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SYNTHESIS OF *O*-β-D-MANNOPYRANOSYL-(1→4)-*O*-α-L-RHAMNOPYRANOSYL-(1→3)-D-GALACTOPYRANOSE, THE TRISACCHARIDE REPEATING-UNIT OF THE O-SPECIFIC POLYSACCHARIDE FROM *Salmonella anatum**

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ABSTRACT

Glycosylation of 1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose with 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-α-L-rhamnopyranosyl bromide, followed by removal of the protecting groups, gave *O*-β-D-mannopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→3)-D-galactose, which is the trisaccharide repeating-unit of the O-specific polysaccharide chain of the lipopolysaccharide from *Salmonella anatum*. The formation of the β-D-mannopyranosyl linkage was achieved by a glucose–mannose conversion *via* stereoselective reduction of the corresponding oxo-disaccharide.

INTRODUCTION

The O-specific chains of the somatic antigens of Gram-negative bacteria are built up of repeating oligosaccharide units, the chemical structures of which are unique for each serological type[1]. The most extensively investigated polymers are the antigenic lipopolysaccharides of the *Salmonella* genus, for many serotypes of which the chemical structures of the O-specific polysaccharide chains have been established[2,3]. However, the synthetic work related to these specific polysaccharides and their fragments, which are important for immunological and biochemical studies, has been limited so far to several disaccharide fragments[4–6]. Obviously, the synthesis of specific, repeating oligosaccharide units could be the first step in the synthesis of specific polysaccharides.

The polysaccharide chain of the somatic antigen of *Salmonella anatum* possesses the simplest repeating-unit, namely the trisaccharide *O*-β-D-mannopyranosyl-(1→4)-*O*-α-L-rhamnopyranosyl-(1→3)-D-galactose (**9**). The polysaccharide chains for all the *Salmonella* serotypes belonging to the serological group E^3 appear to be made up of the trisaccharide unit **9**.

*Dedicated to the memory of Dr. Hewitt G. Fletcher, Jr.

Recently, we described[8,9] the synthesis of the acetylated derivatives of **9** by a scheme which involved construction of the oligosaccharide starting from the non-reducing end, *i.e.*, β-D-Glc*p*-(1→4)-L-Rha → β-D-Man*p*-(1→4)-L-Rha → β-D-Man*p*-(1→4)-α-L-Rha*p*-(1→3)-D-Gal. The formation of the β-D-mannopyranosyl linkage was achieved by conversion of the β-D-glucopyranose moiety of benzyl 2,3-*O*-isopropylidene-4-*O*-(3,4,6-tri-*O*-benzyl-β-D-glucopyranosyl)-α-L-rhamnopyranoside (**1**) by oxidation to benzyl 2,3-*O*-isopropylidene-4-*O*-(3,4,6-tri-*O*-benzyl-β-D-*arabino*-hexopyranosylulose)-α-L-rhamnopyranoside (**2**) followed by platinum-catalysed reduction of the ketone function. The 3-substituted D-galactose residue was synthesised by glycosylation of benzyl 2,6-di-*O*-acetyl-β-D-galactopyranoside[10] and led to two trisaccharide derivatives with (1→4),(1→3) and (1→4),(1→4) linkages, respectively.

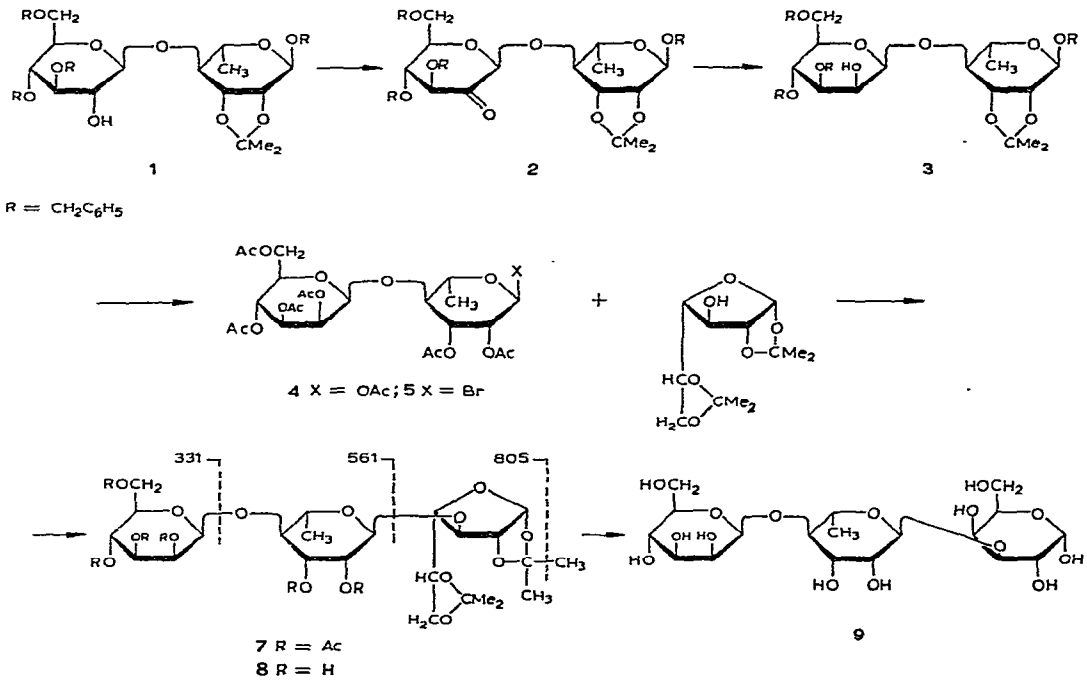
We now describe a synthesis of **9** according to a scheme which includes a new variant for the stereoreduction of the ketone **2** and also the use of 1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose (**6**) for the contruction of the 3-substituted galactopyranose residue.

RESULTS AND DISCUSSION

The disaccharide derivative **1**, which contains a convenient combination of protecting groups for subsequent synthesis, was obtained in high yield by glycosylation of benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[11] in nitromethane with 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl bromide[9] in the presence of mercuric cyanide, followed by deacetylation. The presence of the β-(1→4)-linkage was proved by transformation of **1** into known 4-*O*-β-D-glucopyranosyl-L-rhamnose hepta-acetate[12] by removal of the isopropylidene group with trifluoroacetic acid followed by palladium-catalysed hydrogenolysis and acetylation of the product. To invert the configuration at position 2 of the glucose residue in **1**, HO-2 was oxidised to a keto group which was then stereoselectively reduced[13,14].

Oxidation of **1** with the Pfitzner–Moffatt reagent[15] gave a high yield of the ketone **2** which was isolated as the crystalline ethanolate. The i.r. spectrum of **2** contained an intense carbonyl band (1760 cm^{-1}) and a weak band for hydroxyl.

When **2** was reduced[8,9] over Adams' catalyst, a by-product was formed which apparently arose because of partial hydrogenation of the benzyl groups. According to Theander[13], reduction of methyl β-D-*arabino*-hexopyranosidulose with sodium borohydride at room temperature gave a mixture of *manno* and *gluco* products in the ratio 65:35. We have found that, on reduction of **2** with sodium borohydride, the proportion of the *manno* isomer in the product mixture is increased with the elevation of temperature. At 60°, the reduction was almost stereospecific and afforded mainly benzyl 2,3-*O*-isopropylidene-4-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-α-L-rhamnopyranoside (**3**). When **3** was subjected in sequence to hydrogenation over palladium-on-charcoal to remove benzyl groups, acetylation, hydrolysis with trifluoroacetic acid to remove the isopropylidene group, and acetylation, 4-*O*-β-D-mannopyranosyl-L-rhamnopyranose hepta-acetate (**4**) was obtained. The structure of **4** was proved by



n.m.r. and mass-spectral data. Deacetylation of **4** gave a chromatographically homogeneous disaccharide, acid hydrolysis of which yielded mannose and rhamnose in the ratio 1:1. Methylation analysis of the disaccharide gave 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylmannitol and 1,4,5-tri-*O*-acetyl-2,3-di-*O*-methylrhamnitol which were identified by g.l.c.–m.s. The β-configuration of the mannosidic linkage in **4** was proved by treatment of the corresponding glycosylalditol acetate with chromium trioxide[16,17], which completely oxidised the D-mannopyranose residue. A control sample of 4-*O*-α-D-mannopyranosyl-L-rhamnitol hepta-acetate was resistant to oxidation.

The final step in the synthesis of the trisaccharide **9** consisted of attaching the disaccharide β-D-Man*p*-(1→4)-Rha to D-galactose at position 3. In earlier work[8,9], the selective glycosylation at position 3 of a galactose derivative having HO-3 and HO-4 unsubstituted was attempted (*cf.* ref. 10). However, a mixture of isomeric trisaccharides was obtained.

The development of specific syntheses of 3-linked galactopyranose residues is important since this type of glycosidic linkage occurs in the repeating units of antigenic polysaccharides of bacteria belonging to serological groups A, D, and E of the *Salmonella* genus[3]. 1,2:5,6-Di-*O*-isopropylidene-α-D-galactofuranose (**6**) is a potentially useful derivative for such syntheses, and we have developed a procedure for its preparation by the direct acetonation of galactose[18]. An analogous synthesis of **6**, using different conditions, was reported recently[19].

The glycosylation of **6** in acetonitrile in the presence of mercuric cyanide by 2,3-di-*O*-acetyl-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-α-L-rhamnopyranosyl bromide (**5**), obtained from the hepta-acetate **4**, yielded 22% of the trisaccharide derivative **7**. We have shown[18] that glycosylation of **6** by 2,3-di-*O*-acetyl-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-α-L-rhamnopyranosyl bromide gave up to 60% of product and was not accompanied by isopropylidene migration. The moderate yield of **7** may be due to the instability of the glycosyl bromide **5** which, unlike its glucose analogue, was not obtained in crystalline form. The trisaccharide **7** was homogeneous in g.l.c. and t.l.c., and its structure was confirmed by mass and n.m.r.-spectral data. The principal m.s. fragmentation pathways are shown in formula **7** and are analogous to those reported[18] for the glucose analogue. The assumption of an α-configuration for the (1→3)-linkage in **7** was based on the fact that 2,3,4-tri-*O*-acetyl-α-L-rhamnosyl halides yield α-L-rhamnopyranosides.

In the n.m.r. spectrum of **7**, signals for OAc, CMe, and CMe_2 groups were observed. However, the ratio for OAc to CMe protons was 1.8:1 and not that (1.4:1) expected for seven OAc and five CMe groups, thus indicating the presence of a second product. The side products[20] of $Hg(CN)_2$-catalyzed glycosylation reactions are nitriles of 2,6-anhydroaldonic acids or acetals of pyruvonitrile which are formed from the corresponding acetohalogenoses. It was found that, in acetonitrile in the presence of $Hg(CN)_2$, the glycosyl bromide was readily converted into a mixture of three compounds, one of which had a chromatographic mobility identical to that of **7**. This product may be the contaminant of **7** noted above.

It was expected that the conversion of **7** into the unsubstituted trisaccharide **9** could be performed by successive removal of the protecting groups. However, the galactofuranose residue in **7** was destroyed both in mild acidic and alkaline conditions. An attempt to remove the isopropylidene groups using trifluoroacetic acid in chloroform[21] gave a product which was not a trisaccharide since there were only ions of fragments corresponding to a hexosyl-(1→6)-deoxyhexose in the mass spectrum of its acetate. An attempt to first remove (Zemplén reaction at 0°) the acetyl groups from **7** yielded four compounds with R_{GAL} 0.9 (main product), 1.45, 1.70, and 2.30. The substitution of sodium methoxide by triethylamine gave the same products, but that with R_{GAL} 2.30 preponderated. When the four products were isolated (p.c.) and hydrolysed with acid, the first three gave mannose and rhamnose, whereas that with R_{GAL} 2.30 also gave galactose.

In order to determine whether the foregoing products were due to non-homogeneity of **7**, the product was saponified with methanolic triethylamine, and **8** (R_{GAL} 2.3) was isolated (p.c.) from the product mixture in 31% yield. Acetylation of **8** gave **7**, which when subjected to Zemplén deacetylation gave the mixture of products described above. Thus, the lability of **7** may be a characteristic property and is being further investigated.

When the trisaccharide **8**, which contains a galactofuranose residue, was subjected to mild hydrolysis with acid, it was readily converted into **9**. Complete, acid hydrolysis of **9** gave mannose, rhamnose, and galactose in the ratios of 1:1:0.9, and

acetylation afforded a product which was identical (g.l.c.) with the acetylated trisaccharide previously described[8,9].

EXPERIMENTAL

Melting points were determined with a Kofler apparatus. N.m.r. spectra were recorded on a Varian DA-60-IL spectrometer with hexamethyldisiloxane as internal standard. Mass spectra were obtained with Varian MAT CH-6, and chromato-mass spectra with a Varian MAT 111 "GNOM" spectrometer. Optical rotations were determined with a Perkin–Elmer 141 polarimeter, and i.r. spectra were determined with a Karl-Zeiss UR-20 spectrometer. G.l.c. was carried out using a Pye Unicam 104 model 64 chromatograph. T.l.c. was performed on silica gel "KSK", and p.l.c. on silica gel containing 5% of gypsum. P.c. was carried out by the ascending method on Filtrak FN 11 paper. Reducing sugars were detected with aniline hydrogen phthalate, and alkaline silver nitrate was used for non-specific detection. Solutions were evaporated *in vacuo* at 40°.

Benzyl 4-O-(2-O-acetyl-3,4,6-tri-O-benzyl-2,3-O-isopropylidene-β-D-glucopyranosyl)-α-L-rhamnopyranoside. — To a solution of 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-glucopyranosyl bromide[9] (12 g) and benzyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside[11] (2.6 g) in 260 ml of anhydrous nitromethane, mercuric cyanide (3 g) was added and the mixture was stirred for 3 h at 20°. The mixture was extracted with ether (2 × 500 ml), and the extract was dried (Na_2SO_4) and concentrated to dryness. The residue was eluted from silica gel with ethyl acetate–light petroleum (15:85). Fractions containing the substance with R_F 0.7 (t.l.c., benzene–ether, 10:1) were combined and concentrated to give the title compound (5 g, 80%) as a syrup, $[\alpha]_D^{20}$ −20° (*c* 3.3, chloroform). N.m.r. data (CCl_4): δ 7.0–8.0 (20 H, aromatic protons), 1.9 (3 H, AcO), 1.3 and 1.5 (2 s, 6 H, CMe_2), 1.32 (d, 3 H, $J_{5,6}$ 5 Hz, rhamnose CMe).

Anal. Calc. for $C_{45}H_{52}O_{11}$: C, 70.50; H, 6.78. Found: C, 70.12; H, 6.85.

Benzyl 2,3-O-isopropylidene-4-O-(3,4,6-tri-O-benzyl-β-D-glucopyranosyl)-α-L-rhamnopyranoside (**1**). — To a solution of the foregoing disaccharide derivative (5 g) in methanol (50 ml), 2 ml of 0.1M methanolic sodium methoxide were added, and the mixture was kept overnight at room temperature and then concentrated. The residue was crystallized from methanol to give **1** (4.5 g, 80%), m.p. 101–104°, $[\alpha]_D^{20}$ −20° (*c* 2, chloroform). N.m.r. data ($CDCl_3$): δ 7.0–8.0 (20 H, aromatic protons), 1.3 and 1.5 (2 s, 6 H, CMe_2), 1.32 (d, 3 H, $J_{5,6}$ 5 Hz, rhamnose CMe).

Anal. Calc. for $C_{43}H_{50}O_{10}$: C, 71.05; H, 6.93. Found: C, 71.11; H, 7.03.

Compound **1** (100 mg) was treated with trifluoroacetic acid[20] to remove the isopropylidene group, and the product was debenzylated over palladium-on-charcoal and subsequently acetylated to give 4-*O*-β-D-glucopyranosyl-α-L-rhamnopyranose hepta-acetate, m.p. 98–100°; lit.[12] m.p. 98°.

Benzyl 2,3-O-isopropylidene-4-O-(3,4,6-tri-O-benzyl-β-D-arabino-hexopyranosyl-ulose)-α-L-rhamnopyranoside (**2**). — To a solution of **1** (3 g) in 150 ml of methyl sulphoxide, acetic anhydride (7 ml) was added, and the mixture was kept under nitrogen

for 4 days at room temperature. After lyophilization of the mixture, the residue was eluted from a column of silica gel with a gradient of light petroleum–ethyl acetate. Fractions containing the product with R_F 0.45 (t.l.c., benzene–ether, 10:1) were combined and concentrated to give **2** (2.26 g, 75%), m.p. 102–104° (from ethanol), $[\alpha]_D^{20}$ −40° (*c* 1.7, chloroform), ν_{max} 1760 (strong, C=O) and 3600 cm^{-1} (weak, hydroxyl). N.m.r. data ($CDCl_3$): δ 7.0–8.0 (20 H, aromatic protons), 1.3 and 1.5 (2 s, 6 H, CMe_2), 1.32 (d, 3 H, $J_{5,6}$ 5 Hz, rhamnose CMe).

Anal. Calc. for $C_{43}H_{48}O_{10}\cdot C_2H_5OH$: C, 70.01; H, 7.00. Found: C, 69.62; H, 6.81.

*1,2,3-Tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-mannopyranosyl)-α-*L*-rhamnopyranose* (**4**). — To a solution of **2** in ethanol (150 ml), water (46 ml) and sodium borohydride (1.3 g) were added, and the mixture was kept for 45 min at 60°. More sodium borohydride (1 g) was added, and the mixture was heated for 45 min. The cooled solution was neutralised with KU-2(H^+) resin and filtered, and the resin was washed with methanol. The combined filtrate and washings were concentrated and boric acid was removed from the residue by repeated distillation of methanol therefrom. The residue was then eluted from silica gel with light petroleum to give benzyl 2,3-*O*-isopropylidene-4-*O*-(3,4,6-tri-*O*-benzyl-β-D-mannopyranosyl)-α-L-rhamnopyranoside (**3**; 2.01 g, 88%), R_F 0.4 (t.l.c., ethyl acetate–light petroleum, 3:7), and the *gluco* analogue (0.13 g, 6%).

A solution of **3** (2 g) in ethanol (200 ml) was hydrogenolysed in the presence of 10% palladium-on-charcoal (2 g), the reaction being monitored by u.v. spectroscopy. The mixture was then filtered and concentrated to give a solid (1.1 g), R_F 0.25 (t.l.c.; chloroform–acetone, 7:3), conventional treatment of which with acetic anhydride–pyridine afforded a syrupy product (1.61 g), R_F 0.6 (t.l.c., chloroform–acetone, 7:3). To a solution of this product in chloroform (70 ml), aqueous trifluoroacetic acid (99:1, 8 ml) was added, the mixture was stored for 50 min at room temperature and then concentrated *in vacuo*, and toluene was repeatedly evaporated from the residue to remove trifluoroacetic acid. The residue was then acetylated, and the product was purified by p.l.c. (chloroform–acetone, 9:1) to give syrupy **4** (0.9 g), $[\alpha]_D^{20}$ −57° (*c* 2, chloroform). N.m.r. data ($CDCl_3$): δ 5.9 (d, 1 H, $J_{1,2}$ 2 Hz, rhamnose H-1), 1.9–2.1 (21 H, 7 AcO), 1.3 (d, 3 H, *J* 5 Hz, rhamnose CMe). Mass spectrum: *m/e* 331, 273, and 560 (M − AcOH).

Anal. Calc. for $C_{26}H_{36}O_{17}$: C, 50.32; H, 5.85. Found: C, 49.52; H, 5.82.

Deacetylation of **4** (10 mg) with methanolic sodium methoxide afforded 4-*O*-β-D-mannopyranosyl-L-rhamnose, R_F 0.9 (p.c., 1-butanol–pyridine–water, 6:4:3), hydrolysis of which (M sulphuric acid, 4 h, 100°) afforded (g.l.c. of alditol acetates) mannose and rhamnose. Methylation of the disaccharide and subsequent acid hydrolysis, reduction with sodium borohydride, and acetylation gave (g.l.c.–m.s.) 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methylmannitol and 1,4,5-tri-*O*-acetyl-2,3-di-*O*-methylrhamnitol.

*Oxidation of octa-*O*-acetyl-β- and -α-D-mannopyranosyl-L-rhamnitol with chromium trioxide in acetic acid.* — To a solution of octa-*O*-acetyl-β-D-manno-

pyranosyl-L-rhamnitol (5 mg) and hexa-*O*-acetylgalactitol (2.5 mg) in glacial acetic acid (5 ml), chromium trioxide (20 mg) was added, and the mixture was stirred for 1 h at 50°. The cooled mixture was diluted with water, neutralized with calcium carbonate, and extracted with chloroform (3 × 10 ml). The extract was concentrated and a solution of the residue in aqueous methanol (50%, 5 ml) was reduced with sodium borohydride (30–40 mg) for 10 h at room temperature. The mixture was neutralized with KU-2(H^+) resin, filtered, and concentrated. The residue was treated with acetic anhydride–pyridine and analyzed by g.l.c. (3% ECNSS-M column at 190°). The acetates of mannitol, glucitol, rhamnitol, and galactitol were detected in the ratios 0.7:0.3:1.1.

In the product mixture from the corresponding α-isomer, the starting glycoside and hexa-*O*-acetylgalactitol were identified (g.l.c., SE-30 column) in the same ratio as in the mixture prior to oxidation.

3-O-[2,3-Di-O-acetyl-(2,3,4,6-tetra-O-acetyl-β-D-mannopyranosyl)-α-L-rhamnopyranosyl]-1,2:5,6-di-O-isopropylidene-α-D-galactofuranose (**7**). — A solution of **4** (280 mg) in glacial acetic acid (0.6 ml) was treated with 0.7 ml of a 32% solution of hydrogen bromide in glacial acetic acid for 40 min at room temperature. The mixture was diluted with chloroform (20 ml), washed rapidly with cold water, aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and concentrated to yield 2,3-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl)-α-L-rhamnopyranosyl bromide (**5**), R_F 0.7 (t.l.c.; chloroform–acetone, 9:1), which was used immediately without further purification.

A solution of **5** in acetonitrile (6 ml) was added to a suspension of 1,2:5,6-di-*O*-isopropylidene-α-D-galactofuranose[18] (**6**, 230 mg) and mercuric cyanide (110 mg) in freshly distilled acetonitrile (1 ml), and the mixture was stirred for 12 h. The mixture was diluted with chloroform (60 ml), washed successively with M potassium bromide and water, dried (Na_2SO_4), and concentrated to yield a syrupy product (400 mg) which was eluted from silica gel with a benzene–methanol gradient to give **6** (110 mg) and syrupy **7** (162 mg, 22%), $[\alpha]_D^{20}$ −41.5° (*c* 1.14, chloroform), which was homogeneous on g.l.c. (10% SE-30, 290°, *T* 5.34 min). Mass spectrum: *m/e* 805, 561, 331.

3-O-(4-O-β-D-mannopyranosyl-α-L-rhamnopyranosyl)-D-galactose (**9**). — Compound **7** (51 mg) was deacetylated with 3% methanolic triethylamine (10 ml) for 24 h at 0°. The mixture was then concentrated and methanol was repeatedly distilled from the residue to remove triethylamine. Preparative p.c. (1-butanol–pyridine–water, 6:4:3) of the residue gave 1,2:5,6-di-*O*-isopropylidene-3-*O*-(4-*O*-β-D-mannopyranosyl-α-L-rhamnopyranosyl)-D-galactofuranose (**8**; 11.2 mg, 31%; R_{GAL} 2.30), which contained mannose, rhamnose, and galactose in the ratios 1:1:0.9 (g.l.c. of the alditol acetates). Treatment of **8** (1 mg) with acetic anhydride–pyridine regenerated **7**.

A solution of **8** (9 mg) in aqueous trifluoroacetic acid (1 ml, 90%) was kept for 10 min at room temperature and then concentrated, and toluene was repeatedly distilled from the residue to remove trifluoroacetic acid. The trisaccharide **9** (7.9 mg) remained; it was homogeneous on p.c. (1-butanol–pyridine–water, 6:4:3, R_{GAL} 0.27;

and ethyl acetate–acetic acid–formic acid–water, 18:3:1:4, R_{GAL} 0.29), and had $[\alpha]_D^{20}$ −24° (*c* 0.8, water).

Hydrolysis of **9** (M HCl, 3 h, 100°) afforded mannose, galactose, and rhamnose in the ratios 1:0.9:1, identified by g.l.c. as the alditol acetates.

Treatment of **9** with acetic anhydride–pyridine gave a deca-acetate, identical with that described previously[8,9].

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