THE CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES

IV. FURTHER DEGRADATIONS OF REDUCING DISACCHARIDES TO 2-*O*-GLYCOSYL-GLYCEROLS[1]

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ABSTRACT

The configuration of glycosidic linkages in a number of reducing disaccharides has been determined by converting each compound to the corresponding 2-*O*-glycosyl-glycerol, the configuration of which was readily established. Compounds examined include 3-*O*-β-D-galactopyranosyl-D-galactose, 3-*O*-α-D-galactopyranosyl-L-arabinose, 3-*O*-β-D-arabopyranosyl-L-arabinose, 2-*O*-β-D-xylopyranosyl-L-arabinose, 3-*O*-α-D-xylopyranosyl-L-arabinose, and 4-*O*-β-D-xylopyranosyl-D-xylose, all of which were derived by partial hydrolysis of polysaccharides. 2-*O*-α-L-Arabopyranosyl-glycerol has been synthesized via the Koenigs-Knorr condensation.

A previous paper in this series (3) describes a novel method for determining the configuration of glycosidic linkages in reducing disaccharides containing a hexopyranose non-reducing end-unit. According to this method the reducing end-unit of the disaccharide is degraded selectively by successive lead tetraacetate oxidations and sodium borohydride reductions to a 2-*O*-substituted glycerol. The resulting 2-*O*-glycopyranosyl-glycerol is one of two possible anomeric glycosides the configurations of which are designated by Hudson's nomenclature (9) according to their relative specific rotations.

Studies on the oxidation of reducing disaccharides by lead tetraacetate (4) indicate that many kinds of disaccharides can be degraded to give 2-*O*-glycosyl-glycerols. With the current paper the method has now been applied to each type of disaccharide represented in Fig. 1; the 1,2- and 1,4-aldohexose disaccharides were considered earlier (3). Most of the disaccharides examined had been isolated by other workers through partial hydrolysis of polysaccharides, but many had only tentatively been characterized. Included in the study are several pentopyranosyl disaccharides, and these have furnished three of the four possible 2-*O*-L-arabopyranosyl- and 2-*O*-D-xylopyranosyl-glycerols necessary as reference compounds. The fourth of these was synthesized.

Degradation of the various compounds is summarized by the series of reactions listed below, in which lead tetraacetate is represented by "O" and sodium borohydride by "H". Non-crystalline products were characterized as derived benzoates.

A. 3-*O*-β-L-Arabopyranosyl-L-arabinose (11), from a partial hydrolyzate of larch ε-galactan

$\xrightarrow[(2)\ \mathrm{H}]{(1)\ \mathrm{O}}$ 2-*O*-β-L-arabopyranosyl-L-erythritol (hexabenzoate)

$\xrightarrow[(2)\ \mathrm{H}]{(1)\ \mathrm{O}}$ 2-*O*-β-L-arabopyranosyl-glycerol.

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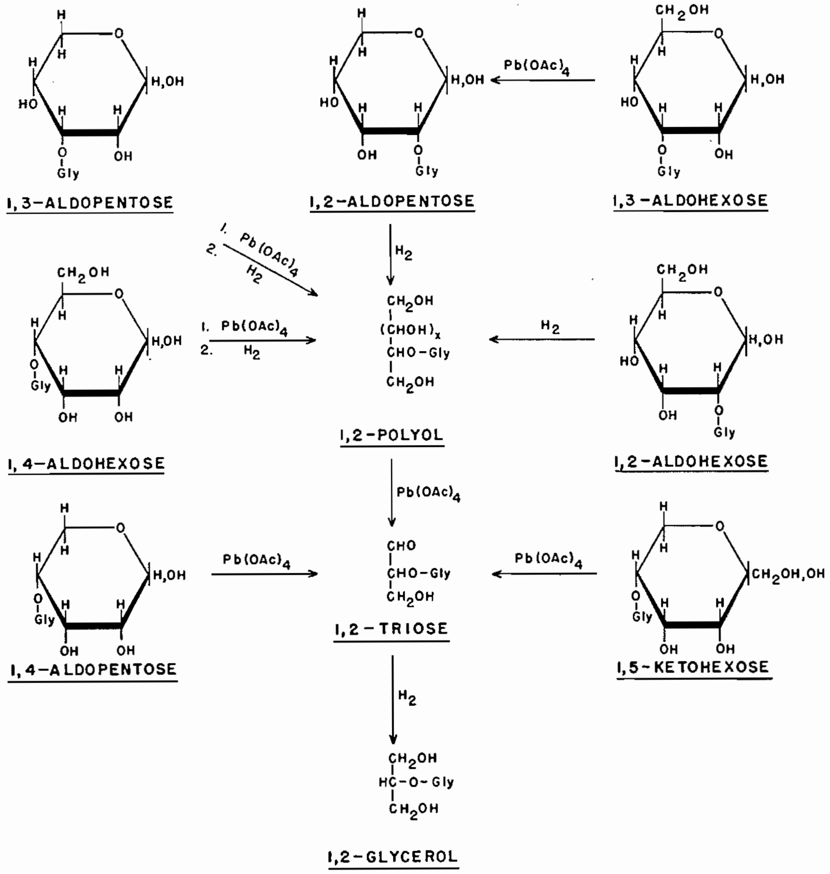

FIG. 1. A schematic representation of the reaction sequence used for degradation of reducing disaccharides to 2-*O*-glycosyl-glycerols. Non-reducing end-units of the disaccharides are denoted by "Gly".

B. 3-*O*-α-D-Xylopyranosyl-L-arabinose (1), from an autohydrolyzate of golden apple gum

$\xrightarrow[(2)\ \mathrm{H}]{(1)\ \mathrm{O}}$ 2-*O*-α-D-xylopyranosyl-L-erythritol (hexabenzoate)

$\xrightarrow[(2)\ \mathrm{H}]{(1)\ \mathrm{O}}$ 2-*O*-α-D-xylopyranosyl-glycerol (pentabenzoate).

C. 4-*O*-β-D-Xylopyranosyl-D-xylose (22) from a partial hydrolysis of wheat flour pentosan (14)

$\xrightarrow[(2)\ \mathrm{H}]{(1)\ 2\mathrm{O}}$ 2-*O*-β-D-xylopyranosyl-glycerol (pentabenzoate).

D. 2-*O*-β-D-Xylopyranosyl-L-arabinose (21) from a partial hydrolyzate of hemicellulose-B of corn cobs

$\xrightarrow{(1)\ \mathrm{H}}$ 2-*O*-β-D-xylopyranosyl-L-arabitol

$\xrightarrow[(2)\ \mathrm{H}]{(1)\ 2\mathrm{O}}$ 2-*O*-β-D-xylopyranosyl-glycerol (pentabenzoate).

E. 3-*O*-α-D-Galactopyranosyl-L-arabinose (17), from a partial hydrolyzate of gum acacia

$\xrightarrow[\text{(2) H}]{\text{(1) O}}$ 2-*O*-α-D-galactopyranosyl-L-erythritol

$\xrightarrow[\text{(2) H}]{\text{(1) O}}$ 2-*O*-α-D-galactopyranosyl-glycerol.

F. 3-*O*-β-D-Galactopyranosyl-D-galactose (6, 17), from a partial hydrolyzate of gum acacia

$\xrightarrow[\text{(2) H}]{\text{(1) O}}$ 4-*O*-β-D-galactopyranosyl-D-arabitol (2-*O*-β-D-galactopyranosyl-D-lyxitol)

$\xrightarrow[\text{(2) H}]{\text{(1) 2O}}$ 2-*O*-β-D-galactopyranosyl-glycerol (hexabenzoate).

G. 5-*O*-α-D-Glucopyranosyl-D-fructose (leucrose) (19), from sucrose by enzymic synthesis with *Leuconostoc mesenteroides*

$\xrightarrow[\text{(2) H}]{\text{(1) 2O}}$ 2-*O*-α-D-glucopyranosyl-glycerol (hexabenzoate).

2-*O*-α-L-Arabopyranosyl-glycerol was synthesized in the following way: 2,3,4-tri-*O*-acetyl-β-L-arabopyranosyl-bromide was condensed with 1,3-*O*-benzylidene-glycerol using the procedure of Carter (2). The crystalline (1′,3′-*O*-benzylidene)-2-*O*-α-L-arabopyranosyl-glycerol thus formed gave a crystalline tribenzoate. Removal of the benzylidene group by catalytic hydrogenolysis (18) afforded sirupy 2-*O*-α-L-arabopyranosyl-glycerol, which was characterized by conversion to its pentabenzoate. The properties of this and other new glycosyl-glycerols and of their respective benzoate derivatives are listed in Table I. The majority of these benzoates appear to be amorphous. However, they have good melting points, give correct analyses, and are readily distinguishable by their specific rotations and infrared absorption spectra.

The results of the present and earlier studies in this series on determining configuration (3, 5) generally agree with those obtained previously by other workers for the same disaccharides. The sole exception is 2-*O*-β-D-xylopyranosyl-L-arabinose, which originally was thought to possess the α-configuration (20). For most of these disaccharides the assignment of configuration had been made by reference to the equilibrium specific rotations of the compounds. This practice has developed as an extension of Hudson's Rules of Isorotation (10), but its correctness has not been rigidly established, chiefly because the rotatory contribution of the reducing end-unit in the equilibrium mixture is not readily assessed. The current results, therefore, characterize more definitively those compounds examined for which configurations had been assigned previously from equilibrium rotation values. Moreover, because of the generally good agreement between the two methods, they provide support for the validity of the polarimetric method.

It appears likely that the configuration of yet other types of reducing disaccharides can be determined by the present procedure. For example, the reducing end-unit of an aldobiuronic acid may be degraded (4) and the carboxyl group of the uronic acid residue reduced to a carbinol group, giving a 2-*O*-glycosyl-glycerol. When glycosyl-glycerols required as reference compounds are not obtainable, e.g., when the related disaccharides

TABLE I

PROPERTIES OF 2-*O*-GLYCOSYL-GLYCEROLS AND DERIVATIVES

				2B	
Compound	Melting point (° C.)	$[\alpha]_D^{27}$*	$[M]_D^{27}$	Found†	Calculated‡
2-*O*-α-L-Arabopyranosyl-glycerol	Sirup	+5°	+1120	+46820	+43140
2-*O*-α-L-Arabopyranosyl-glycerol pentabenzoate	53–57	+93°			
2-*O*-β-L-Arabopyranosyl-glycerol	154–155	+204°	+45700		
2-*O*-β-L-Arabopyranosyl-glycerol pentabenzoate	48–50	+164°			
2-*O*-α-D-Xylopyranosyl-glycerol	Sirup	+95°	+21280	+12990	+14510
2-*O*-α-D-Xylopyranosyl-glycerol pentabenzoate	51–55	+51°			
2-*O*-β-D-Xylopyranosyl-glycerol	Sirup	−37°	−8290		
2-*O*-β-D-Xylopyranosyl-glycerol pentabenzoate	51–53	−36°			
2-*O*-α-D-Galactopyranosyl-glycerol hexabenzoate	156–157	+120°			
2-*O*-β-D-Galactopyranosyl-glycerol hexabenzoate	61–63	+25°			

**Of the glycosyl-glycerols, in water; of the derivatives, in 2,4-lutidine.*

†Sum of the molecular rotations $[M]_D$ for the α- and β-glycosyl-glycerols; temperature 27° C.

‡Sum of the molecular rotations $[M]_D$ for the corresponding α- and β-methyl-glycosides; temperature 20° C. Values taken from Ref. 15.

are unknown, at least one of the anomers may frequently be synthesized. This procedure is likely to prove more simple than synthesis of the disaccharide itself since it involves a condensation with readily available 1,3-disubstituted glycerols, rather than with possibly a rare sugar derivative having one particular hydroxyl group free.

EXPERIMENTAL

Optical rotations were measured at 27° C. Sugars produced by hydrolysis of disaccharides were characterized by paper chromatography. Chromatograms were prepared using Whatman No. 1 filter paper and *n*-butanol–ethanol–water (40: 11: 19, v/v) as solvent. Non-reducing and reducing sugars were detected with ammoniacal silver nitrate (13) and *p*-anisidine hydrochloride sprays (8), respectively. Solutions were concentrated at 40° C. under reduced pressure. Infrared absorption spectra were prepared by the potassium bromide window technique (16).

Disaccharides obtained by partial hydrolysis of polysaccharides were isolated by chromatographic methods. In a typical preparation, wheat flour pentosan (14) (50 g.) was hydrolyzed with 0.1 *N* sulphuric acid (250 ml.) for 5 hours on the steam bath. The products were fractionated on a charcoal column, mono-, di-, and tri-saccharides being separated with varying concentrations of ethanol in water (20). The disaccharide fraction was refractionated on a cellulose column (7) using *n*-butanol half saturated with water as solvent, and the material corresponding to xylobiose (1.0 g.) was recovered. Recrystallized from aqueous methanol it had m.p. 183–185° C., undepressed on admixture with authentic 4-*O*-D-xylopyranosyl-D-xylose.

Some of the disaccharides were sirups, in accordance with the description of these products by other workers. As a check on the isolation procedure, therefore, the component sugars of the compounds were characterized after hydrolysis, and linkage positions determined by lead tetraacetate oxidation (4).

For the sake of brevity, the techniques used in lead tetraacetate oxidations and sodium borohydride reductions are described in full only the first time they are reported. Benzoates were recrystallized from ethanol at −30° C.

*2-O-β-*L*-Arabopyranosyl-glycerol from 3-O-β-*L*-Arabopyranosyl-*L*-arabinose*

Sirupy 3-*O*-β-L-arabopyranosyl-L-arabinose (718 mg.) was dissolved in water (2 ml.), and acetic acid (150 ml.) was then added. The solution was treated with lead tetraacetate (1.2 g., 1.1 molar equivalents) and after 10 minutes the divalent lead was removed from solution by addition of 10% oxalic acid in acetic acid. The suspension was stirred for 0.5 hour, then filtered, and the filtrate was evaporated to dryness. The material obtained was dissolved in water (50 ml.) and deionized with a mixture of Amberlite IR-120 and Dowex-1 resin. Sodium borohydride (0.5 g.) was then added and after 15 minutes excess reagent was decomposed with acetic acid. The solution was treated with Amberlite IR-120 resin and evaporated to a crust, which was dissolved in methanol. The solution was evaporated in order to remove the excess boric acid. This procedure was repeated three times to give sirupy 2-*O*-β-L-arabopyranosyl-L-erythritol (415 mg.) with $[\alpha]_D$ +135° (*c*, 1.70, water).

The erythritol derivative (22 mg.) was benzoylated (procedure described under "2-*O*-α-L-arabopyranosyl-glycerol"). Two recrystallizations of the product from ethanol gave the hexabenzoate as white needles (41 mg.) with m.p. 131–134° C. and $[\alpha]_D$ +114° (*c*, 1.0, 2,4-lutidine). Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found, C, 70.03%; H, 4.84%.

The arabopyranosyl-erythritol (304 mg.) was oxidized with lead tetraacetate (590 mg.) in acetic acid (60 ml.) containing water (1 ml.). After the oxidation was completed the reaction mixture was worked up and the product reduced in the usual way with sodium borohydride. A mixture of compounds was produced and these were fractionated on a cellulose column using *n*-butanol half saturated with water as the mobile phase. The 2-*O*-β-L-arabopyranosyl-glycerol (83 mg.) crystallized and was twice recrystallized from ethanol. The product (64 mg.) had m.p. 154–155° C. and $[\alpha]_D$ +204° (*c*, 1.2, water). Calculated for $C_8H_{16}O_7$: C, 42.85%; H, 7.19%. Found: C, 43.04%; H, 7.20%. Hydrolysis of the material produced arabinose and glycerol. The infrared absorption spectrum of the compound differed from that of its α-anomer.

The glycerol derivative was converted to the pentabenzoate, which had m.p. 48–50° C. and $[\alpha]_D$ +164° (*c*, 0.8, 2,4-lutidine). Calculated for $C_{43}H_{36}O_{12}$: C, 69.35%; H, 4.87%. Found: C, 69.47%; H, 4.43%.

*2-O-α-*D*-Xylopyranosyl-glycerol from 3-O-α-*D*-Xylopyranosyl-*L*-arabinose*

Sirupy 3-*O*-α-D-xylopyranosyl-L-arabinose (452 mg.) was dissolved in water (2 ml.), and acetic acid (100 ml.) was added followed by lead tetraacetate (990 mg.). After 15 minutes the reaction mixture was worked up as described above and the product was reduced with sodium borohydride to give sirupy 2-*O*-α-D-xylopyranosyl-L-erythritol (338 mg.), which had $[\alpha]_D$ +91° (*c*, 0.9, water).

The erythritol derivative (42 mg.) was benzoylated and the product recrystallized three times from ethanol. It (60 mg.) had m.p. 64–67° C. and $[\alpha]_D$ +98° (*c*, 1.1, 2,4-lutidine). Calculated for $C_{51}H_{42}O_{14}$: C_6H_5CO, 71.7%. Found: C_6H_5CO, 71.5%.

2-*O*-α-D-Xylopyranosyl-L-erythritol (209 mg.) was oxidized with lead tetraacetate (400 mg.) in acetic acid (75 ml.) containing water (1.5 ml.). After the oxidation was completed the reaction mixture was worked up and the product reduced with aqueous sodium borohydride. The resulting 2-*O*-α-D-xylopyranosyl-glycerol was contaminated with a little of the erythritol derivative and the mixture was fractionated on a cellulose column using *n*-butanol, one-third saturated with water, as solvent. The purified sirup had $[\alpha]_D$ +95° (*c*, 1.5, water) and gave xylose and glycerol on hydrolysis.

The glycerol derivative (61 mg.) was converted to its pentabenzoate, three recrystallizations from ethanol yielding a product with m.p. 51–55° C. and $[\alpha]_D$ +51° (*c*, 1.1, 2,4-lutidine). Calculated for $C_{43}H_{36}O_{12}$: C_6H_5CO, 70.6%. Found: C_6H_5CO, 70.9%.

2-O-β-D-Xylopyranosyl-glycerol from 4-O-β-D-Xylopyranosyl-D-xylose

The xylobiose (428 mg.) was dissolved in water (2 ml.), and acetic acid (100 ml.) and lead tetraacetate (1.35 g.) added. After 3 hours the 2-*O*-β-D-xylopyranosyl-D-glyceraldehyde was isolated and converted by sodium borohydride reduction to sirupy 2-*O*-β-D-xylopyranosyl-glycerol (200 mg.) with $[\alpha]_D$ −37° (*c*, 1.1, water). Hydrolysis of the material gave xylose and glycerol.

The glycerol derivative (90 mg.) was benzoylated to give the pentabenzoate, which after three recrystallizations from ethanol had m.p. 51–53° C. and $[\alpha]_D$ −36° (*c*, 0.9, 2,4-lutidine). Yield 33 mg. Calculated for $C_{43}H_{36}O_{12}$: C, 69.35%; H, 4.87%. Found: C, 69.62%; H, 4.83%. The infrared absorption spectrum differed from that of the α-anomer.

2-O-β-D-Xylopyranosyl-glycerol from 2-O-β-D-Xylopyranosyl-L-arabinose

Sirupy 2-*O*-β-D-xylopyranosyl-L-arabinose (465 mg.) was reduced to crystalline 2-*O*-β-D-xylopyranosyl-L-arabitol using sodium borohydride. The product was recrystallized twice from methanol–ethanol and had m.p. 185–187° C. and $[\alpha]_D$ −33° (*c*, 1.2, water). Yield 235 mg. Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.45%; H, 7.15%.

The arabitol derivative (152 mg.) was oxidized in water (0.4 ml.) and acetic acid (40 ml.) with lead tetraacetate (0.59 g.) for 18 hours. The resulting glyceraldehyde derivative was reduced with sodium borohydride to sirupy 2-*O*-β-D-xylopyranosyl-glycerol (135 mg.) having $[\alpha]_D$ −30° (*c*, 1.3, water). The infrared absorption spectrum was identical with that of an authentic specimen. The material gave xylose and glycerol on hydrolysis.

The glycerol derivative (72 mg.) was converted to its pentabenzoate, which after three recrystallizations from ethanol had m.p. 51–53° C., undepressed on admixture with an authentic specimen of 2-*O*-β-D-xylopyranosyl-glycerol pentabenzoate; $[\alpha]_D$ −35° (*c*, 1.2, 2,4-lutidine). Yield 41 mg. Calculated for $C_{43}H_{36}O_{12}$: C, 69.35%; H, 4.87%. Found: C, 69.67%; H, 4.50%. The material had an infrared absorption spectrum identical with that of authentic 2-*O*-β-D-xylopyranosyl-glycerol pentabenzoate and different from that of the α-anomer.

2-O-α-D-Galactopyranosyl-glycerol from 3-O-α-D-Galactopyranosyl-L-arabinose

3-*O*-α-D-Galactopyranosyl-L-arabinose (1.84 g.) was oxidized with lead tetraacetate (2.5 g.) for 10 minutes in acetic acid (250 ml.) containing water (4 ml.). The reaction product was converted by sodium borohydride reduction to 2-*O*-α-D-galactopyranosyl-L-erythritol, which on recrystallization from aqueous ethanol had m.p. 156–158° C. and $[\alpha]_D$ +145° (*c*, 1.0, water). Yield 1.0 g. Calculated for $C_{10}H_{20}O_9$: C, 42.25%; H, 7.09%. Found: C, 42.16%; H, 7.11%.

The erythritol derivative (560 mg.) was oxidized for 3 hours with lead tetraacetate (860 mg.) in acetic acid (100 ml.) containing water (2 ml.). The reaction mixture was worked up and the product reduced with aqueous sodium borohydride to give a mixture of unchanged material and 2-*O*-α-D-galactopyranosyl-glycerol. These were separated on a cellulose column using *n*-butanol half saturated with water as solvent. The gylcosyl-glycerol (250 mg.) was recrystallized from ethanol and had m.p. 131–132° C., undepressed on admixture with an authentic specimen of 2-*O*-α-D-galactopyranosyl-glycerol (12); $[\alpha]_D$ +164° (*c*, 0.7, water). Calculated for $C_9H_{18}O_8$: C, 42.52%; H, 7.14%. Found: C, 42.55%; H, 7.17%. The infrared absorption spectra of the product and of the authentic α-anomer were identical.

2-O-α- and 2-O-β-D-Galactopyranosyl-glycerol Hexabenzoates

2-*O*-α-D-Galactopyranosyl-glycerol (46 mg.) was benzoylated to give its hexabenzoate (76 mg.) having m.p. 156–157° C. and $[\alpha]_D$ +120° (*c*, 1.4, 2,4-lutidine) after two recrystallizations from ethanol. Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.24%; H, 4.73%.

The β-anomer (46 mg.) was benzoylated yielding, after four precipitations from ethanol, an amorphous powder (53 mg.) which had m.p. 61–63° C. and $[\alpha]_D$ +25° (*c*, 0.6, 2,4-lutidine). Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.20%; H, 5.37%. The two anomeric hexabenzoates had readily distinguishable infrared absorption spectra.

2-O-β-D-Galactopyranosyl-glycerol from 3-O-β-D-Galactopyranosyl-D-galactose

3-*O*-β-D-Galactopyranosyl-D-galactose (500 mg.) was dissolved in acetic acid (100 ml.) containing water (1 ml.) and oxidized with lead tetraacetate (900 mg.). After 20 minutes the reaction mixture was worked up and reduced with sodium borohydride to give 4-*O*-β-D-galactopyranosyl-D-arabitol (2-*O*-β-D-galactopyranosyl-D-lyxitol (390 mg.), which was recrystallized twice from ethanol to give a material with m.p. 177–179° C. and $[\alpha]_D$ −7° (*c*, 0.6, water). Calculated for $C_{11}H_{22}O_{10}$: C, 42.03%; H, 7.06%. Found: C, 41.99%; H, 7.06%.

The disaccharide (310 mg.), thus obtained, was oxidized with lead tetraacetate (860 mg.) for 2 hours in acetic acid (50 ml.) containing water (0.8 ml.). The product was reduced with aqueous sodium borohydride to give a mixture which contained 2-*O*-β-D-galactopyranosyl-glycerol. This was fractionated on a cellulose column using *n*-butanol half saturated with water as the mobile phase. The D-galactosyl-glycerol (100 mg.) could not be induced to crystallize. Therefore a portion (41 mg.) was converted to its hexabenzoate, which after two successive precipitations from ethanol had m.p. 56–59° C., undepressed on admixture with authentic 2-*O*-β-D-galactopyranosyl-glycerol hexabenzoate, and $[\alpha]_D$ +36° (*c*, 0.7, 2,4-lutidine). Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.53%; H, 4.83%. The infrared absorption spectrum was identical with that of the β-galactose hexabenzoate derivative and differed from that of the α-anomer.

2-O-α-D-Glucopyranosyl-glycerol from 5-O-α-D-Glucopyranosyl-D-fructose

5-*O*-α-D-Glucopyranosyl-D-fructose (225 mg.) was oxidized with lead tetraacetate (580 mg.) in acetic acid (50 ml.) containing water (1 ml.). After 3 hours' reaction time the product was reduced using sodium borohydride to give a mixture of materials from which 2-*O*-α-D-glucopyranosyl-glycerol (85 mg.) was isolated by chromatography on a cellulose column using *n*-butanol half saturated with water as solvent. It had $[\alpha]_D$ +119° (*c*, 0.7, water), an infrared absorption spectrum identical with that of the α-anomer but different from that of the β-anomer, and gave glucose and glycerol on acid hydrolysis.

The glycerol derivative was converted to its hexabenzoate, which was recrystallized twice from ethanol. It had m.p. 137–138° C., unchanged on admixture with authentic 2-*O*-α-D-glucopyranosyl-glycerol hexabenzoate, and $[\alpha]_D$ +94° (*c*, 0.8, $CHCl_3$); it gave an infrared absorption spectrum identical with that of 2-*O*-α-D-glucopyranosyl-glycerol hexabenzoate, but unlike the β-anomer. Calculated for $C_{51}H_{42}O_{14}$: C, 69.69%; H, 4.82%. Found: C, 69.82%; H, 4.80%.

2-O-α-L-Arabopyranosyl-glycerol

A mixture of tri-*O*-acetyl-β-L-arabopyranosyl-bromide (8.4 g.), 1,3-*O*-benzylidene-glycerol (7.5 g.), silver carbonate (20 g.), and Drierite (50 g.) in benzene (125 ml.) was shaken for 3 hours at 55° C. It was then refluxed for 15 minutes, the solution was filtered, and chloroform (200 ml.) was then added to the filtrate followed by sodium methoxide (0.5 g.) in methanol (20 ml.). After 18 hours at room temperature the solution was evaporated to a sirup which was fractionated on a cellulose column. Benzene eluted unchanged 1,3-*O*-benzylidene-glycerol, and benzene–ethanol–water (3 : 1 : trace, v/v) eluted (1′,3′-*O*-benzylidene)-2-*O*-α-L-arabopyranosyl-glycerol (3.1 g.). The product crystallized and was recrystallized twice from methanol–ether, m.p. 121–122° C. and $[\alpha]_D$ +4° (*c*, 1.1, ethanol). Calculated for $C_{15}H_{20}O_7$: C, 57.68%; H, 6.40%. Found: C, 57.73%; H, 6.48%.

The product (46 mg.) was dissolved in chloroform (0.30 ml.) containing pyridine (0.20 ml.) and benzoyl chloride (0.12 ml.). After 18 hours the reaction mixture was dissolved in chloroform to which a little methanol was added, and the solution was washed successively with 1% sulphuric acid, aqueous sodium bicarbonate, and water, then dried with magnesium sulphate, filtered, and evaporated to a sirup which crystallized. Three recrystallizations from ethanol gave a product softening at 160–165° C. and melting at 170–172° C., with $[\alpha]_D$ +114° (*c*, 0.9, 2,4-lutidine). Calculated for $C_{36}H_{32}O_{10}$: C, 69.22%; H, 5.16%. Found: C, 69.47%; H, 5.18%.

The 1,3-benzylidene-L-arabinosyl-glycerol (28 mg.) was dissolved in ethanol (25 ml.) and the solution was shaken with palladium oxide (80 mg.) in an atmosphere of hydrogen for 18 hours. The product, obtained as a sirup by filtration and evaporation of the solution, had $[\alpha]_D$ +5° (*c*, 1.0, water).

2-O-α-L-Arabopyranosyl-glycerol Pentabenzoate

The L-arabopyranosyl-glycerol (93 mg.) was benzoylated and the product, after three recrystallizations from ethanol, had m.p. 53–57° C. and $[\alpha]_D$ +93° (*c*, 0.9, 2,4-lutidine). Yield 61 mg. Calculated for $C_{43}H_{36}O_{12}$: C_6H_5CO, 70.6%. Found: C_6H_5CO, 70.8%.

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REFERENCES

1. Andrews, P. and Jones, J. K. N. J. Chem. Soc. 4134 (1954).
2. Carter, N. M. Ber. **63**, 1684 (1930).
3. Charlson, A. J., Gorin, P. A. J., and Perlin, A. S. Can. J. Chem. **34**, 1811 (1956).
4. Charlson, A. J. and Perlin, A. S. Can. J. Chem. **34**, 1200 (1956).
5. Charlson, A. J. and Perlin, A. S. Can. J. Chem. **34**, 1804 (1956).
6. Hirst, E. L. and Perlin, A. S. J. Chem. Soc. 2622 (1954).
7. Hough, L., Jones, J. K. N., and Wadman, W. H. J. Chem. Soc. 2511 (1949).
8. Hough, L., Jones, J. K. N., and Wadman, W. H. J. Chem. Soc. 1702 (1950).
9. Hudson, C. S. J. Am. Chem. Soc. **31**, 66 (1909).
10. Hudson, C. S. J. Am. Chem. Soc. **38**, 1566 (1916).
11. Jones, J. K. N. J. Chem. Soc. 1672 (1953).
12. Nunn, J. R. and Holdt, M. M. von. J. Am. Chem. Soc. **77**, 2551 (1955).
13. Partridge, S. M. Nature, **158**, 270 (1946).
14. Perlin, A. S. Cereal Chem. **28**, 370 (1951).
15. Polarimetry, saccharimetry, and the sugars. Natl. Bur. Standards (U.S.), Circ. C440, Govt. Printing Office, Washington, D.C. 1942.
16. Schiedt, U. and Reinwein, H. Z. Naturforsch. **7b**, 270 (1952).
17. Smith, F. J. Chem. Soc. 744 (1939).
18. Stimmel, B. F. and King, C. G. J. Am. Chem. Soc. **56**, 1774 (1934).
19. Stodola, F. H., Koepsell, H. J., and Sharpe, E. S. J. Am. Chem. Soc. **74**, 3202 (1952).
20. Whistler, R. L. and Durso, D. F. J. Am. Chem. Soc. **72**, 677 (1950).
21. Whistler, R. L. and McGilvray, D. I. J. Am. Chem. Soc. **77**, 1884 (1955).
22. Whistler, R. L. and Tu, C. C. J. Am. Chem. Soc. **73**, 1389 (1951).