SYNTHESIS OF GLYCOSIDES DERIVED FROM POLYHYDRIC ALCOHOLS*

PART I. 2-DEOXYGLYCER-2-YL GLYCOSIDES

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ABSTRACT

2-Deoxyglycer-2-yl α- and β-L-arabinopyranoside, α-L-arabinofuranoside, α- and β-D-xylopyranoside, β-D-glucopyranoside, β-maltoside, and α- and β-cellobioside have been synthesized in good yields from the respective 1,3-dichloropropyl glycoside acetates by displacement of the chloride ion with sodium or ammonium benzoate in *N*,*N*-dimethylformamide at 165°, followed by alkaline hydrolysis.

INTRODUCTION

As part of a program to synthesize the deoxyglyceryl glycosides required as reference compounds in structural investigations of polysaccharides, the synthesis of glycer-2-yl glycosides was undertaken. The 1,3-dihalopropyl glycosides offered a simple route to these glycosides by means of a nucleophilic displacement of the halide ions ultimately giving the glycerol derivative.

DISCUSSION

Previous methods for preparing 2-deoxy-2-yl glycosides involve either the selective degradation of an appropriate oligosaccharide with lead tetraacetate in acetic acid[1–3], an extremely useful reaction when the oligosaccharide is readily available, or a Koenigs–Knorr condensation of the acylglycosyl halide with a 1,3-disubstituted glycerol, such as 1,3-*O*-benzylideneglycerol[1,4]. Attempts, in this laboratory, to condense acylglycosyl halides with 1,3-di-*O*-triphenylmethyl- and

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1,3-di-*O*-*p*-nitrobenzoylglycerol and with the dimethyl ester of tartronic acid were unsuccessful. 1,3-*O*-Benzylideneglycerol, therefore, appears to be one of the few suitable compounds for this type of reaction. The acid lability of the benzylidene acetal, however, limits the use of this compound to the Koenigs–Knorr type reaction.

The effective displacement of the halide residue from the unreactive aryl halides by sodium benzoate has been recognized for a long time and shown to be catalyzed by tertiary amines[5]. More recently, it has been established that sodium benzoate in *N*,*N*-dimethylformamide is a powerful nucleophilic reagent. It seemed advisable, therefore, to investigate sodium benzoate in hot *N*,*N*-dimethylformamide as the nucleophilic reagent for the displacement of the halide from the 1,3-dihalopropyl glycosides.

When 1,3-dichloropropyl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside was heated with sodium benzoate in *N*,*N*-dimethylformamide for 48 h at 165°, the corresponding dibenzoate crystallized in a 74% yield. Saponification of this compound afforded glycer-2-yl β-D-xylopyranoside. Further experiments indicated an overall yield of 95% in these two reactions (see Table I).

TABLE I

INFLUENCE OF THE REACTION CONDITIONS ON THE YIELDS OF 2-DEOXYGLYCER-2-YL β-D-XYLOPYRANOSIDE FROM 1,3-DIHALOPROPYL β-D-XYLOPYRANOSIDE TRIACETATE

Glycoside of β-D-xylopyranoside triacetate	*Reaction time (h)*	*Nucleophile, Benzoate*	*Yield*[a] (%)
1,3-Dichloropropyl	48	Sodium	95[b]
	18	Ammonium	90[c]
1,3-Dibromopropyl	24	Sodium	50[c]
	18	Ammonium	95[b]

[a]The yields were determined from the weights of 2-deoxyglycer-2-yl β-D-xylopyranoside isolated by paper chromatography of the saponified reaction products. [b]No other products were detected. [c]The crude product contained traces of 3 other components including 1,3-dichloropropyl or 1,3-dibromopropyl β-D-xylopyranoside.

In order to demonstrate its usefulness, this reaction was applied successfully to acetylated 1,3-dichloropropyl furanosides, pyranosides, and disaccharides; the corresponding dibenzoates were isolated in 40–75% yields. The properties of the 2-deoxy-glycer-2-yl glycosides synthesized by this method are reported in Table II.

Since the rate of displacement is proportional to the concentration of the nucleophile, ammonium benzoate, which is much more soluble in *N*,*N*-dimethylformamide than the sodium salt, was more effective in displacing the halide, as shown for the 1,3-dihalopropyl β-D-xylopyranoside triacetates (Table I). Furthermore, the rate of reaction of alkyl halides in these displacement reactions depends on the polarizability of the bond in the order C–Br > C–Cl. Although preliminary experiments indicated a slightly faster rate of reaction with the 1,3-dibromopropyl glycosides (Table I), considerable color formation accompanied the reaction.

The required 1,3-dichloro- or 1,3-dibromo-propyl β-glycosides were prepared by Koenigs–Knorr condensation, whereas direct condensation of the sugar with 1,3-dichloro-2-propanol in the presence of an acid catalyst provided the α-anomer. The anomeric configuration of the glycosides have been assigned on the basis of their molecular rotations according to Hudson's rules.

EXPERIMENTAL

General. — Paper and thin-layer chromatography was performed with the following solvent systems: (A) 2:5:7 (v/v) pyridine–ethyl acetate–water, upper phase[9], (B) 13:2:5 (v/v) propyl alcohol–ethyl acetate–water[10], and (C) 200:47:15:1 (v/v) benzene–ethanol–water–acetic acid, upper phase[11]. Silica gel G was used for t.l.c. Components were visualized on paper with the ammoniacal silver nitrate reagent[12] and on thin-layer plates by spraying with sulfuric acid and heating at 150°. Melting points were determined on a Fisher–Johns block and are uncorrected.

1,3-Dichloropropyl 2,3,4-tri-O-acetyl-β-L-arabinofuranoside. — A mixture of redistilled 1,3-dichloro-2-propanol (5 g), anhyd. ether (200 ml), mercuric cyanide (5.95 g), and Drierite (1 g) was shaken for 1 h at room temperature. Crystalline 2,3,4-tri-*O*-acetyl-α-L-arabinopyranosyl bromide[13] (4 g) was added, and the mixture was shaken for 4 h when more bromide (4 g) was added. After the mixture had been shaken for 10 h, the solvent was evaporated and the residue was extracted with chloroform. The extract was filtered, washed with water to remove the 1,3-dichloro-2-propanol and salts, dried with magnesium sulfate, and evaporated to give a syrup. This was deacetylated catalytically with sodium methoxide in methanol and the solvent evaporated. 1,3-Dichloro β-L-arabinopyranoside was crystallized from acetone (1.9 g), m.p. 141°, $[\alpha]_D^{24}$ +188.0° (*c* 0.3, water).

Acetylation of this glycoside (1 g) in pyridine (10 ml) with acetic anhydride (3 ml) for 24 h at room temperature afforded the triacetate which was crystallized from 50% ethanol (1.57 g), m.p. 105°, $[\alpha]_D^{24}$ +235.0° (*c* 0.3, chloroform).

Anal. Calc. for $C_{14}H_{20}Cl_2O_8$: C, 43.42; H, 5.21; Cl, 18.31. Found: C, 43.58; H, 5.30; Cl, 18.40.

1,3-Dichloropropyl 2,3,4-tri-O-acetyl-α-L-arabinopyranoside. — Ether was added to the mother liquor of 1,3-dichloropropyl β-L-arabinopyranoside and the turbid solution was stored for 12 h at 0°. It was filtered and evaporated to a syrup (0.45 g), which was acetylated with pyridine (15 ml) and acetic anhydride (4 ml) for 24 h at room temperature. The triacetate was crystallized from 50% ethanol (0.43 g), m.p. 106°, $[\alpha]_D^{26}$ +0.75° (*c* 1.4, chloroform).

Anal. Calc. for $C_{14}H_{20}Cl_2O_8$: C, 43.42; H, 5.21; Cl, 18.31. Found: C, 43.43; H, 5.30; Cl, 18.48.

1,3-*Dichloropropyl α-L-arabinofuranoside.* — A mixture of redistilled 1,3-dichloro-2-propanol (5 g), anhyd. ether (20 ml), mercuric cyanide (2.5 g), and Drierite (3 g) was shaken for 1 h at 25°. 2,3,5-Tri-*O*-benzoyl-α-L-arabinofuranosyl bromide (5 g), prepared according to Scheurer and Smith[13] and isolated as described by Ness

and Fletcher[14], was added and shaking was continued for 12 h at 25°. The reaction mixture was diluted with chloroform (50 ml) and filtered, and the filtrate was washed with water, dried with magnesium sulfate, and evaporated. After debenzoylation with sodium methoxide in methanol, the solution was evaporated *in vacuo*. The residue was stirred with water and the suspension was filtered without suction to eliminate the immiscible methyl benzoate. Continuous extraction of the aqueous solution with ether afforded 1.4 g which was crystallized from ether (1.24 g), m.p. 74–75°, $[\alpha]_D^{22}$ −95.0° (*c* 0.13, water).

Anal. Calc. for $C_8H_{14}Cl_2O_5$: C, 36.80; H, 5.40; Cl, 27.16. Found: C, 36.49; H, 5.44; Cl, 26.32.

Benzoylation of this glycoside (1.35 g) with pyridine (4 ml) and benzoyl chloride (1.8 ml) gave the tribenzoate (2.4 g) which failed to crystallize, $[\alpha]_D^{24}$ ±0° (*c* 10, chloroform).

*1,3-Dichloropropyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside.* — A mixture of redistilled 1,3-dichloro-2-propanol (18 ml), mercuric cyanide (6.15 g), and Drierite (5 g) was shaken for 1 h at 25°. 2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl bromide[13] was added and the reaction mixture was shaken for 12 h, and then filtered. The filtrate was diluted with chloroform, washed with water to remove the excess of 1,3-dichloro-2-propanol and salts, and dried with magnesium sulfate. Evaporation and addition of ethanol to the residue, afforded crystals (4.5 g) which were recrystallized from ethanol, m.p. 123°, $[\alpha]_D^{25}$ −8.9° (*c* 1.3, chloroform).

Anal. Calc. for $C_{17}H_{24}Cl_2O_{10}$: C, 44.46; H, 5.27; Cl, 15.44. Found: C, 44.21; H, 5.24; Cl, 15.30.

The conditions and molar proportions of reagents just described were used to prepare the following compounds:

*1,3-Dibromopropyl 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranoside.* — Yield 38%, m.p. 123°, $[\alpha]_D^{25}$ −12.4° (*c* 0.5, chloroform).

Anal. Calc. for $C_{17}H_{24}Br_2O_{10}$: C, 37.25; H, 4.41; Br, 29.15. Found: C, 37.50; H, 4.42; Br, 29.06.

*1,3-Dichloropropyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranoside.* — Yield 53%, m.p. 183°, $[\alpha]_D^{25}$ −54.2° (*c* 1.5, chloroform).

Anal. Calc. for $C_{14}H_{20}Cl_2O_8$: C, 43.42; H, 5.21; Cl, 18.31. Found: C, 43.58; H, 5.40; Cl, 18.27.

*1,3-Dibromopropyl 2,3,4-tri-*O*-acetyl-β-*D*-xylopyranoside.* — Yield 55%, m.p. 150–152°, $[\alpha]_D^{25}$ −48.8° (*c* 1.0, chloroform).

Anal. Calc. for $C_{14}H_{20}Br_2O_8$: C, 35.31; H, 4.23. Found: C, 35.49; H, 4.23.

1,3-Dichloropropyl β-maltoside heptaacetate. — A mixture of hexa-*O*-acetyl-α-D-maltosyl bromide[13] (4.4 g), redistilled 1,3-dichloro-2-propanol (4.5 g), mercuric cyanide (2.2 g), and Drierite (1 g) was shaken for 2 days, and the product was isolated as just described. Since it did not crystallize spontaneously, it was chromatographed on silica gel G plates with solvent C as eluent. Elution of the fastest-moving component with acetone afforded the heptaacetate (1.38 g) which was crystallized from ethanol, m.p. 135–136°, $[\alpha]_D^{22}$ +52.4° (*c* 5.6, chloroform).

Anal. Calc. for $C_{29}H_{40}Cl_2O_{18}$: C, 46.59; H, 5.39; Cl, 9.49. Found: C, 46.55; H, 5.45; Cl, 9.47.

1,3-Dichloropropyl β-cellobioside heptaacetate. — A mixture of redistilled 1,3-dichloro-2-propanol (10 ml), mercuric cyanide (5 g), anhydrous silica gel (3 g), and hexa-*O*-acetyl-α-D-cellobiosyl bromide[13] (8 g) was shaken for 12 h. The product was isolated as just described and dissolved in ethanol (60 ml) from which a crystalline product was obtained (4.5 g). Four recrystallizations from ethanol gave a product (4.0 g) which showed 2 components (R_F 0.44 and 0.39) in t.l.c. on silica gel G with solvent C. Repeated crystallizations from ethanol–benzene (1:1 and 2:1, v/v), ethanol, and 95% aqueous ethanol afforded pure 1,3-dichloropropyl β-cellobioside heptaacetate (0.33 g), R_F 0.44, m.p. 220–224°, $[\alpha]_D^{24}$ −16.7° (*c* 6.0, chloroform), and 1,3-dichloropropyl α-cellobioside heptaacetate (0.40 g), R_F 0.39, m.p. 193–194°, $[\alpha]_D^{24}$ +54.9° (*c* 8.8, chloroform).

Anal. Calc. for $C_{29}H_{40}Cl_2O_{18}$: C, 46.59; H, 5.39; Cl, 9.49. Found for the β-anomer: C, 46.35; H, 5.32; Cl, 9.58. For the α-anomer: C, 46.26; H, 5.37; Cl, 9.53.

1,3-Dichloropropyl 2,3,4-tri-O-acetyl-α-D-xylopyranoside. — D-Xylose (5 g) was stirred with 1,3-dichloro-2-propanol (20 ml) at 140° until dissolved. Amberlite IR-120 (H^+, 5 g) was added and the mixture was stirred for 24 h at 75°. The resin was removed by filtration, and the solution was concentrated to a syrup and chromatographed on a starch column with solvent A as eluent. The fastest-moving component, 1,3-dichloropropyl α-D-xylopyranoside (3 g) was crystallized from ethyl acetate, m.p. 141–143°, $[\alpha]_D^{26}$ +124.0° (*c* 0.5, water).

Anal. Calc. for $C_8H_{14}Cl_2O_5$: C, 36.80; H, 5.40. Found: C, 36.50; H, 5.32.

Acetylation of this glycoside (0.10 g) with pyridine (3 ml) and acetic anhydride (2 ml) for 24 h at 25° afforded the triacetate which was crystallized from ethanol (0.10 g), m.p. 67°, $[\alpha]_D^{21}$ +116.0° (*c* 0.4, chloroform).

Anal. Calc. for $C_{14}H_{20}Cl_2O_8$: C, 43.42; H, 5.21; Cl, 18.31. Found: C, 43.60; H, 5.36; Cl, 18.25.

2-Deoxyglycer-2-yl β-D-xylopyranoside. — 1,3-Dichloropropyl β-D-xylopyranoside triacetate (0.20 g) and sodium benzoate (0.50 g) were heated in freshly-distilled *N*,*N*-dimethylformamide (10 ml) in a sealed tube for 48 h at 165°. Ether was added to the cooled reaction mixture which was then filtered. Evaporation of the filtrate and addition of ethanol to the residue gave crystalline 1,3-dibenzoylglycer-2-yl 2,3,4-tri-*O*-acetyl-β-D-xylopyranoside (0.21 g), m.p. 141–146°, which was recrystallized from ethanol (0.17 g), m.p. 151.5–152°, $[\alpha]_D^{24}$ −14.3° (*c* 1.1, chloroform).

Anal. Calc. for $C_{28}H_{30}O_{12}$: C, 60.21, H, 5.41. Found: C, 60.18; H, 5.48.

After saponification with M sodium hydroxide, the solution was deionized with an ion-exchange resin and evaporated. Glycer-2-yl β-D-xylopyranoside was recrystallized from ethanol, m.p. 109–111°, $[\alpha]_D^{24}$ −47° (*c* 1.0, water); lit.[7]: m.p. 109–111°, $[\alpha]_D^{24}$ −47°.

The molar proportions of the 1,3-dichloropropyl glycoside acetates and sodium benzoate and the conditions just described were used to prepare glycer-2-yl β-D-glucopyranoside, α- and β-L-arabinopyranoside, and α-L-arabinofuranoside in nearly

TABLE II

2-DEOXYGLYCER-2-YL GLYCOSIDES AND DERIVATIVES

2-Deoxyglycer-2-yl	*This work*				*Literature*				
	M.p. (°C)	$[\alpha]_D^{25}$ (*degrees*)	*Solvent*	*c*	*M.p.* (°C)	$[\alpha]_D$ (*degrees*)	*Solvent*	*c*	*Ref.*
α-L-Arabinopyranoside		+7	Water	5.0		+5	Water	10	1
pentabenzoate	55–59	+91.9	Chloroform	2.0	53–57	+93	Chloroform	0.9	1
β-L-Arabinopyranoside	151	+204	Water	0.5	154–155	+204	Water	1.2	1
pentabenzoate	48–50	+162	Chloroform	1.6	48–50	+164	Chloroform	0.8	1
α-L-Arabinofuranoside		−101	Water	2.0		−129	Water	1.0	6
penta-*p*-nitrobenzoate	88–92	±0	2,4-Dimethylpyridine	3.5	88–92	±0	2,4-Dimethylpyridine	1.1	6
α-D-Xylopyranoside		+133	Water	1.7		+91	Water	1.5	1
pentabenzoate	127–128	+72.2	Chloroform	0.1	51–55	+51	Chloroform	1.1	1
β-D-Xylopyranoside									
pentabenzoate	105–106	−35.8	2,4-Dimethylpyridine	0.5	105–106	−36	2,4-Dimethylpyridine	0.9	7
β-D-Glucopyranoside	164	−30.0	Water	1.0	163	−30.2	Water	1.0	2, 3
hexabenzoate	136–137	−3.3	Chloroform	0.7	145–146	−4	Chloroform	0.7	2

quantitative yields. The properties of the glycosides and of their crystalline benzoates and *p*-nitrobenzoates are reported in Table II.

2-Deoxyglycer-2-yl β-maltoside. — 1,3-Dichloropropyl β-maltoside heptaacetate (0.40 g) was heated with sodium benzoate (1.2 g) in *N,N*-dimethylformamide (10 ml) for 18 h at 165°. The product, which was isolated as just described, failed to crystallize and was purified by t.l.c. (solvent C). The fastest-moving component, 1,3-dibenzoyl-2-deoxyglycer-2-yl hepta-*O*-acetyl-β-maltoside, was crystallized from ethanol (0.20 g), m.p. 90–92°, $[\alpha]_D^{26}$ +38.5° (*c* 4.5, chloroform).

This product was deacetylated with sodium methoxide in methanol to give glycer-2-yl β-maltoside which failed to crystallize. The glycoside had $R_{Maltose}$ 0.97 and 1.13 on paper chromatography in solvents A and B, respectively. Acid hydrolysis of the glycoside liberated glucose and glycerol, as shown by paper chromatography.

Acetylation of the glycoside gave glycer-2-yl β-maltoside nonaacetate which was recrystallized from ethanol, m.p. 81–82°, $[\alpha]_D^{21}$ +47.5° (*c* 0.5, chloroform).

Anal. Calc. for $C_{33}H_{46}O_{22}$: C, 49.87; H, 5.84. Found: C, 49.67; H, 5.82.

2-Deoxyglycer-2-yl α-cellobioside. — 1,3-Dichloropropyl α-cellobioside heptaacetate (0.20 g) and sodium benzoate (0.60 g) were heated in *N,N*-dimethylformamide (7 ml) in a sealed tube for 2 days at 165°. The product was isolated as just described and crystallized from ethanol (0.12 g), m.p. 188–197°. The crude product was recrystallized from ethanol to give 1,3-dibenzoylglycer-2-yl hepta-*O*-acetyl-α-cellobioside (89 mg), m.p. 204°, $[\alpha]_D^{26}$ +32.3° (*c* 13.7, chloroform).

Deacylation of this product with sodium methoxide in methanol afforded 2-deoxyglycer-2-yl α-cellobioside which failed to crystallize. On acid hydrolysis, only glucose and glycerol were detected by paper chromatography.

Acetylation with pyridine and acetic anhydride gave the nonaacetate which was crystallized and recrystallized from ethanol, m.p. 193–194°, $[\alpha]_D^{31}$ +61.3° (*c* 1.2, chloroform).

Anal. Calc. for $C_{33}H_{46}O_{22}$: C, 49.87; H, 5.84. Found: C, 49.28; H, 5.76.

2-Deoxyglycer-2-yl β-cellobioside. — The displacement reaction was performed for 18 h as described for the α-anomer to give crude 1,3-dibenzoylglycer-2-yl hepta-*O*-acetyl-β-cellobioside (yield, 54%), m.p. 154–155°, which on recrystallization from ethanol had m.p. 159–160°, $[\alpha]_D^{25}$ −18.2° (*c* 2.0, chloroform).

On deacylation with sodium methoxide in methanol, glycer-2-yl β-cellobioside was obtained, m.p. 142–145°, $[\alpha]_D^{24}$ −15.3° (*c* 2.3, water); lit.[14]: m.p. 138–141°, $[\alpha]_D$ −15.6°.

The glycoside was acetylated with pyridine and acetic anhydride to give the nonaacetate which was crystallized from ethanol, m.p. 146–147°, $[\alpha]_D^{25}$ −17.8° (*c* 3.7, chloroform).

Anal. Calc. for $C_{33}H_{46}O_{22}$: C, 49.87; H, 5.84. Found: C, 49.35; H, 5.78.

Comparison of yields of glycer-2-yl β-D-xylopyranoside obtained under various conditions. — 1,3-Dichloropropyl and 1,3-dibromopropyl β-D-xylopyranoside triacetate (0.1 g) were heated with either sodium benzoate or ammonium benzoate (0.3 g) in *N,N*-dimethylformamide (3 ml) in sealed tubes for various lengths of time

at 165°. At the end of the reaction time, the products were isolated as described in the previous paragraph and the chloroform extracts were washed with water, dried, and evaporated. The residues were treated with sodium methoxide. The crude products were examined by paper chromatography and the glycer-2-yl β-D-xylopyranoside was isolated from each reaction product by chromatography on Whatman No. 3 paper with solvent A. The yields are shown in Table I.

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