11.19 m, 8.85 vs (1), 7.76 s, 6.66 vs (3), 6.19 w, 5.50 m, 4.44 s, 37.4 w, 3.43 vs (2), 3.27 m, 3.01 s, and 2.88 m.

Anal. Calcd for $C_{17}H_{19}N_5O_{10}$: C, 45.03; H, 4.22; N, 15.45. Found: C, 44.77; H, 4.36; N, 15.34.

Attempts to remove the 2,4-dinitroanilino group in this compound with Dowex 1 (OH^-) resin encountered the same difficulties as were found in like experiments with the glycoside derivative **3**.

B.—Compound **4** (300 mg) was dissolved in methylene chloride (10 ml) and methanol (30 ml). The cooled solution was nearly saturated with hydrogen chloride and was then maintained at room temperature for 25 hr. Solvent removal under diminished pressure left a crystalline residue which was recrystallized from ethanol to yield 190 mg, mp and mmp 249–250°; infrared spectrum and X-ray powder diffraction data are identical with those of **5** prepared by method A above.

O → N Rearrangement[10] of the Glycoside Derivative 2 into the Nucleoside Derivative 4.—Compound **2** (200 mg) was refluxed with toluene (10 ml) and mercuric bromide (500 mg) for 20 hr. The dark mixture was diluted with methylene chloride (50 ml), washed with water, dried, and concentrated to dryness. The residue was purified by thick layer (1.25 mm) chromatography on silica gel G with ethyl acetate–benzene (1:1 v/v) as developer. The band of R_f 0.5 was eluted with ethyl acetate to give a lemon yellow, crystalline product which was recrystallized from acetone to yield 15 mg (7.5%), mp and mmp 219°; infrared spectrum and X-ray powder diffraction data are identical with those of **4**.

1-(2-Amino-2-deoxy-β-D-glucopyranosyl)thymine (6).—A mixture of 1-[2-deoxy-2-(2,4-dinitroanilino)-β-D-glucopyranoysl]thymine (**5**, 0.5 g), barium hydroxide octahydrate (3.0 g), and water (100 ml) was gently refluxed for 2 hr. After cooling, the mixture was treated with 1 *N* sulfuric acid to pH 3.0. After settling, the barium sulfate was filtered and the orange filtrate was extracted three times with ethyl acetate. The aqueous layer was stirred with barium carbonate (1.0 g) to pH 8.0 and filtered through Celite. The filtrate was evaporated to dryness; the residue was dissolved in dilute methanol (2 ml) and chromatographed on two silica gel G plates using ethyl acetate–methanol (1:1 v/v) as developer. The band of R_f 0.5 was extracted with 95% ethanol. Evaporation of the ethanol extract gave a colorless residue which was readily crystallized from methanol to yield 210 mg (80%): mp 240–242°; $[\alpha]^{22}D$ +6.0° (*c* 3.46, water); X-ray powder pattern identical with the sample prepared previously.[11]

Registry No.—2, 13388-99-3; **3**, 13389-00-9; **4**, 13421-40-4; **5**, 13428-21-2; **6**, 13389-01-0; methyl 2-deoxy-2-(2,4-dinitroanilino)-D-glucopyranoside, 13389-02-1.

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Optically Pure *N*-substituted Derivatives of Benzyl 2-Amino-2-deoxy-α- and -β-D-glucopyranoside[1-3]

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Treatment of 2-acetamido-2-deoxy-D-glucose with benzyl alcohol and hydrogen chloride at 70° gave both anomers of the benzyl glucopyranoside; they were separated as 3,4,6-tri-*O*-acetyl- or 3-*O*-acetyl-4,6-*O*-benzylidene derivatives. Treatment of both anomers of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-D-glucopyranoside with potassium hydroxide in ethanol at 110° gave the 2-amino derivatives. Treatment of these two derivatives with acid chlorides or with acids in the presence of a carbodiimide derivative gave, in both series, the *N*-benzyloxycarbonyl, *N*-phenoxycarbonyl, and *N*-chloroacetyl derivatives and, in the α series, the *N*-benzoyl and *N*-bromoacetyl derivatives. In addition, the *N*-*p*-methoxybenzylidene Schiff bases of both 2-amino derivatives were obtained.

The study of a new synthesis of muramic acid [2-amino-3-*O*-(D-1-carboxyethyl)-2-deoxy-D-glucose][4] and of the conversion of 2-amino-2-deoxy-D-glucose into 2-amino-2-deoxy-D-galactose[5] required the preparation of optically pure glycosides of 2-amino-2-deoxy-D-glucose. The benzyl glycosides were selected for this purpose because removal of the aglycone by hydrogenolysis required only mild conditions. In addition, the aromatic nucleus facilitates the solubility in organic solvent and crystallization. The benzyl glycosides may be detected by the extinction of the ultraviolet fluorescence of thin layer plates coated with silicic acid containing zinc silicate, thus omitting the need for spray reagents. Since derivatives of 2-amino-2-deoxy-D-glucose are present in natural products as *N*-acetyl derivatives, the glycosidation of 2-acetamido-2-deoxy-D-glucose (**1**) was reinvestigated. Although both anomers of benzyl 2-acetamido-2-deoxy-D-glucopyranoside have been previously synthesized,[6,7] the method[6] for obtaining the α-D anomer is not completely satisfactory. This procedure involves heating under reflux **1** in benzyl alcohol in the presence of hydrogen chloride, thus causing extensive degradation, and low yields. Although samples of both anomers with optical rotations approaching the highest value could occasionally be obtained after several recrystallizations, the method was not always reproducible. Moreover, no solvent system could be found to separate both anomers by thin layer chromatography in order to control their purity.

When 2-acetamido-2-deoxy-D-glucose (**1**) was heated at 70° with benzyl alcohol in the presence of hydrogen

(1) Amino Sugars LII. This is publication no. 435 of the Robert W. Lovett Memorial Group for the Study of Crippling Diseases, Harvard Medical School at the Massachusetts General Hospital, Boston, Mass.

(2) This investigation was supported by research grants from the National Institute of Allergy and Immunology, National Institutes of Health, U. S. Public Health Service (AI-04282 and 06692), and the National Science Foundation (GB-5031).

(3) A preliminary communication was presented at the Winter Meeting of the American Chemical Society, Phoenix, Ariz., Jan 1966: P. Gross and R. W. Jeanloz, Abstracts, C-032 and C-033.

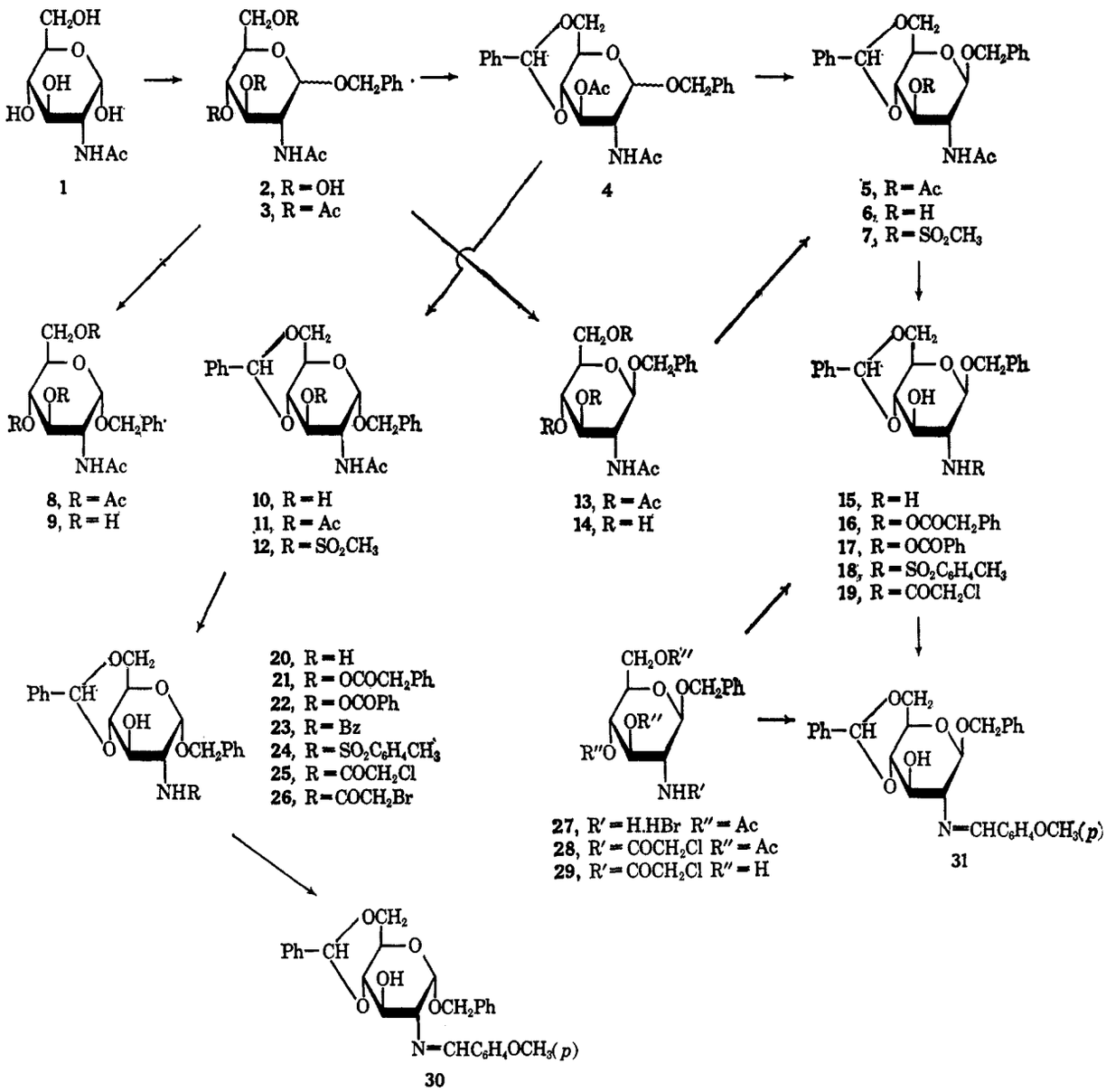
(4) P. H. Gross and R. W. Jeanloz, unpublished results.

(5) P. H. Gross, F. Du Bois, and R. W. Jeanloz, *Carbohydrate Res.*, **4**, 244 (1967).

(6) R. Kuhn, H. H. Baer, and A. Seeliger, *Ann.*, **611**, 236 (1958).

(7) A. Kuhn and W. Kirschenlohr, *Ber.*, **86**, 1331 (1953).

SCHEME I



chloride, equilibrium was reached after 1 to 2 hr. A crude mixture of benzyl 2-acetamido-2-deoxy-α- and -β-D-glucopyranoside (**2**) was precipitated in high yield by addition of 2-isopropoxypropane. It was recrystallized once and then either peracetylated into the 3,4,6-tri-*O*-acetyl derivatives (**3**) or condensed with benzaldehyde to give the 4,6-*O*-benzylidene derivatives, which were subsequently acetylated into the derivatives **4**. The fully substituted pairs of anomers could be resolved by crystallization, the separation of the 3,4,6-tri-*O*-acetyl derivatives (**3**) being the easiest.[8] The β-D anomer (**13**) was crystallized first from pyridine–toluene, and then the α-D anomer (**8**) was isolated from methanol–water (Scheme I). The anomers could be separated on thin layer plates of silica gel with a chloroform-methanol mixture. Thus, the purity of each compound could be easily determined.

De-*O*-acetylation of **8** with aqueous potassium hydroxide in dioxane gave the α-D anomer (**9**). From this product, the 4,6-*O*-benzylidene derivative (**10**), reported previously by Kuhn, Baer, and Seeliger,[6] was prepared. It showed the same constants as the product prepared by fractionation of **4**, followed by de-*O*-acetylation of **11**. A similar sequence of reactions was applied to the β-D anomers (**13** → **14** → **6**; **4** → **5** → **6**). The products obtained had constants similar to those reported by Kuhn and Kirschenlohr,[7] but different from those reported by Yoshimura, *et al.*[9]

Both anomers of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-D-glucopyranosides (**10** and **6**) were treated with methanesulfonyl chloride to give the 3-*O*-methanesulfonyl derivatives **12** and **7**, respectively. Treatment of both anomers of benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-D-glucopyranoside (**10** and **6**) with a concentrated solution of potassium hydroxide in ethanol at 110° gave benzyl 2-amino-4,6-*O*-benzylidene-2-deoxy-α- and -β-D-glucopyranoside (**20** and **15**), respectively. The good yields obtained show the high stability of the benzyl glycosides toward alkali. These results are in agreement with the observation that

(8) After this work has been completed and reported,[3] a similar separation of the 3,4,6-triacetate was published.[9]

(9) J. Yoshimura, M. Funabashi, S. Ishige, and T. Sato, *Bull. Chem. Soc. Japan*, **38**, 1760 (1966).

methyl glycosides have a far greater stability toward alkali than have phenyl glycosides. Both free bases (**20** and **15**) crystallized readily, thus showing the favorable promoting influence of the aromatic ring on the crystallization properties. Both bases were used as starting materials for the preparation of various optically pure *N* derivatives that could not be prepared by the conventional methods of glycosidation because of lability toward alkali or acid.

This approach was first tested for the *N*-acylation of **20** and **15** by treatment with an acid chloride. Thus, benzyloxycarbonyl chloride gave the known benzyl 2-[(benzyloxycarbonyl)amino]-4,6-*O*-benzylidene-2-deoxy-α- and -β-D-glucopyranoside (**21** and **16**).[10] Similarly, the *N*-phenoxycarbonyl (**22** and **17**) and *N*-*p*-tolylsulfonyl (**24** and **18**) derivatives in both the α-D and β-D series, respectively, and the *N*-benzoyl derivative (**23**) in the α-D series were obtained by treatment with the corresponding acid chloride.

N-acylation of the bases **20** and **15** with an acid in the presence of a carbodiimide derivative was then investigated. The 2-*N*-chloroacetyl derivatives (**25** and **19**) of the α-D and β-D series, respectively, and the 2-*N*-bromoacetyl derivative (**26**) of the α-D series were prepared. The structure of benzyl 4,6-*O*-benzylidene-2-[(chloroacetyl)amino]-2-deoxy-β-D-glycopyranoside (**19**) was ascertained by its synthesis from benzyl 2-[(chloroacetyl)amino]-2-deoxy-β-D-glucopyranoside hydrobromide (**27**)[10] *via* the intermediates **28** and **29**. In both *N*-acylation procedures, very little *O*-acetylation took place.

Finally, condensation of the bases **20** and **15** with *p*-methoxybenzaldehyde gave benzyl 4,6-*O*-benzylidene-2-deoxy-2-[(*p*-methoxybenzylidene)amino]-α-D-glucopyranoside (**30**) and its β-D anomer (**31**), respectively. Both compounds were very acid labile and were hydrolyzed on thin layer plates coated with silic acid.

Experimental Section

Melting points were taken on a hot stage, equipped with a microscope, and correspond to "corrected melting points." Rotations were determined with a polarimeter equipped with a Rudolph photoelectric polarimeter attachment, Model 200, or with the Perkin-Elmer No. 141 polarimeter. The chloroform used was A.R. grade and contained approximately 0.75% ethanol. The homogeneity of the compounds synthesized was determined by chromatography on plates covered with a thin layer of a 3:1 mixture of silica gel G (Merck) and silica gel GF (Merck). The plates were irrigated with chloroform containing a sufficient proportion of methanol to produce R_F values between 0.2 and 0.6. The compounds were detected with ultraviolet light or by spraying with concentrated sulfuric acid and heating for 20 min at 120°. Evaporations were carried out *in vacuo*, with an outside bath temperature kept below 45°. Amounts of volatile solvent smaller than 20 ml were evaporated under a stream of dry nitrogen. The microanalyses were performed by Dr. M. Manser, Zürich, Switzerland.

Benzyl 2-Acetamido-2-deoxy-α,β-D-glucopyranosides (2).—A mixture of 93.2 g (0.4 mole) of 2-acetamido-2-deoxy-α-D-glucopyranose (**1**) and 2000 ml of a 2% solution of hydrogen chloride in benzyl alcohol was stirred for 1.5 hr at 70°. The solution was neutralized with 350 g of lead carbonate and filtered. The product was precipitated from the filtrate by addition of 6000 ml of 2-isopropoxypropane. After being kept overnight at −10°, the suspension was filtered. The crystalline precipitate was suspended in 1000 ml of ether, stirred, filtered, washed with hexane, and dried. It was recrystallized once from ethanol, at −10°. The mother liquor was evaporated, and the syrupy residue was combined with the ether and the hexane washings to give additional material. The total yield, after drying for 20 hr at 70° *in vacuo*, was 100–110 g.

Benzyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside (13).—The mixture of anomers (**2**, 93.5 g, 0.3 mole), was dissolved in 300 ml of absolute pyridine and treated with 90 ml of acetic anhydride overnight at room temperature. The mixture was then concentrated to one-third of its volume and diluted with 1500 ml of hot toluene. It was seeded with pure benzyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-β-D-glucopyranoside and kept for 3 days at −10 to −15°. The crystals were filtered off, washed with cold toluene and hexane, and recrystallized from a mixture of methanol and water to give 13–16 g (10–12%), mp 170°, $[\alpha]^{25}D$ −43° (*c* 1, methanol). Kuhn and Kirschenlohr[7] reported mp 165–167°, $[\alpha]^{20}D$ −43.4° (methanol).

Benzyl 2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside (8).—The mother liquor of the preparation of **13** was evaporated, and ethanol was added and evaporated twice in order to remove all traces of toluene. The residue was recrystallized by dissolution in methanol and addition of water. After a short time, the crystalline material was collected and recrystallized from the same solvent mixture. Thin layer chromatography on silica gel F (Merck), with chloroform–methanol as solvent, showed only one spot. The α-D anomer moved faster than the β-D anomer. The yield was 90–100 g of elongated prisms (69–76%), mp 111°, $[\alpha]^{25}D$ +129° (*c* 1.11, pyridine), $[\alpha]^{20}D$ +103° (*c* 0.59, chloroform). Yoshimura, Funabashi, Ishige, and Sato[9] reported mp 108°, $[\alpha]^{20}D$ +120° (*c* 1.0, methanol).

Anal. Calcd for $C_{21}H_{27}NO_9$: C, 57.66; H, 6.22; N, 3.21; O, 32.92. Found: C, 57.52; H, 6.20; N, 3.21; O, 33.08.

Benzyl 2-Acetamido-2-deoxy-β-D-glucopyranoside (14).—Compound **13** (13.1 g, 0.03 mole) was dissolved in 350 ml of dioxane, and 200 ml of 0.5 *N* potassium hydroxide was slowly added. The homogeneous mixture was stirred for 5 hr at 25°, concentrated to one-third of its volume, and cooled to 0°. The pH was adjusted to 4 by addition of 20 ml of 5 *N* hydrochloric acid and the solution was concentrated to a small volume. The crystals were filtered off and washed with a small amount of water. The filtrate was evaporated to dryness and the residue was extracted with hot 2-propanol to give an additional crop of crystals. Both crops were combined and recrystallized from ethanol to give 8.5 g (92%) of prisms, mp 207–208°, $[\alpha]^{25}D$ −48° (*c* 1, water). Kuhn and Kirschenlohr[7] reported mp 205–206°, $[\alpha]^{20}D$ −48° (*c* 2, water).

Benzyl 2-Acetamido-2-deoxy-α-D-glucopyranoside (9).—Compound **8** (87.5 g, 0.2 mole) was dissolved in 1 l. of absolute methanol, and 90 ml of 0.5 *N* barium methoxide was added at −10°. The solution was kept overnight at −10°. The solution was neutralized by addition of Dowex-1 (H^+ form). The suspension was stirred for 1 hr at 0° and then filtered through a short column containing an equal amount of Dowex-1. The column was washed with 1000 ml of methanol and the eluents were evaporated. The residue was crystallized from absolute ethanol to give 57 g (92%) of prismatic needles, mp 187–189°, $[\alpha]^{23}D$ +170° (*c* 0.9, water) and +183° (*c* 1.1, pyridine). Kuhn, Baer, and Seeliger[6] reported mp 183–184°, $[\alpha]^{23}D$ +168.5° (c 0.9, water).

Benzyl 2-Acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (11).—To 6.2 g (0.02 mole) of the mixture of anomers of benzyl 2-acetamido-2-deoxy-D-glucopyranoside (**2**), dried *in vacuo* for 5 hr at 100°, was added 90 ml of benzaldehyde and 5 g of fused zinc chloride. The mixture was shaken overnight and then poured into a solution of 300 ml of 2-isoproxypropane, 200 ml of water, and 10 g of ammonium chloride. The mixture was stirred and the precipitate was filtered off, washed with water and with a small amount of 2-propanol, and then recrystallized from a mixture of dioxane and acetone to give 6 g, $[\alpha]^{25}D$ +75° (*c* 1, pyridine). The dry product was dissolved in 35 ml pyridine and 5 ml of acetic anhydride and kept overnight at room temperature. To the mixture was added 10 ml of dioxane, 15 ml of butanone, and 180 ml of toluene. After being kept for 10 hr at room temperature and for 30 hr to 0°, the crystalline material was filtered off to give 2.1 g, mp 211–215°, $[\alpha]^{25}D$ −20° (*c* 0.7, pyridine). The filtrate was heated to 40° and 400 ml of pentane were added. The first brownish precipitate, which appeared upon seeding with **11**, was filtered off. After being kept for 1 hr at room temperature, the solution deposited fine, cottonlike threads. The suspension was reheated twice to 45°. After 4 hr at room temperature and 60 hr at −5°, the product was filtered off, washed with toluene and pentane, and recrystallized from ethanol to give 4 g of fine

(10) G. Fodor and L. Ötvös, *Ann.*, **604**, 29 (1957).

TABLE I

N DERIVATIVES OF BENZYL-2-AMINO-4,6-*O*-BENZYLIDENE-2-DEOXY-α- AND -β-D-GLUCOPYRANOSIDE (20 AND 15) [PREPARED BY TREATMENT WITH AN ACYL CHLORIDE

Compound	Yield, %	Solvents of crystallization	Mp, °C	$[\alpha]^{25}D$, deg[a]	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % O	Found, % C	Found, % H	Found, % N	Found, % O
α-D-Glucopyranoside												
2-(Benzyloxycarbonyl)amino (21)[b]	67	Tetrahydrofuran–hexane	229–231	+84	68.42	5.95	2.85	22.79	68.15	6.19	2.90	22.70
2-(Phenoxycarbonyl)amino (22)	83	Tetrahydrofuran–2-isopropoxypropane	184–185	+72	67.91	5.70	2.93	23.46	67.92	5.87	2.87	23.40
2-Benzamido (23)[c]	73	Dioxane–ether	218–220	+115	70.27	5.90	3.09	20.80	69.66	6.10	3.03	21.27
β-D-Glucopyranoside												
2-(Benzyloxycarbonyl)amino (16)[d]	60	Pyridine–1,2-dimethoxyethane	239–240	−82	68.42	5.95	2.85	22.79	68.49	5.96	2.92	22.74
2-(Phenoxycarbonyl) amino (17)	48	Dioxane–butanone–ether	201–202	−88	67.91	5.70	2.93	23.46	67.65	5.65	2.90	23.53

[a] In pyridine, *c* 1. [b] P. H. Gross and H. K. Zimmerman [*Ann.*, **674**, 211 (1964)] reported mp 225–226°, $[\alpha]^{25}D$ +79° (*c* 1, pyridine). [c] The product forms a very stable hydrate [K. Miyai, M.S. Thesis, University of the Pacific, Stockton, Calif. (1965)], and it was difficult to remove the water of crystallization. [d] Gross and Zimmerman (footnote *b*) reported mp 232–234°, $[\alpha]^{25}D$ −82° (*c* 1, pyridine).

needles, mp 198–200°, $[\alpha]^{25}D$ +82° (*c* 1, pyridine). The product was homogeneous on thin layer plates of silica gel with chloroform containing 3% ethanol.

Anal. Calcd for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.16; N, 3.18; O, 25.37. Found: C, 65.24; H, 6.22; N, 3.26; O, 25.25.

The same compound was obtained by acetylation, with acetic anhydride and pyridine, of pure benzyl 2-acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**10**).

Benzyl 2-Acetamido-3-*O*-acetyl-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**5**).—The fraction, rich in β-D anomer (2.1 g, mp 211–215°), of the preceding preparation was recrystallized from a mixture of dioxane and toluene (1:1) until the product showed a homogeneous spot on thin layer plates of silica gel with chloroform containing 3% ethanol. The final yield was 0.7 g of prismatic needles, mp 273–274°, $[\alpha]^{25}D$ −111° (*c* 1, pyridine). Yoshimura, Funabashi, Ishige, and Sato[9] reported mp 258–259° dec, $[\alpha]^{20}_{578}$ −56° (*c* 0.30, pyridine).

Anal. Calcd for $C_{24}H_{27}NO_7$: C, 65.29; H, 6.17; N, 3.18; O, 25.37. Found: C, 65.21; H, 6.12; N, 3.07; O, 25.28.

Acetylation of pure compound **6** with acetic anhydride and pyridine gave the same compound.

Benzyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**6**) **from 14.**—Compound **14** (6.2 g, 0.02 mole) was dried *in vacuo* for 5 hr at 100° and then added to a mixture of 5 g of zinc chloride, 100 ml of benzaldehyde, and 60 ml of ether. The mixture was shaken overnight at room temperature. After addition of a few milliliters of ammonium chloride to prevent precipitation of the zinc hydroxide, 2-isopropoxypropane and ice were added. The three-phase system was filtered, and the precipitate was washed with water and with a small amount of 2-propanol. Recrystallization from dioxane gave 5.9 g (74%) of prismatic needles, mp 270–271°, $[\alpha]^{25}D$ −89° (*c* 0.8, pyridine). Yoshimura, Funabashi, Ishige, and Sato[9] reported mp 260–261° dec $[\alpha]^{20}_{578}$ −40° (*c* 0.50, pyridine).

Anal. Calcd for $C_{22}H_{25}NO_6$: C, 66.16; H, 6.51; N, 3.51; O, 24.03. Found: C, 66.04; H, 6.36; N, 3.42; O, 24.08.

From 5.—To a solution of 440 mg of **5** (1 mmole) in 2 ml of pyridine were added 10 ml of dioxane and 5.2 ml of 0.2 *N* sodium hydroxide. The solution was stirred for 4 hr at 40° and then evaporated. The residue was stirred with 100 ml of water for 15 hr, filtered off, and washed with water. Recrystallization from a mixture of dioxane, 2-butanone, and hexane gave 360 mg (90%), mp 267°, $[\alpha]^{25}D$ −89° (*c* 0.8, pyridine). The product showed no depression of melting point on admixture with the product described above.

Benzyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**10**) **from 9.**—Compound **9** (62 g, 0.2 mole) was dried *in vacuo* for 5 hr at 100° and then dissolved in a mixture of 50 g of zinc chloride and 900 ml of benzaldehyde. The solution was kept overnight at room temperature. After addition of 3000 ml of 2-isopropoxypropane with vigorous stirring, the solution was kept at −15°. After 3 hr, most of the compound had precipitated and it was filtered off. The filtrate was shaken with ice–water, whereupon a second crop precipitated. It was filtered and washed with 2-propanol. Both crops were combined and recrystallized from a mixture of dioxane and 2-propanol to give 71 g (89%) of elongated prisms, mp 263–264°, $[\alpha]^{26}D$ +120° (*c* 1, pyridine). Kuhn, Baer, and Seeliger[6] reported mp 262°, $[\alpha]^{23}D$ +114° (*c* 1, pyridine).

From 11.—Deacetylation of compound **11**, as described for the preparation of **6** from **5**, gave compound **10** in 89% yield, having identical melting point and optical rotation with those of the compound described above.

Benzyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methylsulfonyl-α-D-glucopyranoside (**12**).—A solution of 0.4 g (1 mole) of **10** in 3 ml of pyridine was cooled to −10° with the exclusion of moisture, and 0.3 ml of freshly distilled methanesulfonyl chloride was slowly added at −10°. After being kept for 30 hr at 0°, the mixture was poured onto ice and further diluted with water. The precipitate was filtered off, washed with water, and dried. It was recrystallized from a mixture of dioxane, 2-propanol, and 2-isopropoxypropane to give 262 mg (55%) of needles, mp 198–199° dec, $[\alpha]^{25}D$ +76° (*c* 1, pyridine).

Anal. Calcd for $C_{23}H_{27}NO_8S$: C, 57.84; H, 5.70; N, 3.00; S, 6.71. Found: C, 57.60; H, 5.89; N, 2.86; S, 6.69.

Benzyl 2-Acetamido-4,6-*O*-benzylidene-2-deoxy-3-*O*-methylsulfonyl-β-D-glucopyranoside (**7**).—This compound was prepared from **6** by a procedure similar to that used for the preparation of **12**. After recrystallization from a mixture of dioxane and 2-propanol, 238 mg (50%) of fine needles were obtained, mp 195° dec, $[\alpha]^{25}D$ −80° (*c* 0.5, pyridine).

Anal. Calcd for $C_{23}H_{27}NO_8$: C, 57.84; H, 5.70; N, 3.00; S, 6.71. Found: C, 57.77; H, 5.79; N, 2.93; S, 6.83.

Benzyl 2-Amino-4,6-*O*-benzylidene-2-deoxy-α-D-glucopyranoside (**20**).—A solution of 16 g (0.04 mole) of **10** in a hot mixture of 60 g of potassium hydroxide (86%) and 200 ml of ethanol (96%) was heated under reflux for 5–6 hr at 120°. The hot solution was poured with caution into 1500 ml of hot water. After being cooled to room temperature, the crystalline mass was kept overnight at −10°. The crystals were filtered off and washed with water. After dissolution in methanol and treatment of the solution with charcoal, a compound containing methanol of crystallization was obtained. A second crystallization from a mixture of toluene and heptane yielded 13 g (91%) of fine needles, mp 173–174°, $[\alpha]^{25}D$ +90° (*c* 1, pyridine).

Anal. Calcd for $C_{20}H_{23}NO_5$: C, 67.20; H, 6.49; N, 3.92; O, 22.39. Found: C, 67.11; H, 6.40; N, 3.95; O, 22.38.

Benzyl 2-Amino-4,6-*O*-benzylidene-2-deoxy-β-D-glucopyranoside (**15**).—This compound was prepared by a procedure identical with that used for the preparation of the α-D anomer. After recrystallization from methanol, 11.5 g (80%) of prismatic needles were obtained, mp 145–146°, $[\alpha]^{25}D$ −131° (*c* 1, pyridine).

Anal. Calcd for $C_{20}H_{23}NO_5$: C, 67.20; H, 6.49; N, 3.92; O, 22.39. Found: C, 67.28; H, 6.48; N, 3.80; O, 22.27.

Treatment of Benzyl 2-Amino-4,6-*O*-benzylidene-2-deoxy-α- and -β-D-glucopyranoside (**20 and 15**) **with Acid Chlorides.**—To a cooled solution of 1 mole of **15** or **20** in 100 ml of a mixture of chloroform and a solution of 3% potassium hydrogen carbonate (1:1) was added, with stirring, 1.1 mole of acid chloride. The mixture was stirred vigorously overnight at 0°. The organic layer was separated, washed once with water, then with 5% citric acid, and again with water, dried with sodium sulfate, and evaporated. The compounds prepared with this procedure are reported in Table I.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-[(*p*-tolylsulfonyl)amino]-α-D-glucopyranoside (**24**).—To a cold solution of 357 mg (1 mmole) of **20** was added, with stirring, 100 ml of pure chloroform, 50 ml of cold 3% potassium hydrogen carbonate solution, and 0.23 g (1 mmole) of *p*-toluenesulfonyl chloride. The mixture was stirred vigorously overnight at 20°. Pyridine (0.5 ml) was added and stirring continued for 1 hr. The organic layer was separated and was washed once with water, twice with 5% citric acid, twice with sodium hydrogen carbonate, and finally with water. The solution was dried with sodium sulfate and evaporated. The residue was crystallized from 2-propanol, after treatment of the solution with charcoal, to give 390 mg

(76%) of small prisms, mp 192–194°, $[\alpha]^{25}D$ +51° (*c* 1, pyridine).

Anal. Calcd for $C_{27}H_{29}NO_7S$: C, 63.39; H, 5.71; N, 2.74; O, 21.88; S, 6.27. Found: C, 63.44; H, 5.72; N, 2.75; O, 21.96; S, 6.15.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-[(*p*-tolylfonyl)amino]-β-D-glucopyranoside (18).—The procedure was identical with that used for the preparation of **24**. Crystallization from ethanol and then from a mixture of acetone, ether, and pentane gave fine needles (61% yield), mp 215–216°, $[\alpha]^{25}D$ −65° (*c* 1, pyridine).

Anal. Calcd for $C_{27}H_{29}NO_7S$: C, 63.39; H, 5.71; N, 2.74; O, 21.88; S, 6.27. Found: C, 63.44; H, 5.77; N, 2.82; O, 21.98; S, 6.14.

Benzyl 4,6-*O*-Benzylidene-2-[(chloroacetyl)amino]-2-deoxy-α-D-glucopyranoside (25).—A solution of **21** (375 mg, 1 mmole) in 4 ml of pure chloroform was mixed, at −10° under exclusion of moisture, with a solution of 100 mg (1.05 mmoles) of chloroacetic acid and 450 mg (1.1 mmoles) of 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-*p*-toluenesulfonate (Aldrich Co.) in 4 ml of pure chloroform. The mixture was kept overnight at −5° and 3 hr at room temperature in a closed vessel and then poured on ice (50 g). The suspension was stirred for 1 hr, 50 ml of hexane was added, and the precipitate was filtered and washed with water and with 2-propanol. Crystallization from a mixture of dioxane and acetone gave 370 mg (85%) of needles, mp 255–256°, $[\alpha]^{25}D$ +110° (*c* 1, pyridine).

Anal. Calcd for $C_{22}H_{24}NO_6Cl$: C, 60.90; H, 5.57; N, 3.23; O, 22.13; Cl, 8.17. Found: C, 61.05; H, 5.52; N, 3.17; O, 22.00; Cl, 8.02.

Benzyl 4,6-*O*-Benzylidene-2-[(bromoacetyl)amino]-2-deoxy-α-D-glucopyranoside (26).—This product was obtained from **20** and bromoacetic acid by following a procedure identical with that described for the preparation of **26**. Crystallization from a mixture of dioxane and 2-propanol gave needles (80% yield), mp 235–236°, $[\alpha]^{27}D$ +110° (*c* 1, dioxane).

Anal. Calcd for $C_{22}H_{24}NO_6Br$: C, 55.24; H, 5.06; N, 2.93; O, 20.07; Br, 16.70. Found: C, 55.17; H, 5.09; N, 3.03; O, 20.02; Br, 16.73.

Benzyl 3,4,6-Tri-*O*-acetyl-2-[(chloracetyl)amino]-2-deoxy-β-D-glucopyranoside (28).—Ethanol-free chloroform (200 ml) was stirred with 100 ml of 10% potassium hydrogen carbonate solution for 1 hr at 0°. Benzyl 3,4,6-tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranoside hydrobromide[10] (**27**, 4.8 g, 0.01 mole) and 1.5 ml of chloroacetyl chloride were added and vigorous stirring was continued for 5 hr at 0°. The chloroform layer was separated, washed with water, and evaporated after addition of 50 ml of benzene. The dry residue gave, after crystallization from ethanol, 4.2 g (88%) of plates, mp 186–187°, $[\alpha]^{25}D$ −8° (*c* 1, pyridine).

Anal. Calcd for $C_{21}H_{26}NO_9Cl$: C, 53.44; H, 5.55; N, 2.97; O, 30.52; Cl, 7.51. Found: C, 53.61; H, 6.07; N, 2.80; O, 30.32; Cl, 7.67.

Benzyl 2-Chloroacetamido-2-deoxy-β-D-glucopyranoside (29).—To a solution of 4.7 g (0.01 mole) of **28** in 100 ml of dioxane was added 20 ml of water, followed by the dropwise addition, with stirring, of 2.2 g of potassium hydroxide (85%) in 50 ml of water in 30 min at 0°. After being stirred for 2 hr at 0° and for 2 hr at room temperature, the clear solution was evaporated twice to dryness after addition of water. After addition of 50 ml of water to the residue, the suspension was shaken and filtered. The filtrate was evaporated to a small volume and filtered. Both precipitates were combined and dissolved in 180 ml of a hot mixture of dioxane and ethanol (1:1). Addition of 50 ml of ether gave 3.3 g (95%) of fine needles, mp 211–212°, $[\alpha]^{25}D$ −42° (*c* 1, pyridine).

Anal. Calcd for $C_{15}H_{20}NO_6Cl$: C, 52.10; H, 5.83; N, 4.05; O, 27.77; Cl, 10.26. Found: C, 52.21; H, 5.66; N, 4.00; O, 27.64; Cl, 10.31.

Benzyl 4,6-*O*-Benzylidene-2-[(chloroacetyl)amino]-2-deoxy-β-D-glucopyranoside (19) from 15.—This product was obtained by treatment of **15** with chloroacetic acid; the procedure was identical with that followed for the preparation of **25**. Crystallization from a mixture of dioxane and toluene gave needles (82% yield), mp 261–262°, $[\alpha]^{25}D$ −89° (*c* 1, pyridine).

From 29.—A solution of 1.4 g (4 mmoles) of **29** in a mixture of 2 g of zinc chloride and 60 ml of benzaldehyde was shaken vigorously overnight. After addition of 300 ml of ether, the mixture was kept for 20 hr at −10°. The crystalline precipitate was filtered off, washed with ether, and recrystallized from dioxane to give 1.4 g (81%), mp 261–262°, $[\alpha]^{25}D$ −89° (*c* 1, pyridine). The product showed no depression of melting point on admixture with product **19** described above.

Anal. Calcd for $C_{22}H_{24}NO_6Cl$: C, 60.90; H, 5.51; N, 3.23; O, 22.13; Cl, 8.17. Found: C, 60.82; H, 5.58; N, 3.30; O, 22.22; Cl, 8.23.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-[(*p*-methoxybenzylidene)-imino]-α-D-glucopyranoside (30).—A solution of 1.70 g of **20** (3 mmoles) and 0.7 ml of freshly distilled *p*-methoxybenzaldehyde in 20 ml of 0.15 *N* sodium methoxide in methanol was heated under reflux for 10 min. After addition of 50 g of ice, the mixture was shaken for 1 hr and then kept overnight at −10°. After filtration, the crystalline product was recrystallized from 2-propanol to give 1.25 g (88%) of prismatic needles, mp 180–181°, $[\alpha]^{25}D$ +69° (*c* 1, pyridine).

Anal. Calcd for $C_{28}H_{29}NO_6$: C, 70.72; H, 6.15; N, 2.95; O, 20.19. Found: C, 70.42; H, 6.67; N, 3.19; O, 20.34.

Benzyl 4,6-*O*-Benzylidene-2-deoxy-2-[(*p*-methoxybenzylidene)-imino]-β-D-glucopyranoside (31).—This compound was prepared from **15** following a procedure similar to that used in the preparation of **30**. Recrystallization from a mixture of ethanol and 2-isopropoxypropane gave needles (74% yield), mp 178–179°, $[\alpha]^{25}D$ −119° (*c* 1, pyridine).

Anal. Calcd for $C_{28}H_{29}NO_6$: C, 70.72; H, 6.15; N, 2.95; O, 20.19. Found: C, 70.64; H, 6.21; N, 2.99; O, 20.29.

Registry No.—**2**, 3055-51-4; **5**, 13320-00-8; **6**, 13343-61-8; **7**, 13395-56-7; **8**, 13318-46-2; **9**, 13343-62-9; **10**, 13343-63-0; **11**, 13343-64-1; **12**, 13343-65-2; **13**, 13343-66-3; **14**, 13343-67-4; **15**, 13347-79-0; **16**, 2864-31-5; **17**, 13347-81-4; **18**, 13347-82-5; **19**, 13318-86-0; **20**, 13347-83-6; **21**, 2862-11-5; **22**, 13347-85-8; **23**, 13347-86-9; **24**, 13347-87-0; **25**, 13347-88-1; **26**, 13347-89-2; **28**, 13347-90-5; **29**, 13318-87-1; **30**, 13347-91-6; **31**, 13347-92-7.

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