are involved. The same reservation may be noted with regard to the H-5 and H-5a signals in the spectrum of tri-*O*-acetyl-α-D-xylopyranosyl bromide, measured in chloroform-*d* at 60 MHz.[2]

Registry No.—1, 10343-54-1; 2, 10300-18-2.

Acknowledgments.—The authors thank Mr. J. D. Wander for some of the 60-MHz nmr spectral measurements, and Mr. W. Jankowski (Varian Associates, Pittsburgh, Pa.) for 100-MHz spectral measurements.

Trichloroacetyl and Trifluoroacetyl as *N*-Blocking Groups in Nucleoside Synthesis with 2-Amino Sugars[1]

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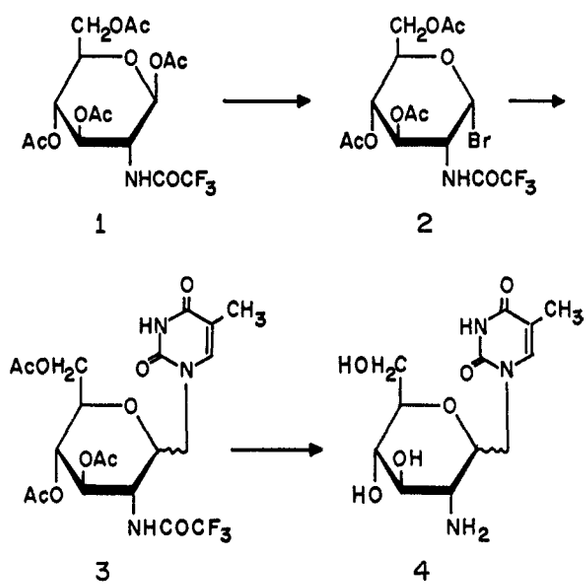
1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucose (1) was converted into the glycosyl halide and this in turn into a fully blocked pyrimidine nucleoside derivative on fusion with bis(trimethylsilyl)thymine. Complete deacylation was effected with methanolic hydrogen chloride or methanolic ammonia. Analogous experiments with the *N*-trichloroacetyl blocking group showed that the products were obtained in lower yield and the *N*-trichloroacetyl group required strong acid or hot barium hydroxide treatment for removal.

There has been a need for an easily removable and conveniently prepared *N*-blocking group in nucleoside synthesis utilizing 2-amino-2-deoxy sugars, especially for these with a *trans* configuration on C-2 and C-3.

In the present work, the trichloroacetyl group was initially tried as an *N*-blocking group. 1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride[2] was converted into its 2-trichloroacetamido derivative (1, F = Cl) and this in turn into a syrupy glycosyl chloride which on fusion[3] with bis(trimethylsilyl)thymine[4] yielded the crystalline 1-nucleoside derivative (3, F = Cl). Treatment of the latter with methanolic hydrogen chloride or methanolic ammonia then gave crystalline 1-(2-trichloroacetamido-2-deoxy-D-glucopyranosyl)thymine. Complete deblocking could be effected only by vigorous acid treatment or by hot barium hydroxide. In this manner the acid-stable pyrimidine nucleoside 4 was obtained in one anomeric form. (See Scheme I.) Since these conditions are too drastic to be employed for purine nucleosides, the use of the more labile *N*-trifluoroacetyl group was explored.

SCHEME I



The trifluoroacetyl group had been used as an *N*-blocking group in the amino acid series[5] and Newman[6] had employed it in the synthesis of steroid glycosides with the glycosyl bromide of a 3,4,6-trideoxy-3-methylaminohexose. At the time our work was communicated,[1] Hirschmann and co-workers[7] reported the crystalline tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-α-D-glucopyranosyl bromide (2) and utilized it for the synthesis of ethyl 2-amino-2-deoxy-β-D-glucopyranoside. In the work herein reported we prepared the bromide 2 by a more convenient method starting from 1,3,4,6-tri-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucose prepared in turn from the 1,3,4,6-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose of Bergmann and Zervas.[2] When 2 was brought into reaction with bis(trimethylsilyl)thymine the crystalline acylated nucleoside 3 was obtained in high yield and this on deacylation with methanolic hydrogen chloride, gave crystalline 1-(2-amino-2-deoxy-D-glucopyranosyl)-thymine hydrochloride (4-HCl). The anomeric nature of this nucleoside is not herein established. The free base 4 is also reported. It was found possible to remove the *O*-acetyl and *N*-trifluoroacetyl groups by prolonged methanolysis and to so obtain the thymine nucleoside 4 in high yield. These alkaline conditions should be suitable for application to purine nucleosides.

A review of all *N*-blocking groups utilized so far in the sugar series has been made.[8] The thymine nucleoside was chosen in the present study as a model substance because of its ease of formation by the trimethylsilyl method and because the thymine nucleoside of 2-amino-2-deoxy-D-glucopyranose had not been synthesized. The trifluoroacetamido group should be

(1) Preliminary communication: M. L. Wolfrom and H. B. Bhat, *Chem. Commun.*, 146 (1966). The syrupy glycosyl chloride reported in the preliminary communication has been replaced herein by the crystalline bromide with better results. In addition, we now report the experiments with the trichloroacetyl *N*-blocking group as well as the removal of the *N*-trifluoroacetyl group under alkaline conditions.

(2) M. Bergmann and L. Zervas, *Ber.*, **64**, 975 (1931); D. Horton, *J. Org. Chem.*, **29**, 1776 (1964).

(3) T. Nishimura, B. Shimizu, and I. Iwai, *Chem. Pharm. Bull.* (Tokyo), **12**, 1471 (1964); *Chem. Abstr.*, **62**, 9223 (1965).

(4) L. Birkofer and A. Ritter, *Angew. Chem.*, **71**, 372 (1959); L. Birkofer, P. Richter, and A. Ritter, *Ber.*, **93**, 2804 (1960); E. Wittenburg, *Z. Chem.*, **4**, 303 (1964).

(5) F. Weygand and E. Scendes, *Angew. Chem.*, **64**, 136 (1952).

(6) H. Newman, *J. Org. Chem.*, **30**, 11287 (1965).

(7) R. G. Strachan, W. V. Ruyle, T. Y. Shen, and R. Hirschmann, *ibid.*, **31**, 507 (1966).

(8) M. L. Wolfrom, P. J. Conigliaro, and E. J. Soltes, *ibid.*, **32**, 653 (1967).

of especial value in the synthesis of purine nucleosides. As the pyrimidine nucleosides are stable to acidity, an *N*-acetyl group can be removed under such acid conditions. The *N*-acetyl group is, however, a strongly participating group, and can lead to oxazoline formation, especially with the highly reactive furanosyl halides.[9] Other *N*-blocking groups, such as the 2,4-dinitrophenyl,[10] may be less or nonparticipating and may also lower favorably the reactivity of the sensitive furanosyl halides. The *N*-trichloroacetyl group is not so advantageous as the *N*-trifluoroacetyl group for the synthesis of thymine nucleosides; yields are distinctly lower and the protecting group is more difficult to remove. Probably this function is somewhat participating, as previous work[11] from this laboratory has indicated.

Experimental Section[12]

1,3,4,6-Tetra-O-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucose (1).—1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucose hydrochloride[2] (20 g) was suspended in methylene chloride (200 ml) and pyridine (20 ml), and trifluoroacetic anhydride (20 ml) was added under cooling with stirring. After stirring for 20 min, the solution was washed with iced water, dried (sodium sulfate), and concentrated to a low volume. Addition of ether yielded crystals which were removed by filtration to give 21.5 g (90%): mp 167°; $[\alpha]^{22}D$ −13° (*c* 2.4, chloroform); λ_{max}^{KBr} 3.0 (NH), 5.7 (OAc), 5.8, 6.4, 7.2, 7.9, 8.1–8.3 (ester), 8.6 (CF), 9.2, 9.3, 10.8, 11.1, 11.2, and 11.5 μ; X-ray powder diffraction data 10.92 (s), 9.51 (vs, 1), 8.12 (w), 6.86 (w), 5.72 (s), 5.04 (vs, 2), 4.53 (vs, 3), 4.31 (s) 4.06 (m), 3.85 (s) 3.74 (m), 3.58 (s), 3.38 (m), 3.24 (s), 2.92 (m), 2.84 (m), 2.75 (m), and 2.08 (s).

Anal. Calcd for $C_{16}H_{20}F_3NO_{10}$: C, 43.35; H, 4.51; N, 3.20. Found: C, 43.35; H, 4.86; N, 3.26.

Preparation of 3,4,6-Tri-O-acetyl-2-deoxy-2-trifluoroacetamido-α-D-glucosyl Bromide (2).—1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-trifluoroacetamido-β-D-glucose (1, 3.0 g) was suspended in methylene chloride (3 ml) and to this was added a solution of acetic acid (3 ml) nearly saturated at 0° with hydrogen bromide. After 3 hr of standing at room temperature, the solvent was removed, the residual syrup was dissolved in ether, and the solution was again evaporated. The syrup was crystallized from ether–hexane to yield 2.8 g (92%): mp 96°, $[\alpha]^{21}D$ +126° (*c* 2.92, chloroform) (lit.[7] 95–97°).

1-(Tri-O-acetyl-2-deoxy-2-trifluoroacetamido-D-glucopyranosyl)thymine (3).—The above bromide (2, 3.5 g) was mixed intimately with bis(trimethylsilyl)thymine[4] (3.5 g) and the mixture was evacuated with a water pump. The system was closed and the mixture was heated slowly to fusion (140°) and so maintained for 30 min whereupon the material was cooled and evacuated to dryness. The dark residue was treated with 80% methanol and evaporated to dryness. The residue was extracted with hot chloroform and the extract was filtered, washed, and dried. The residual syrup obtained on solvent removal was crystallized from methanol–water to yield 3.1 g (80%): mp 236°; $[\alpha]^{22}D$ −47° (*c* 2.50, chloroform); λ_{max}^{EtOH} 265 mμ (ε 9915); λ_{max}^{KBr} 3.0 (NH), 5.7 (OAc), 5.8 (thymine), 6.4, 6.8, 7.3, 7.75, 8.1–8.25 (ester), 9.2, 9.5, 9.7, 10.2, 10.7, and 11.2 μ; X-ray powder diffraction data 12.81 (m), 9.72 (vs, 1), 8.59 (s), 7.38 (s), 6.11 (w), 5.64 (w), 4.98 (vs, 2), 4.46 (vs, 3), 4.27 (s), 3.95 (s), 3.80 (s), 3.62 (s), 3.52 (s), 3.35 (m), 3.24 (s), 3.03 (s), 2.86 (m), and 2.74 (s).

Anal. Calcd for $C_{19}H_{22}F_3N_3O_{10}$: C, 44.79; H, 4.32; N, 8.25. Found: C, 44.79; H, 4.43; N, 8.67.

Thin layer chromatography (silica gel G, E. Merck, Darmstadt; 1:1 ethyl acetate–benzene developer; sulfuric acid indication) of the mother liquor material from the above gave no evidence of an anomer.

1-(2-Amino-2-deoxy-D-glucopyranosyl)thymine Hydrochloride (4-HCl).—The above nucleoside derivative (3, 1.0 g) was dissolved in methanol (25 ml) and the solution was nearly saturated at 0° with hydrogen chloride. After the solution had stood for 16 hr at room temperature, the solvent was removed and the residue was crystallized from methanol to yield 0.55 g (85%): mp 301–304° dec; $[\alpha]^{22}D$ +35° (*c* 2.34, water); λ_{max}^{EtOH} 265 mμ (ε 9240); λ_{max}^{KBr} 2.9–3.0 (OH,NH), 5.8, 5.95 (thymine), 6.1, 6.2, 6.5, 6.8, 7.3, 7.5, 7.85, 9.1, 10.0, 10.5, 11.3, 11.8, and 12.8 μ; X-ray powder diffraction data 13.6 (s), 8.51 (w), 7.08 (vs, 1), 4.46 (s), 4.13 (s), 3.85 (vs, 2), 3.59 (vs, 3), 3.30 (m), 3.04 (m), 2.54 (s), and 2.32 (s).

Anal. Calcd for $C_{11}H_{18}ClN_3O_6$: C, 40.87; H, 5.57; Cl, 10.83; N, 12.92. Found: C, 40.89; H, 5.64; Cl, 10.96; N, 13.26.

1-(2-Amino-2-deoxy-D-glucopyranosyl)thymine (4).—The above hydrochloride (295 mg) was dissolved in water (3 ml) and the solution was treated with sodium hydrogen carbonate (85 mg) in water (3 ml). The product was isolated by thin layer chromatography on silica gel G using ethyl acetate–methanol (1:1, v/v) with indication by sulfuric acid and elution with methanol to yield 200 mg (75%): mp 240–242°, $[\alpha]^{26}D$ +5.4° (*c* 2.44, water); λ_{max}^{EtOH} 266 mμ (ε 9630); λ_{max}^{KBr} 2.93–3.1 (OH,NH), 5.85, 6.02 (thymine), 6.75, 7.0, 7.25, 7.55, 7.8, 8.0, 8.3, 9.1, 9.3, 10.0, 10.8, 12.3, 13.1, and 13.15 μ; X-ray powder diffraction data 13.6 (s), 9.21 (vs, 1), 7.25 (vs, 2), 5.1 (s), 4.67 (s), 4.19 (vs, 3), 3.99 (s), 3.56 (s), 3.34 (s), 3.04 (s), 2.88 (s), 2.75 (m), and 2.63 (m).

Anal. Calcd for $C_{11}H_{17}N_3O_6$: C, 45.99; H, 5.92; N, 14.63. Found: C, 45.50; H, 5.90; N, 14.62.

This compound was also prepared by the prolonged ammonolysis of **3**. The acetylated derivative **3** (540 mg) was dissolved in methanol (20 ml) and nearly saturated at 0° with ammonia. After keeping at room temperature for 5 days, it was evaporated to dryness and the residue was crystallized from methanol to yield 245 mg (80%), mp and mmp 240–242°; X-ray powder diffraction data were identical with those of the previous preparation.

1,3,4,6-Tetra-O-acetyl-2-trichloroacetamido-2-deoxy-β-D-glucose (1, F = Cl).—This compound was prepared in the same manner as its trifluoroacetamido analog (1) except that trichloroacetyl chloride was used in place of trifluoroacetic anhydride. The product was crystallized in the same manner and was obtained in 90% yield: mp 159–160°, $[\alpha]^{22}D$ +7° (*c* 2.5, chloroform); λ_{max}^{KBr} 3.0 (NH), 5.7 (OAc), 5.85, 6.5, 7.3, 8.1–8.2 (ester), 8.9, 9.2, 9.6, 10.3, 10.7, 11.0, 11.9, and 12.1 μ; X-ray powder diffraction data 12.45 (vs, 3), 8.67 (vs, 2), 6.33 (w), 5.79 (w), 5.37 (vs, 1), 5.13 (w), 4.40 (s), 4.02 (m), 3.69 (s), and 2.80 (m).

Anal. Calcd for $C_{16}H_{20}Cl_3NO_{10}$: C, 39.10; H, 4.06; Cl, 21.38. Found: C, 39.30; H, 4.50; Cl, 21.36.

1-(Tri-O-acetyl-2-trichloroacetamido-2-deoxy-D-glucopyranosyl)thymine (3, F = Cl).—The above derivative (9.5 g) was suspended in a mixture of acetic anhydride (30 ml) and methylene chloride (20 ml) and the whole was nearly saturated at 0° with hydrogen chloride. After 16 hr at room temperature, the solution was diluted with methylene chloride (200 ml), neutralized with an aqueous solution of sodium hydrogen carbonate, washed with water, dried, and evaporated. The resulting syrup (9.0 g) was fused with bis(trimethylsilyl)thymine (8.0 g) for 20 min at 150° under diminished pressure, as described above for the synthesis of **3** and the resultant, crystalline product was isolated in the same manner and was recrystallized from methanol to yield 6.0 g (51%): mp 257°; $[\alpha]^{22}D$ −37° (*c* 2.57, chloroform); λ_{max}^{EtOH} 263 mμ (ε 9530); λ_{max}^{KBr} 3.1 (NH), 5.7 (OAc), 5.85 (thymine), 6.5, 6.85, 7.3, 8.1, 9.2, 9.6, 11.1, 11.9, and 12.1 μ; X-ray powder diffraction data 10.78 (vs, 1), 8.85 (w), 7.38 (w), 6.33 (m), 5.34 (vs, 2), 4.82 (m), 3.92 (vs, 3), 3.66 (w), 4.13 (m), and 3.2 (m).

Anal. Calcd for $C_{19}H_{22}Cl_3N_3O_{10}$: C, 40.94; H, 3.95; Cl, 18.85; N, 7.54. Found: C, 40.74; H, 4.17; Cl, 18.69; N, 7.56.

Thin layer chromatography (silica gel, 1:1 ethyl acetate–benzene developer, sulfuric acid indication) of the mother liquor material from the above gave no evidence of an anomer.

1-(2-Trichloroacetamido-2-deoxy-D-glucopyranosyl)thymine.—The above tri-*O*-acetyl derivative (1.0 g) was dissolved in metha-

(9) M. L. Wolfrom and M. W. Winkley, *J. Org. Chem.*, **31**, 3711 (1966).

(10) M. L. Wolfrom, H. G. Garg, and D. Horton, *Chem. Ind.* (London), 930 (1964); *J. Org. Chem.*, **30**, 1556 (1965).

(11) D. R. Lineback, Ph.D. Dissertation, The Ohio State University, 1962, p 295.

(12) All infrared spectra were measured with a Perkin-Elmer Infracord spectrophotometer and ultraviolet spectra were measured with a Bausch and Lomb Spectronic 505 spectrophotometer. X-Ray powder diffraction data refer to interplanar spacing in angstroms (A) with Cu Kα radiation. Relative intensities were estimated visually: s, strong; m, medium; w, weak; v, very. The stronger lines are numbered in order (1, strongest). Polarimetric readings were taken in a 2-dm tube. All evaporations were performed under diminished pressure below 45°. Microanalyses were by W. N. Rond.

nol (25 ml) nearly saturated at 0° with ammonia. After keeping the solution for 8 hr at room temperature, the crystalline product obtained on solvent removal was recrystallized from ethanol to yield 300 mg (40%): mp 281–283° dec; $[\alpha]^{22}D$ +23° (*c* 2.69, ethanol); λ_{max}^{EtOH} 264 mμ (ε 8800); λ_{max}^{KB} 2.9–3.1 (OH, NH), 5.85, 5.9 (thymine), 6.5, 6.8, 7.8, 8.1, 8.8, 9.1, 10.9, 11.9, and 12.2 μ; X-ray powder diffraction data 9.51 (vs, 2), 8.35 (vs, 3), 7.03 (m), 5.22 (vs, 1), 4.6 (s), 4.44 (s), 4.1 (s), 3.79 (s), 3.53 (s), 3.28 (s), 3.13 (s), 2.98 (s), 2.69 (s), and 2.58 (s).

Anal. Calcd for $C_{13}H_{16}Cl_3N_3O_7$: C, 36.19; H, 3.71; Cl, 24.36; N, 9.74. Found: C, 35.98; H, 4.04; Cl, 24.62; H, 9.73.

This substance was also obtained (35% yield) of treating the tri-*O*-acetyl derivative with methanolic hydrogen chloride as described above for the analogous acetylated trifluoroacetamido derivative.

1-(2-Amino-2-deoxy-D-glucopyranosyl)thymine (and Hydrochloride) from 3 (F = Cl).—1-(Tri-*O*-acetyl-2-trichloroacetamido-2-deoxy-β-D-glucopyranosyl)thymine (0.5 g) was refluxed with water (6.2 ml) and concentrated hyrochloric acid (6.2 ml) in an oil bath for 1.5 hr. The solution was evaporated to dryness and the residue was crystallized from methanol to yield 210 mg (75%) of **4**-HCl, mp 320–304° dec; X-ray powder diffraction data were identical with those of the product obtained through the *N*-trifluoroacetyl derivative.

A mixture of 1-(tri-*O*-acetyl-2-trichloroacetamido-2-deoxy-D-glucopyranosyl)thymine (**3**, F = Cl, 0.5 g), barium hydroxide octahydrate (3.0 g), and water (100 ml) was refluxed for 30 min. After cooling, the solution was treated with 1 *N* sulfuric acid to pH 3.0 and the barium sulfate formed was removed by filtration. The filtrate was evaporated to dryness and the residue was treated with ether to remove trichloroacetic acid. The residue, separated by decantation, was dissolved in water (25 ml) and stirred with barium carbonate (1.0 g) to pH 8.0. The solution was filtered through Celite and the filtrate was evaporated to dryness. The syrupy residue was chromatographed on two silica gel G plates using ethyl acetate–methanol (1:1, v/v) as developer and sulfuric acid guideline indication. The band at R_f 0.5 was extracted with 95% ethanol. Evaporation of the solvent yielded a colorless residue which was readily crystallized from methanol to yield 170 mg (80%) of **4**, mp 240–242°; the mixture melting point with **4** was undepressed.

Registry No.—**1**, 7139-63-1; **1** (F = Cl), 10353-00-1; **2**, 6736-63-6; **3**, 7057-54-7; **3** (F = Cl), 10385-54-3; **4**, 10353-03-4; **4** hydrochloride, 7111-40-2; 1-(trichloroacetamido-2-deoxy-D-glucopyranosyl)thymine, 10380-83-3.

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Anomeric Purine Nucleosides of the Furanose Form of 2-Amino-2-deoxy-D-ribose[1]

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Ethyl 2-deoxy-2-(2,4-dinitroanilino)-1-thio-α-D-ribofuranoside (**1**) was converted into the acetylated glycosyl chloride (**3**) which was coupled with chloromercuriadenine to give, when purified through the picrate, an essentially equal mixture of the anomeric forms of 9-(2-amino-2-deoxy-D-ribofuranosyl)adenine. Evidence was adduced that this crystalline mixture was a molecular compound. Anomeric separation was achieved by elution from a column of ion-exchange resin and each of the anomers was obtained in crystalline form.

This laboratory has been interested in devising and applying methods for the synthesis of nucleosides of 2-amino-2-deoxyaldoses, preferably in their furanose forms. In this communication we report the synthesis of the anomeric forms of 9-(2-amino-2-deoxy-D-ribofuranosyl)adenine. 2-Amino-2-deoxy-D-ribose was first synthesized in this laboratory[2] and we later reported a synthesis of this rare sugar from 2-amino-2-deoxy-D-glucose which involved the synthesis of ethyl 2-acetamidodi-*O*-acetyl-2-deoxy-1-thio-α-D-ribofuranoside as a step in the process; from this latter compound there was obtained the crystalline ethyl 2-deoxy-2-(2,4-dinitroanilino)-1-thio-α-D-ribofuranoside (**1**).[3] The 1-thiofuranoside **1** was acetylated to the syrupy diacetate **2**. Treatment of **2** with chlorine[4] in dichloromethane produced the glycosyl chloride **3** which was immediately brought into reaction with 6-acetamido-9-chloromercuripurine in refluxing toluene. The crude product from this reaction was purified by preparative thin layer chromatography on silica gel and the major product was converted into a crystalline picrate in order to *N*-deacetylate the adenine moiety according to the method of Burger and co-workers.[5] Removal of the *O*-acetyl and the *N*-(2,4-dinitroanilino) groups in **4** was effected with basic ion-exchange resin to obtain **5**. The nmr spectrum of **5**, measured in deuterium oxide at ambient temperature, revealed a pair of clearly defined doublets in the anomeric region of the spectrum. These doublets, of essentially equal areas, were at δ 6.05 ($J_{1,2}$ = 7.9 cps) and 6.51 ($J_{1,2}$ = 6.6 cps). Compound **5** was, therefore, a mixture of essentially equal amounts of each anomer. This was attested to also by the optical rotatory power of the mixture, $[\alpha]D$ +17 ± 3°, compared with the mean, +12 ± 2°, of that of the components, $[\alpha]D$ +90 ± 2° and −66 ± 2°, as later isolated. The optical rotatory data, obtained in methanol, were not precise owing to the low solubility of the compounds. Furthermore, the X-ray powder diffraction pattern of the anomeric mixture was distinctly not indicative of a crystalline mixture of essentially equal amounts of the anomers, when com-

(1) Preliminary communication: M. L. Wolfrom and M. W. Winkley, *Chem. Commun.*, 533 (1966). In this communication there was reported a successful separation of the β-D anomer **7** through isolative silica gel chromatography of the anomeric mixture **4** with subsequent removal of all blocking groups. This procedure was very laborious, did not lead to the isolation of the α-D anomer, and was abandoned in favor of the separation method herein described.

(2) M. L. Wolfrom, F. Shafizadeh, R. K. Armstrong, and T. M. Shen Han, *J. Am. Chem. Soc.*, **81**, 3716 (1959).

(3) M. L. Wolfrom and M. W. Winkley, *J. Org. Chem.*, **31**, 1169 (1966).

(4) M. L. Wolfrom and W. Groebke, *ibid.*, **28**, 2986 (1963).

(5) J. R. Parikh, M. E. Wolff, and A. Burger, *J. Am. Chem. Soc.*, **79**, 2778 (1957).