93%) of crystalline product (**5**), mp 124.0–126.5°. The analytical sample had mp 124.5–125.5°; $[\alpha]^{21}D$ +216° (*c* 1, methanol); λ_{max}^{Nujol} 2.90, 2.98 (OH), 8.42 μ (OSO_2).

Anal. Calcd for $C_7H_{14}O_7S$: C, 34.7; H, 5.83; S, 13.2. Found: C, 34.6; H, 5.76; S, 13.1.

Methyl 4-Azido-2,3-di-*O*-benzoyl-4-deoxy-α-D-xylopyranoside (6).—A mixture of 1.0 g (1.9 mmoles) of methyl 2,3-di-*O*-benzoyl-4-*O*-(*p*-tolylsulfonyl)-β-L-arabinopyranoside (**3**) and 0.37 g (5.7 mmoles) of sodium azide in 23 ml of DMF (dried over neutral alumina) was heated with stirring under a nitrogen atmosphere at 115° for 15 hr. The reaction mixture was cooled and evaporated to dryness *in vacuo*. The residue was partitioned between ether and water. The ether layer was dried, then evaporated to dryness *in vacuo* to give 0.64 g of a syrup which was crystallized and recrystallized from methanol to give 0.48 g (64%) of product, mp 75.5–77.5°. The analytical sample had mp 77–79°; $[\alpha]^{21}D$ +174° (*c* 1, chloroform); λ_{max}^{Nujol} 4.70 (N_3), 5.73 μ (C=O).

Anal. Calcd for $C_{20}H_{19}N_3O_6$: C, 60.5; H, 4.82; N, 10.6. Found: C, 60.7; H, 5.00; N, 10.7.

Subsequent preparations starting with 30 g of **3** gave yields up to 89%.

Methyl 4-Azido-4-deoxy-α-D-xylopyranoside (7).—A solution of 4.5 g (11.3 mmoles) of methyl 4-azido-2,3-di-*O*-benzoyl-α-D-xylopyranoside (**6**) in 28 ml of methanol was stirred with 2.8 ml of 1 *N* methanolic sodium methoxide at reflux for 2 hr, then was cooled to room temperature and neutralized to pH 7 with IRC 50 (H). The resin was removed and the methanol solution was evaporated to dryness *in vacuo*. The residue was partitioned between 20 ml each of chloroform and water. The aqueous layer was evaporated to dryness *in vacuo* to give a solid which was crystallized from 65 ml of benzene–hexane (2:1) to give 1.71 g (79%) of colorless needles: mp 74–76°; $[\alpha]^{23}D$ +232° (*c* 1, methanol); λ_{max}^{Nujol} 2.93, 3.0 (OH), 4.68 μ (N_3).

Anal. Calcd for $C_6H_{11}N_3O_4$: C, 38.1; H, 5.86; N, 22.2. Found: C, 38.2; H, 5.80; N, 21.9.

Methyl 4-Amino-4-deoxy-α-D-xylopyranoside (8).—To a solution of 0.5 g (2.64 mmoles) of methyl 4-azido-4-deoxy-α-D-xylopyranoside (**7**) in 9 ml of water was added 200 mg of 5% palladium on carbon and the mixture was hydrogenated at room temperature and atmospheric pressure for 4 hr. The catalyst was removed by filtration and the filtrate was evaporated to dryness *in vacuo* to give 0.47 g of a colorless gum which crystallized on standing. Recrystallization from 2-propanol gave 0.3 g (68%) of crystalline product, mp 110–114°. The analytical sample, obtained by one more recrystallization from 2-propanol, had mp 116–118°, $[\alpha]^{23}D$ +167° (*c* 1, methanol).

Anal. Calcd for $C_6H_{13}NO_4$: C, 44.2; H, 8.03; N, 8.58. Found: C, 44.2; H, 8.00; N, 8.54.

A larger run using 6.8 g of **7** gave similar results.

Methyl 4-Acetamido-4-deoxy-α-D-xylopyranoside (9).—To a solution of 2.5 g (15.3 mmoles) of methyl 4-amino-4-deoxy-α-D-xylopyranoside (**8**) in 61 ml of water was added 6.1 ml (60 mmoles) of acetic anhydride dropwise with stirring. The reaction was kept at room temperature for 20 min and then was evaporated to dryness *in vacuo* to a colorless syrup. Crystallization from acetone gave 2.54 g (81%) of white crystals, mp 150–151°. The analytical sample, recrystallized from ethyl acetate, had mp 152–153°; $[\alpha]^{23}D$ +147° (*c* 0.8, methanol); λ_{max}^{Nujol} 6.1 (amide I), 6.4 μ (amide II).

Anal. Calcd for $C_8H_{15}NO_5$: C, 46.8; H, 7.37; N, 6.83. Found: C, 47.0; H, 7.50; N, 6.67.

Methyl 4-Deoxy-4-trifluoroacetamido-α-D-xylopyranoside (10).—A solution of 2.0 g (12.3 mmoles) of methyl 4-amino-4-deoxy-α-D-xylopyranoside (**8**) in 9 ml of trifluoroacetic anhydride was stirred at room temperature for 2 hr and then was evaporated to dryness *in vacuo* to a yellow syrup which was crystallized from acetone–ether to give 2.5 g (79%) of product, mp 178–179°. The analytical sample was recrystallized from methanol–chloroform and had mp 179.5–180.5°; $[\alpha]^{21}D$ +124° (*c* 1, methanol); λ_{max}^{Nujol} 2.93, 3.0 (OH, NH), 5.84 (amide I), 6.45 μ (amide II).

Anal. Calcd for $C_8H_{12}F_3NO_5$: C, 37.1; H, 4.67; N, 5.40. Found: C, 37.2; H, 4.69; N, 5.60.

4-Azido-4-deoxy-D-xylopyranose (12).—To a cold (0°) solution of 4.2 g (10.6 mmoles) of methyl 4-azido-2,3-di-*O*-benzoyl-4-deoxy-α-D-xylopyranoside (**6**) in 40 ml each of acetic anhydride and glacial acetic acid was added 4 ml of concentrated sulfuric acid dropwise with stirring and continued cooling. After the addition was complete, the reaction was stored at 0° for 16 hr, then was decomposed by the addition of 7.3 g of anhydrous sodium acetate, and the mixture was evaporated to dryness *in vacuo*. The residue was partitioned between 100 ml each of ether and water. The ether layer was washed with two 20-ml portions of saturated aqueous sodium bicarbonate and 20 ml of water then was dried and evaporated to dryness *in vacuo* to give 4.41 g of crude blocked azide (**11**): λ_{max}^{film} 4.68 (N_3), 5.7 (C=O), 7.85 (benzoate C–O–C), 8.1 μ (acetate C–O–C).

Deacetylation, at room temperature for 4 hr, of crude **11** in 55 ml of methanol which contained 10 ml of 1 *N* methanolic sodium methoxide was followed by neutralization with IRC 50 (H) to pH 7. The neutralized solution was filtered, then evaporated to dryness *in vacuo*. The residue was partitioned between 60 ml each of chloroform and water. The aqueous phase was evaporated to dryness *in vacuo* to give a gummy solid. Extraction of this solid with several portions of hot acetone gave 1.06 g of crude product (**12**) as a syrup. Purification of crude **12** was effected by silica gel chromatography. Thus, a solution of 1.0 g of **12** in the minimum amount of acetone was applied to a column which contained 20 g of silica gel. Elution was started with chloroform, then proceeded through 50% ethyl acetate in chloroform and finally 100% ethyl acetate. The 100% ethyl acetate fraction contained crystalline product and weighed 0.45

g. Crystallization from methanol–chloroform gave the analytical sample of 4-azido-4-deoxy-D-xylose (**12**), mp 110–114°, $[\alpha]^{21}D$ +81° (*c* 1, water).

Anal. Calcd for $C_5H_9N_3O_4$: C, 34.3; H, 5.18; N, 24.0. Found: C, 34.1; H, 5.30; N, 23.8.

4-Acetamido-1,2,3,5-tetra-*O*-acetyl-4-deoxy-D-xylofuranose (14).—To a cold (0°) mixture of 254 ml of glacial acetic acid, 254 ml of acetic anhydride, and 15.1 ml of concentrated sulfuric acid was added 4.9 g (23.7 mmoles) of methyl 4-acetamido-4-deoxy-α-D-xylopyranoside (**9**) with stirring. The reaction was stored at *ca.* 0° for 47 hr, then 59 g of anhydrous sodium acetate was added, and the mixture was evaporated to dryness *in vacuo*. The residue was partitioned between water and ether. The ether layer was washed with water, saturated aqueous sodium bicarbonate, and, finally, water, and then it was dried and evaporated to dryness *in vacuo* to give 5.85 g (69%) of product (**14**) as a syrup, λ_{max}^{film} 5.70 (OAc), 5.95 μ (NAc). There was no evidence for NH absorption at 3.0 μ or amide II absorption at 6.5 μ. The nmr spectrum was compatible with the furanose structure (**14**) and showed H-1 absorption occurring as a singlet (τ 3.62) and a doublet (τ 3.42, J = 5 cps) to suggest approximately equal amounts of α and β anomers.

Anal. Calcd for $C_{15}H_{21}NO_9$: C, 50.1; H, 5.89; N, 3.90. Found: C, 50.4; H, 6.15; N, 3.75.

The original aqueous extract from the ether–water partition was further extracted with chloroform. The chloroform layer was washed and dried in same fashion as was the previously described ether layer, then was evaporated to dryness to yield 1.88 g of a syrup. Thin layer chromatography using ethyl acetate as the developing solvent showed that in addition to the furanose (**14**) there was also another slower moving component. The infrared spectrum showed the presence of NH absorption at 2.9 μ and amide II absorption at 6.5 μ in addition to the expected carbonyl bands, thus indicating the presence of small amounts of the pyranose (**16**). An additional 1.4 g (16%) of pure furanose was obtained by partition of this fraction between benzene and water. The pure furanose component was obtained from the benzene fraction.

9-(4-Acetamido-4-deoxy-β-D-xylofuranosyl)adenine (17).—To a mixture of 5.13 g (14.3 mmoles) of 4-acetamido-1,2,3,5-tetra-*O*-acetyl-4-deoxy-D-ribofuranose and 13.2 g (18 mmoles) of chloromercuri-6-benzamido purine (64% on Celite) on 540 ml of 1,2-dichloroethane was added 2.3 ml (19.5 mmoles) of titanium tetrachloride. The reaction was refluxed with stirring for 24 hr, then was cooled to room temperature and stirred for 4 hr with 12 ml of saturated aqueous sodium bicarbonate. The mixture was filtered and the precipitate was washed with chloroform. The organic layer was separated and washed with 10 ml of 30% aqueous potassium iodide, then with two 10-ml portions of water. The solution was dried, then evaporated to dryness to give 5.7 g (73%) of crude blocked nucleoside.

A solution of the crude blocked nucleoside in 133 ml of methanol was treated with 13.3 ml of 1 *N* methanolic sodium methoxide at room temperature for 15 hr, then was neutralized to pH 7 with IRC 50 (H) and evaporated to dryness *in vacuo*. The residue was partitioned between chloroform and water; then the aqueous phase was evaporated to dryness to give 2.48 g of crude nucleoside (**17**). Crude **17** was dissolved in the minimum amount of water and applied to a column of 150 g of Dowex 1 (OH).[15] Elution of the column began with 500 ml of pure water, then proceeded through 100 ml of methanol–water (3:7), 300 ml of methanol–water (1:1), 900 ml of methanol–water (7:3), and finally 500 ml of pure methanol. Two ultraviolet absorbing peaks were eluted using methanol-water (7:3). The main fraction weighed 0.98 g and was crystallized from methanol–chloroform to give 0.97 g (22%) of crystalline **17**, mp 227–230°, which was homogeneous on thin layer chromatography using 1-propanol–ethyl acetate–water (3:2:1) as the developing agent.

Recrystallization from methanol gave the analytical sample: mp 228–230° dec; $[\alpha]^{21}D$ −101° (*c* 0.55, water); $\lambda_{max}^{pH\ 1}$ 258 mμ (ε 14,520); $\lambda_{max}^{pH\ 7}$ 259 mμ (ε 14,590); $\lambda_{max}^{pH\ 13}$ 260 mμ (ε 14,640); λ_{max}^{Nujol} 2.90, 3.04, 3.22 (OH and NH), 6.00, 6.16, 6.24 μ (aromatic). There was no amide II absorption at 6.5 μ.

Anal. Calcd for $C_{12}H_{16}N_6O_4$: C, 46.8; H, 5.23; N, 27.3. Found: C, 46.7; H, 5.30; N, 27.1.

9-(4-Acetamido-2,3,5-tri-*O*-acetyl-4-deoxy-β-D-xylofuranosyl)-adenine (19).—To a cold (0°) mixture of 0.5 g (14.4 mmoles) of 9-(4-acetamido-4-deoxy-β-D-xylofuranosyl)adenine (**17**) in 35 ml of dry pyridine was added 1.4 ml of acetic anhydride with stirring. The reaction was stirred at 0° for 1 hr, then stored at *ca.* 0° for 44 hr and decomposed by the addition of 10 ml of methanol, with stirring and cooling. The reaction was evaporated to dryness *in vacuo* and the residue was partitioned between 30 ml each of chloroform and water. The water layer was extracted with two additional 10-ml portions of chloroform. The organic extracts were combined and washed with 10 ml of water, dried, and evaporated to dryness *in vacuo* to give 0.87 g of syrup. Treatment of this syrup with ether caused the product to solidify. Precipitation from benzene with petroleum ether gave 0.52 g (83%) of **19**: mp 101–110°; $[\alpha]^{22}D$ −66° (*c* 1, chloroform).

Anal. Calcd for $C_{18}H_{22}N_6O_7$: C, 49.8; H, 5.11; N, 19.4. Found: C, 49.9; H, 5.08; N, 18.9.

Registry No.—**2**, 13143-91-4; **3**, 13143-92-5; **4**, 13143-93-6; **5**, 13143-94-7; **6**, 13143-95-8; **7**, 13143-96-9; **8**, 13143-97-0; **9**, 13143-98-1; **10**, 13143-99-2; **11**, 13131-52-7; **12**, 13144-00-8; **14**, 13144-01-9; **17**, 13144-02-0; **19**, 13144-03-1.

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Silica Gel Catalyzed Detritylation of Some Carbohydrate Derivatives[1]

JACOB LEHRFELD

Northern Regional Research Laboratory,[2] Peoria, Illinois 61604

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Methyl 2,3,4-tri-*O*-acetyl-α-D-glucopyranoside (I) and 1,2,3,4-tetra-*O*-acetyl-β-D-glucopyranose (II) were prepared in 81 and 87% yields, respectively, from methyl 2,3,4-tri-*O*-acetyl-6-*O*-trityl-α-D-glucopyranoside (III) and 1,2,3,4-tetra-*O*-acetyl-6-*O*-trityl-β-D-glucopyranose (IV). A column of silica gel was used as the acidic detritylation catalyst and it also served as an adsorbent for the chromatographic separation of the reaction products.

In 1924, Helferich and Becker[3] prepared the first trityl[4] ether of a carbohydrate. Since then, the trityl ether has been extensively used in carbohydrate chemistry as a protecting group for primary hydroxyl groups.[5] The ethers are base stable and acid labile. A number of procedures have been developed for cleaving trityl ethers and regenerating the hydroxyl groups, but each has its limitations. For example, catalytic hydrogenolysis proceeds with difficulty in the presence of sulfur-containing compounds[6] and is

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

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(4) This is an abbreviation for the triphenylmethyl group.

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