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Note

Complete structure of the repeating unit of the O-specific polysaccharide chain of *Shigella dysenteriæ* type 3 lipopolysaccharide

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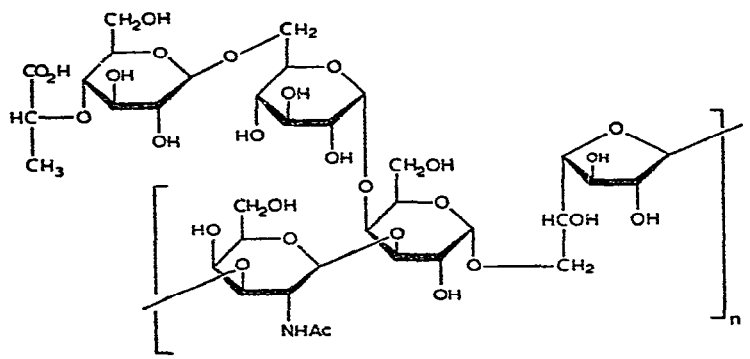
The complete structure of the pentasaccharide repeating-unit of the O-specific polysaccharide chain of the lipopolysaccharide of *Sh. dysenteriae* type 3 has now been established as **1**. Previous investigations[1–3] revealed all the structural features except the configuration of the glycosidic linkages of the 4-*O*-[(*R*)-1-carboxyethyl)-D-glucose] and D-galactofuranose residues.



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When the disaccharide 6-*O*-{4-*O*-[(*R*)-1-carboxyethyl]-D-glucopyranosyl}-D-glucose, obtained[1] by partial hydrolysis of the polysaccharide with acid, was treated with boron trichloride[4], a neutral disaccharide was formed together with 4-*O*-[(*R*)-1-carboxyethyl]glucose and glucose, as shown by paper chromatography and electrophoresis. The neutral fraction, obtained after removal (Dowex-1 x8 resin) of the acidic components, was investigated by using a Technicon sugar analyzer and found to contain gentiobiose and glucose. Thus, the 4-*O*-[(*R*)-1-carboxyethyl]-D-glucose residue was β-linked in the polysaccharide. From the optical rotation data in Table I

for the methyl ester of the polysaccharide and the methyl glycosides of the component sugars, it therefore follows that the D-galactofuranose residue also has the β configuration.

TABLE I

OPTICAL ROTATION DATA

Compound	$[\alpha]_D^a$ *(degrees)*	*Ref.*	$[M]_D$ *(degrees)*
Methyl α-D-glucopyranoside	+158.9	6	+308
Methyl α-D-galactopyranoside	+178.8	6	+347
Methyl 2-acetamido-2-deoxy-β-D-galactopyranoside	−12.0	7	−28
Methyl 4-*O*-[(*R*)-1-(methoxycarbonyl)ethyl]-β-D-glucopyranoside	+5.0	3	+14
Methyl α-D-galactofuranoside	+104.0	6	+202
Methyl β-D-galactofuranoside	−102.0	8	−198
Methyl ester of polysaccharide, calc. for repeating unit containing an α-D-galactofuranose residue	+90.03		+843
calc. for repeating unit containing a β-D-galactofuranose residue	+47.34		+443
Methyl ester of polysaccharide	+36.5		+342

[a]For aqueous solutions.

Calculation according to Klyne's rule[5] shows that the molecular rotation (+443°) of the methyl ester of the polysaccharide containing β-D-galactofuranose residues corresponds much more closely to the observed value (+342°) than does the value (+843°) calculated on the basis of α-D-galactofuranose residues.

The above assignment of linkage configuration in the polysaccharide was confirmed by p.m.r. spectroscopy; signals of five anomeric protons at δ 4.40, 4.50, 4.76, 4.94, and 5.06 were observed[1] for a solution of the polysaccharide in D_2O. In accordance with literature data[9,10], the anomeric protons of α- and β-hexopyranoside residues resonate at $\delta \sim 5.0$ and ~ 4.50, respectively. Thus, the signals at δ 4.94 and 5.06 for the polysaccharide correspond to the α-linked residues of D-gluco- and D-galacto-pyranose, whereas the signals at δ 4.40, 4.50, and 4.76 are due to the β-linked residues of 2-acetamido-2-deoxy-D-galactopyranose, 4-*O*-[(*R*)-1-carboxyethyl]-D-glucose, and D-galactofuranose.

EXPERIMENTAL

The isolation of oligosaccharides from a partial hydrolysate of the polysaccharide was carried out as previously described[1]. Treatment of the acidic disaccharide with boron trichloride was carried out according to the standard procedure[4]. P.c. (descending) was performed on Filtrak FN-11 paper with 1-butanol–pyridine–water (6:4:3). Paper electrophoresis was performed with a 25mM pyridinium acetate buffer

(pH 4.50) at 28 V/cm. Sugars were identified by using a Technicon SC-2 system with a column (25 × 0.6 cm) of DAx4 resin (Durrum, USA), a 0.5M sodium borate buffer (pH 9.0) at 85°, and an elution rate of 60 ml/h. Optical rotations were determined on a Perkin–Elmer polarimeter Model 141.

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