lized from a small amount of acetone, 530 mg (46%), mp 191–193°, $[\alpha]_D$ +7.2° (*c* 1.3, pyridine).

Anal. Calcd for $C_{14}H_{18}O_7N_3I$: C, 35.99; H, 3.88; N, 8.99. Found: C, 35.93; H, 3.87; N, 8.92.

(1-(3-Acetamido-2-*O*-acetyl-3,6-dideoxy-β-D-*xylo*-hex-5-eno-pyranosyl)uracil (34).—A mixture of compound **33b** (708 mg) and silver fluoride (1.83 g) in pyridine (20 ml) was shaken for 3 hr and filtered. The filtrate was evaporated to dryness and the residue was dissolved in methanol (100 ml). A small amount of insoluble material was removed by filtration. Hydrogen sulfide was bubbled into the methanol solution to precipitate silver ion. The dark mixture was filtered through a Celite bed and the filtrate was concentrated to dryness. The residue was dissolved in a small amount of methanol and applied to two silica gel PF_{254} plates (20 × 20 cm, 2 mm). The plates were developed with chloroform–methanol (4:1). The main band was removed and extracted with acetone–methanol (4:1) and concentrated to dryness. The residue was crystallized from acetone, 297 mg, mp 145–146°, $[\alpha]_D$ −63° (*c* 1.2, pyridine).

Anal. Calcd for $C_{14}H_{17}O_7N_3$: C, 49.56; H, 5.05; N, 12.38. Found: C, 49.40; H, 5.07; N, 12.32.

Registry No.—**4**, 4338-36-7; **5**, 32254-26-5; **7**, 32254-27-6; **8**, 32254-28-7; **9**, 32254-29-8; **10**, 32254-30-1; **11**, 32254-31-2; **12**, 32254-32-3; **13**, 32254-33-4; **14**, 32254-34-5; **15**, 32254-35-6; **16**, 32254-36-7; **17**, 32367-45-6; **18**, 32254-37-8; **19**, 32254-38-9; **20**, 32254-39-0; **21**, 32304-21-5; **22**, 32254-40-3; **23**, 32254-41-4; **24**, 32254-42-5; **25**, 32254-43-6; **26**, 32254-44-7; **30**, 32304-22-6; **32**, 32254-45-8; **33a**, 32254-46-9; **33b**, 32254-47-0; **34**, 32254-48-1.

Nucleosides. LXXIII. Ribosyl Analogs of Chloramphenicol[1]

R. S. KLEIN, M. P. KOTICK, K. A. WATANABE, AND J. J. FOX*

Division of Organic Chemistry, Sloan-Kettering Institute for Cancer Research, Sloan-Kettering Division, Graduate School of Medical Sciences, Cornell University, New York, New York 10021

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The synthesis of *p*-(5-dichloroacetamido-5-deoxy-β-D-ribofuranosyl)nitrobenzene (**20b**) and *p*-(β-D-ribofuranosyl)nitrobenzene 5-phosphate (**12**) from β-D-ribofuranosylbenzene (**6**) are described. Precursor **6** was obtained by condensation of diphenylcadmium with tri-*O*-benzoyl-D-ribofuranosyl chloride (**2**) and the β configuration of **6** was established by periodate and nmr studies. Acetylation and nitration of **6** afforded a mixture of the *o*- and *p*-nitro isomers **10a** and **10b** which was resolved after deacetylation to *o*- and *p*-(β-D-ribofuranosyl)-nitrobenzene (**11a** and **11b**). The para isomer **11b** was acetonated, phosphorylated, and deisopropylidenated to give the 5-phosphate **12**. Acetonation of **6** followed by mesylation, azidation, and reduction afforded the amine **16**. Dichloroacetylation of **16** followed by deisopropylidenation gave (5-dichloroacetamido-5-deoxy-β-D-ribofuranosyl)benzene (**18**) which was converted in two steps to the *o*- and *p*-nitro derivatives **20a** and **20b**.

It was reported[2] that the antibiotic chloramphenicol (a protein synthesis inhibitor) adopts a "curled" conformation (Figure 1) in solution and, as such, resembles the nucleotide, uridine 5′-phosphate. It has been suggested further that the mode of action of this antibiotic may be related to this conformation.[2,3] If this hypothesis is valid, one might expect that *p*-(5-dichloroacetamido-5-deoxy-β-D-ribosyl)nitrobenzene(**20b**) or *p*-(β-D-ribofuranosyl)nitrobenzene 5-phosphate (**12**) may also be inhibitors of protein synthesis. This paper deals with the synthesis of **12** and **20** as part of our program directed toward the preparation of nucleoside analogs of potential biochemical significance.

The glucopyranosylbenzene derivative (**1**, Figure 2) has been prepared by Hurd and Bonner[4] by condensation of poly-*O*-acetyl-α-D-glucosyl chloride with phenylmagnesium bromide. Zhdanov, *et al.*,[5] have prepared ribopyranosylbenzene analogously by using the corresponding ribopyranosyl chloride. The β configuration was assumed for **1**[6] solely by analogy of optical rotation data with a related derivative of the xylo series. With diphenylcadmium as the condensing agent, Hurd and Holysz[7] also obtained compound **1**, albeit in lower yield. Mertes, *et al.*,[8] reacted bis(2,6-dibenzyloxypyridyl-3)cadmium with tri-*O*-benzoyl-D-ribofuranosyl chloride (**2**) and obtained the corresponding 3-ribosylpyridine derivative. Attempts in our laboratory to apply the condensation of phenylmagnesium bromide with **2** in order to prepare **6** were unsuccessful. However, the use of diphenylcadmium with **2** in refluxing benzene solution afforded the "nucleoside" **3** in 20% yield. The major product of this reaction (**2** → **3**) was the sugar ketal **4** which, after saponification with methoxide, afforded the crystalline ketal **5**. Proof of the structure of **5** as 1,2-*O*-diphenylmethylidene-α-D-ribofuranose was obtained by elemental analyses, by nmr measurements, and by acid hydrolysis to benzophenone and ribose. Ketals analogous to **5** had been reported[7] from similar type reactions. Debenzoylation of **3** with sodium methoxide in methanol yielded the unblocked nucleoside **6**.

The β configuration for **3** and **6** was established as follows. Periodate oxidation of **6** afforded the dialdehyde **7**, which was reduced with sodium borohydride to the trialcohol **8**. Deacetylation of **1** followed by a similar oxidation and reduction afforded a trialcohol which was identical (melting point, mixture melting point, optical rotation) with compound **8** obtained from **3**. The nmr spectrum of **1** in pyridine-d_5 and of its deacetylated derivative in DMSO-d_6 all show large splittings for H-1–H-2 ($J \cong 10$ Hz) which establishes definitively the β configuration for **1** and, thereby, the β configuration for **3** and **6**.

Nitration of the tri-*O*-acetate **9** of **6** was accomplished

(1) This investigation was supported in part by funds from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA 08748). Paper LXXII: *Carbohyd. Research*, in press.

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(4) C. D. Hurd and W. A. Bonner, *J. Amer. Chem. Soc.*, **67**, 1972 (1945).

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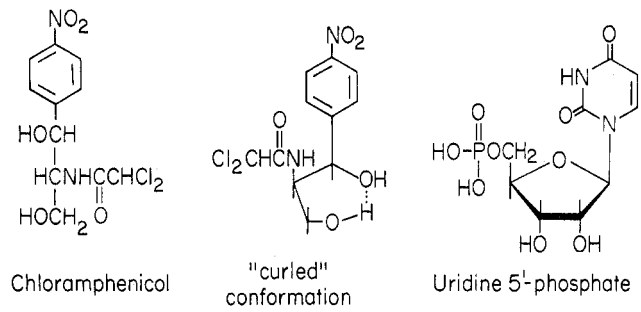

Figure 1.

The synthesis of the 5-dichloroacetamido-5-deoxy-β-D-ribosylnitrobenzenes (**20**) was achieved from **6** by the following route. Isopropylidenation of **6** to **13** followed by mesylation gave the 5-mesylate **14**, which was treated with sodium azide in DMF to afford the 5-azido derivative **15**. Reduction of the latter derivative with borohydride in refluxing 2-propanol[11] gave the 5-amino analog **16** which, after acylation, afforded the 5-dichloroacetamido derivative **17** as an analytically pure syrup in 65% overall yield from **6**. Deacetonation of **17** gave an almost quantitative

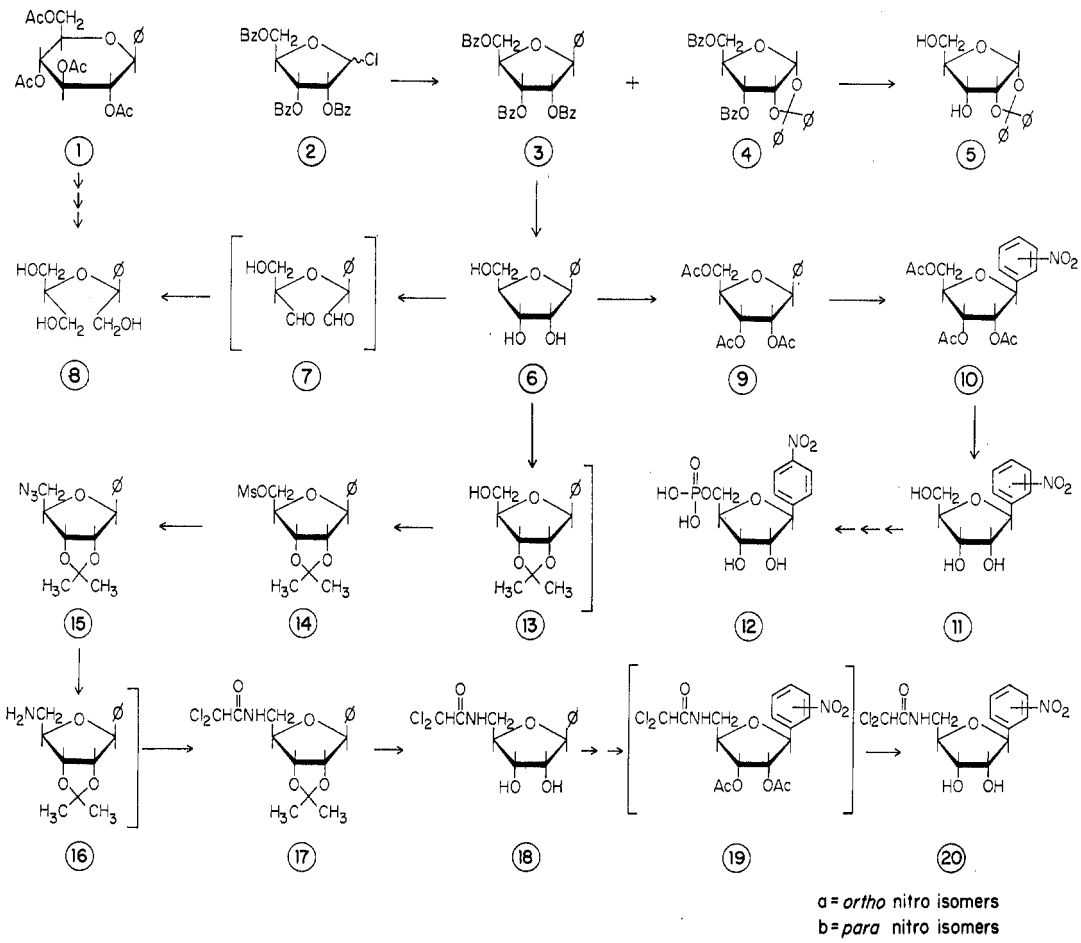

Figure 2.

in an acetic anhydride–cupric nitrate mixture[9] to give both the ortho and para isomers (**10**) in approximately equal amounts in a combined yield of 58%. Attempts to obtain separation of this mixture by tlc were unsuccessful. Even after deacetylation to **11**, the isomeric mixture exhibited similar migration properties on tlc in a variety of solvent systems. It was found that fractional crystallization of the mixture (**11**) could be achieved from ethyl acetate, whereby each crop was characterized by its ir and nmr spectrum. Isopropylidenation of the *p*-nitro isomer **11b** followed by phosphorylation with 2-cyanoethyl phosphate and dicyclohexylcarbodiimide[10] and removal of the protecting groups gave the "nucleotide" **12**, which was isolated as the calcium salt.

(9) J. M. Craig and W. A. Bonner, *J. Amer. Chem. Soc.*, **72**, 4808 (1950); A. Gerecs and M. Windholz, *Acta Chim. Acad. Sci. Hung.*, **18**, 231 (1957) [*Chem. Abstr.*, **52**, 11778 (1958)].

(10) P. T. Gilham and G. M. Tener, *Chem. Ind. (London)*, 542 (1959).

yield of crystalline **18**, which was acetylated and then nitrated with acetic anhydride–cupric nitrate reagent[9] to a mixture of ortho and para isomers in fair yield. Separation of these isomers was accomplished by use of thick layer chromatography on alumina. The dissimilar migratory properties of these isomers (**19**) are probably related to the susceptibility of the ortho isomer to intramolecular hydrogen bonding between the nitro and amido groups. Deacetylation of each of the isomers (**19**) was performed under mild conditions with triethylamine in methanol. Each of the isomers (**20**) was obtained in crystalline form.

A more direct route to **20b** was attempted from **11b**, which involved acetonation, mesylation, and displacement of the 5-mesylate with ammonia. Though this approach was satisfactory for the ortho series, the para 5-mesylate isomer underwent extensive

(11) H. Ohrui and S. Emoto, *Agr. Biol. Chem. (Tokyo)*, **32**, 1371 (1968).

decomposition in the presence of ammonia. This approach to **20b** was therefore abandoned.

The ribofuranosylnitrobenzenes described herein have been submitted to another laboratory for biochemical evaluation. The results of these studies, when completed, will be reported elsewhere.

Experimental Section

General Procedure.—Melting points were determined on a Thomas–Hoover apparatus (capillary method) and are uncorrected. The nmr spectra were measured on a Varian A-60 spectrometer using TMS as internal standard. Chemical shifts are reported in parts per million (δ) and signals are described as s (singlet), d (doublet), t (triplet), q (quartet), or m (complex multiplet). Values given for coupling constants are first order. Thin layer chromatography was performed on silica gel GF_{254} (Merck); spots were detected by uv absorbance or by spraying with 20% v/v sulfuric acid–ethanol and heating. Column chromatography was performed[12] over silica gel G under positive pressure. Microanalyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. All evaporations were carried out *in vacuo*.

β-D-Ribofuranosylbenzene (6) and 1,2-*O*-Diphenylmethylidene-α-D-ribofuranose (5).—To a suspension of 36.7 g (0.200 mol) of finely powdered $CdCl_2$ (previously dried for 1 hr at 100°) in 1 l. of anhydrous tetrahydrofuran was added 133 ml of 3.13 *M* phenylmagnesium bromide in ether (Alfa Inorganics, Ventron). The gray suspension was heated to reflux and 300 ml of solvent were distilled off. To the resulting clear mixture was added a solution of 2,3,5-tri-*O*-benzoyl-D-ribosyl chloride (**2**) (from 0.2 mol of 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribose) in 500 ml of benzene. After addition of another 500 ml of benzene the solution was heated for 1 additional hr as 700 ml were distilled off. After cooling, the mixture was poured into 0.8 l. of an ice–water mixture and enough acetic acid was added to dissolve all precipitated solid (pH of aqueous layer was ~7.0). After separation, the aqueous layer was washed with more benzene and the organic extracts were washed with aqueous $NaHCO_3$ and H_2O, dried over Na_2SO_4, and evaporated to dryness. The residue was dissolved in 1 l. of warm methanol containing 1 mmol of NaOMe. After complete reaction the solution was neutralized with Dowex AG 50 (H^+), filtered, and evaporated to dryness. The residue was partitioned between 500 ml each of water and ether and each layer was back-extracted again. The ether extracts were pooled and dried over Na_2SO_4. Evaporation to dryness and crystallization of the residue from benzene–petroleum ether (bp 30–60°) gave 35 g (55%) of crude **5**, which was recrystallized from the same solvent pair to give analytically pure material: mp 139–140°; nmr ($CDCl_3$) δ 7.20–7.60 (10, m, 2 C_6H_5), 5.84 (1, d, H-1), 4.53 (1, q, H-2), 4.15–3.50 (4, m, H-3, H-4, and H-5), 2.20 (2, s, OH's), $J_{1,2} = 4$, $J_{2,3} = 4$ Hz.

Anal. Calcd for $C_{18}H_{18}O_5$: C, 68.78; H, 5.77. Found: C, 68.82; H, 5.77.

The aqueous extract was evaporated to give a semicrystalline residue which crystallized from ethyl acetate–benzene to afford 7.8 g of crude **6**. Column chromatography of the mother liquor on 400 g of silica gel G (7.5:1, chloroform–methanol) afforded another 2.6 g of **6** (25% total yield). Recrystallization from ethyl acetate–benzene gave the pure product: mp 121–122°; nmr (DMSO-d_6) δ 7.40 (5, m, C_6H_5), 4.75–5.02 (3, m, OH's), 4.64 (1, d, H-1), 3.55–4.05 (5, m, H-2, H-3, H-4, and H-5), $J_{1,2} = 6.5$ Hz.

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.45; H, 6.51.

2-[2-(1,3-Dihydroxy)propyloxy]-2-phenyl-2(*R*)-ethanol (8). Method A, from 6.—To a solution of 2.67 g (0.0147 mol) of **1** in 50 ml of water was added 3.45 g (0.0161 mol) of $NaIO_4$. The mixture was left at ambient temperature for 1 hr, then poured into 200 ml of absolute ethanol and stirred for 15 min at room temperature. After filtration from the white solid the solution was reduced in volume to 50 ml and added slowly to a stirred solution protected from light, containing sodium borohydride (3.06 g, 0.080 mol) dissolved in 70 ml of water. After stirring for 30 min the mixture was stored at 0–5° overnight. The pH was then adjusted to 7 with Dowex AG-50 (H^+) and the resin was removed by filtration. The aqueous solution was then evaporated to dryness and the residue (one major spot on tlc) was chromatographed on 100 g of silica gel G (4:1, chloroform–methanol). The fractions containing the product were evaporated to dryness and the residue was recrystallized from ethyl acetate. Compound **8** (1.59 g, 51%) was very hygroscopic and had to be filtered under a nitrogen atmosphere and stored over phosphorus pentoxide: mp 69–71°; $[\alpha]^{23}D$ +86 ± 1° (*c* 1.3, water); nmr (DMSO-d_6) δ 7.31 (5, s, C_6H_5), 4.36–5.40 (4, m, 3 OH's and anomeric), 3.40–3.70 (7, m).

Anal. Calcd for $C_{11}H_{16}O_4$: C, 62.25; H, 7.60. Found: C, 62.05; H, 7.49.

Method B, from 1.—Tetra-*O*-acetyl-β-D-glucopyranosylbenzene (6.70 g, 0.0164 mol) was deblocked with 300 ml of methanol containing 100 mg of sodium methoxide. The mixture was neutralized with Dowex AG 50 (H^+), filtered, and evaporated to dryness. The syrupy glucopyranosylbenzene was then subjected to cleavage by metaperiodate (2 equiv) and borohydride reduction in a manner similar to that described in method A. Purification by column chromatography and recrystallization of the product from ethyl acetate gave compound **8** (2.41 g, 69%) identical in all respects with the product obtained by method A: mp and mmp 69–71°; $[\alpha]^{23}D$ +86 ± 1° (*c* 1.3, water).

***o*- and *p*-(β-D-Ribofuranosyl)nitrobenzene (11a and 11b).**—β-D-Ribofuranosylbenzene **6** (1.90 g, 0.0104 mol) in 20 ml of pyridine was treated with 2 ml of acetic anhydride and kept overnight at room temperature. Excess acetic anhydride was hydrolyzed by addition of a small amount of water and the mixture was evaporated to dryness. After partition (chloroform–sodium bicarbonate, then water) the organic phase was dried over sodium sulfate and evaporated. Tlc (10:1, benzene–ethyl acetate) of the syrup indicated the presence of only one component (R_f 0.2). The triacetate **9** was dissolved in 45 ml of acetic anhydride and 15 g of cupric nitrate trihydrate was added in three portions. The mixture was kept at 50° for 35 min. It was then rapidly cooled and poured into 120 ml of ice-water. It was extracted with 300 ml of benzene in two portions and the organic layer was washed with aqueous sodium bicarbonate and water and was finally dried over anhydrous sodium sulfate. After evaporation to dryness, the yellow syrupy residue (3.4 g) was chromatographed on 150 g of silica gel G (7:1 benzene–ethyl acetate). The major fractions were pooled and evaporated to give 2.3 g of syrup (~58%). This ortho–para mixture was deacetylated in methanol with sodium methoxide and the product was crystallized from ethyl acetate to give 1.14 g (48% based on **6**) of mixed *o*- and *p*-(β-D-ribofuranosyl)nitrobenzene (**11a** and **11b**) in four crops. Pure samples of each isomer were obtained using fractional crystallization from ethyl acetate by alternately seeding the concentrated mother liquor after the isolation of each pure fraction with crystals of the other isomer. Each crop was identified by its crystalline form and its ir spectrum.

The ortho isomer (**11a**, 0.225 g) was obtained as small spherical fibrous aggregates: mp 155–157°; nmr (DMSO-d_6) δ 7.30–8.30 (4, m, C_6H_4), 5.12 (1, d, H-1), 4.72–5.06 (3, m, OH's), 3.50–3.95 (5, m, H-2, H-3, H-4, and H-5), $J_{1,2} = 4.5$ Hz; ir ν_{max}^{KBr} 790 (1:2 disubstituted), 1005 and 1015 (1:2 disubstituted), 1180 and 1200 (1:2 disubstituted), 1550 and 1575 cm^{-1} (NO_2).

Anal. Calcd for $C_{11}H_{13}NO_6$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.94; H, 5.09; N, 5.47.

The para isomer (**11b**, 0.524 g) crystallized from ethyl acetate as stout prisms: mp 151–153°; nmr (DMSO-d_6) δ 7.72 and 8.30 (4, 2d, C_6H_4), 4.85–5.25 (3, m, OH's), 4.79 (1, d, H-1), 3.55–4.05 (5, m, H-2, H-3, H-4, and H-5), $J_{1,2} = 7.0$ Hz; ir ν_{max}^{KBr} 850 (1:4 disubstituted), 1180 (1:4 disubstituted), 1575 cm^{-1} (NO_2).

Anal. Calcd for $C_{11}H_{13}NO_6$: C, 51.77; H, 5.13; N, 5.49. Found: C, 51.94; H, 5.09; N, 5.47.

***p*-(β-D-Ribofuranosyl)nitrobenzene 5-(Calcium phosphate) (12).**—To a solution of **11b** (0.454 g, 0.0018 mol) in 40 ml of acetone were added two drops of concentrated sulfuric acid and 0.25 ml of dimethoxypropane. The mixture was left overnight and neutralized by shaking with anhydrous sodium carbonate. The suspension was filtered and the filtrate was evaporated to dryness. The residue was dissolved in chloroform, which was extracted with water and dried over sodium sulfate. The residue, in 4 ml of dry pyridine, was added to a solution of 2-cyanoethyl phosphate (0.54 g, 0.00356 mol) and dicyclohexylcarbodiimide (1.46 g, 0.00712 mol) in 25 ml of anhydrous pyridine. The mixture was left for 2 days at room temperature and treated with 3.5 ml of H_2O and filtered. The filtrate was evaporated under vacuum below 35° and the residue was dissolved in 100 ml of 70% acetic

(12) B. J. Hunt and W. Rigby, *Chem. Ind. (London)*, 1868 (1967).

acid and heated for 30 min at 100°. The mixture was evaporated to dryness; the residue was dissolved in 70 ml of H_2O; and the solution was filtered again. To the filtrate was added 10 ml of 6 *M* KOH and the solution was heated on a steam bath for 30–40 min. After cooling, it was passed through a short Dowex AG 50 (H^+) column, washed, and adjusted to pH 7.5–8 with NH_4OH. The solution was concentrated and chromatographed on six sheets of Whatman No. 3 MM with 5:2 ethanol–1 *M* ammonium formate. The aqueous eluates from the appropriate bands were pooled, evaporated to a small volume, and passed through a short Dowex AG 50 (Na^+) column. The solution was then evaporated to dryness to give 1.03 g of a white solid. Optical density measurements (based on **11**) indicated that the solid obtained was 40% pure **12** (as the Na salt in 60% yield) and was present together with a uv-nonabsorbing salt (possibly HCOONa). Paper chromatography (Whatman No. 1, 5:2 ethanol–0.5 *M* ammonium formate; R_f 0.35) and paper electrophoresis (Whatman No. 3 MM, 0.05 *M* ammonium bicarbonate, pH 5, R_{UMP} 0.91) indicated the presence of only one uv-absorbing component. The product was purified by precipitation as the sparingly soluble calcium salt of **12** (0.244 g).

Anal. Calcd for $C_{11}H_{12}NO_9PCa \cdot H_2O$: C, 33.76; H, 3.60; N, 3.58; P, 7.91; Ca, 10.24. Found: C, 33.69; H, 3.60; N, 3.58; P, 7.82; Ca, 10.12.

(2,3-Isopropylidene-5-dichloroacetamido-5-deoxy-β-D-ribofuranosyl)benzene (17).—Compound **6** (4.30 g, 0.0236 mol) in 100 ml of acetone was treated with three drops of concentrated H_2SO_4 and 2.5 ml of dimethoxypropane at room temperature overnight. Tlc (20:1, chloroform–methanol) showed complete conversion to product **13** (R_f 0.65). Excess sodium carbonate was added to the solution and the suspension was filtered. The solution was evaporated to a syrup that did not crystallize. This was dissolved in 30 ml of pyridine and 3.2 g (0.0028 mol) of mesyl chloride. Mesylation was completed within 2 hr at room temperature. The mixture was evaporated to dryness and partitioned between chloroform and water, and the organic layer was dried over Na_2SO_4 and evaporated to a syrup (**14**) (tlc, 10:1 benzene–ethyl acetate, R_f 0.4). This was dissolved in 50 ml of DMF, and finely powdered sodium azide (4.87 g, 0.0750 mol) was added in portions. The suspension was heated over a steam bath with frequent shaking. After 45 min tlc indicated complete conversion to compound **15** (10:1 benzene–ethyl acetate, R_f 0.7). The mixture was cooled, filtered, and evaporated and the residue was partitioned between chloroform and water. The organic layer was dried and evaporated to give **15** as a syrup. This was dissolved in 160 ml of 2-propanol and sodium borohydride (2.85 g, 0.075 mol) was added. The mixture was heated to reflux for a total of 22 hr, evaporated to dryness, and partitioned between dichloromethane and water (150 ml each). The organic layer was dried and evaporated to give **16** as an oil. Tlc of the product (20:1 chloroform–methanol, $R_f \cong 0.3$) revealed only small amounts of side products. The amine **16** was therefore used without further purification. It was dissolved in 50 ml of dry pyridine, chilled to 0°, and treated with dichloroacetic anhydride (6.0 g, 0.025 mol). The mixture was left for 2 hr at room temperature, treated with a small amount of methanol, and evaporated to dryness. The residue was partitioned between water and chloroform and the organic layer was decolorized with charcoal and dried over Na_2SO_4. After evaporation of the filtrate, the residue was chromatographed on 400 g of silica gel G (5:1 benzene–ethyl acetate). Appropriate fractions were collected and after evaporation to dryness compound **17** (5.60 g, 65% based on **6**) was obtained pure as a colorless syrup: nmr ($CDCl_3$) δ 7.33 (5, s, C_6H_5), 7.00 (1, t, NH), 5.94 (1, s, $CHCl_2$), 4.88 (1, m, H-1), 4.52 (2, m, H-2 and H-3), 4.02–4.30 (1, m, H-4), 3.65 (2, q, H-5).

Anal. Calcd for $C_{16}H_{19}NO_4Cl_2 \cdot {}^1/_2H_2O$: C, 52.05; H, 5.46; N, 3.79; Cl, 19.20. Found: C, 52.03; H, 5.40; N, 3.81, Cl, 19.25.

(5-Dichloroacetamido-5-deoxy-β-D-ribofuranosyl)benzene (18). Compound **17** (4.94 g, 0.0134 mol) was dissolved in 100 ml of 70% acetic acid and the solution was heated on the steam bath for 30 min. The mixture was evaporated to dryness and the residue was crystallized from ethyl acetate–ether to give 4.09 g of compound **18** (95%). Recrystallization from the same solvent pair gave the analytical sample (mp 109–111°) as long white needles: nmr (DMSO-d_6) δ 8.65 (1, t, NH), 7.31 (5, s, C_6H_5), 6.50 (1, s, $CHCl_2$), 5.00 (2, m, OH's), 4.60 (1, d, H-1), 3.30–3.95 (5, m, H-2, H-3, H-4, and H-5), $J_{1,2}$ = 6.0 Hz.

Anal. Calcd for $C_{13}H_{15}NO_4Cl_2$: C, 48.78; H, 4.72; N, 4.37; Cl, 22.12. Found: C, 48.68; H, 4.64; N, 4.36; Cl, 22.03.

***o*- and *p*-(5-Dichloroacetamido-5-deoxy-β-D-ribofuranosyl)-nitrobenzene (20a and 20b).**—Compound **18** (4.70 g, 0.016 mol) was acetylated in 30 ml of pyridine with 6.1 g (0.060 mol) of acetic anhydride. The mixture was worked up as for **9** and compound **19** (obtained as a syrup) was dissolved in 60 ml of acetic anhydride. It was nitrated with 20 g of cupric nitrate and worked up in the manner described above. The crude mixture of products was separated on 800 g of silica gel G (50:1, $CHCl_3$–MeOH) and appropriate fractions were collected and evaporated to give 2.90 g of a mixture of **20a** and **20b**. The two isomers were separated on ten plates (20 × 40 cm, 2 mm alumina HF_{254}, $CHCl_3$) where the ortho isomer migrated slightly ahead of the para isomer. All bands were eluted with ethyl acetate and the appropriate eluates were pooled and evaporated to give 0.269 g of **19a** (ortho) and 0.581 g of **19b** (para) as syrups: nmr (**19a** in $CDCl_3$) δ 7.50–8.10 (4, m, C_6H_4), 7.08 (1, broad t, NH), 5.98 (1, s, $CHCl_2$), 5.57 (1, d, H-1), 4.90–5.40 (2, m, H-2 and H-3), 4.05–4.45 (1, m, H-4), 3.50–3.95 (2, m, H-5), 2.09 and 2.17 (6, 2 s, $2CH_3CO$–), $J_{1,2}$ = 3.5 Hz; nmr (**19b** in $CDCl_3$) δ 8.20 and 7.57 (4, 2 d, C_6H_4), 7.14 (1, broad t, NH), 6.00 (1, s, $CHCl_2$), 5.07 (3, broad s, H-1, H-2, and H-3), 4.30 (1, m, H-4), 3.80 (2, m, H-5), 2.13 (6, s, $2CH_3CO$–). All of **19a** obtained above was dissolved in 4 ml of methanol and treated with 0.2 ml of triethylamine. The mixture was left at room temperature for 16 hr and evaporated to dryness. The semicrystalline residue was recrystallized from ethanol to give 120 mg of analytically pure **20a**: mp 157–158°; nmr (DMSO-d_6) δ 8.69 (1, broad t, NH), 7.30–8.00 (4, m, C_6H_4), 6.50 (1, s, $CHCl_2$), 4.95–5.30 (3, m, H-1 and OH's), 3.40–4.00 (5, m, H-2, H-3, H-4, and H-5), $J_{1,2}$ = 4.0 Hz.

Anal. Calcd for $C_{13}H_{14}N_2O_6Cl_2$: C, 42.76; H, 3.86; N, 7.67; Cl, 19.41. Found: C, 42.85; H, 3.72; N, 7.66; Cl, 19.56.

All of **19b** obtained above was similarly deacetylated in 8 ml of methanol with 0.4 ml of triethylamine. After complete evaporation of the solvent, the syrupy residue was crystallized very slowly from ethanol. Recrystallization was repeated several times until **20b** separated as analytically pure white needles (221 mg). Compound **20b** showed no definite melting point but, after cooling, the melt resolidified and melted sharply at 131–133°: nmr (DMSO-d_6) δ 8.69 (1, broad t, NH), 8.20 and 7.63 (4, 2 d, C_6H_4), 6.50 (1, s, $CHCl_2$), 5.00–5.30 (2, m, OH's), 4.75 (1, d, H-1), 3.25–4.00 (5, m, H-2, H-3, H-4, and H-5), $J_{1,2}$ = 6.5 Hz.

Anal. Calcd for $C_{13}H_{14}N_2O_6Cl_2$: C, 42.76; H, 3.86; N, 7.67; Cl, 19.41. Found: C, 42.55; H, 3.77; N, 7.68; Cl, 19.48.

Registry No.—**5**, 32252-02-1; **6**, 32252-03-2; **8**, 32304-19-1; **11a**, 32252-04-3; **11b**, 32252-05-4; **12**, 32304-20-4; **17**, 32252-06-5; **18**, 32251-31-3; **19a**, 32251-32-4; **20a**, 32251-33-5; **20b**, 32251-34-6.