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Note

Type-specific pneumococcal polysaccharides: Concerning the anomeric configuration of the (1→3)-D-galactofuranosyl residues in S-31

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Pneumococcal types 10 and 31 have long been known to exhibit a minor, usually one-way, cross-reaction[1,2]. As the relationship between the chemical constitution and immunological specificities of polysaccharides is now securely established[3–5], it is to be expected that D-galactose, the only sugar common to S-10 (refs. 6 and 7) and S-31 (refs. 8–10), will be found to be present in similar linkage in the two polysaccharides.

Mainly on the basis of methylation studies, Roy[10] proposed structure **1** for the repeating unit of S-31.

→4)-β-D-Glc*p*A-(1→3)-α-D-Gal*f*-(1→3)-β-L-Rha*p*-(1→3)-α-D-Gal*f*-(1→2)-β-L-Rha*p*-(1→

1

Structure **1** suggests that D-galactose occurs in S-31 as (1→3)-linked furanosyl residues which are arbitrarily assigned an α-anomeric configuration on the basis of (a) the low specific rotation ($[\alpha]_D$ −19°)[8–10] of the polysaccharide, (b) the characterization of the aldobiouronic acid released on acid hydrolysis of S-31 as 3-*O*-(β-D-glucopyranosyluronic acid)-D-galactose[9], and (c) the demonstration[10], from studies of oxidation by chromium trioxide, that β-linked L-rhamnosyl and D-glucosyl residues are present in reduced, peracetylated S-31.

However, as only β-linked D-galactofuranosyl residues have thus far been identified in other type-specific, pneumococcal polysaccharides [S-13 (ref. 11), S-29 (ref. 12), S-33B (ref. 13), and S-34 (ref. 14)], in galactocarolose[15,16] from *Penicillium charlesii*, in a galactan from *Mycoplasma mycoides*[17], and in capsular polysaccharides of *Klebsiella* [K12 (ref. 18) and K41 (ref. 19)], an arbitrary assignment of an α-linkage to the (1→3)-D-galactofuranosyl residues of S-31 warrants comment. Indeed, it is only very rarely that α-D-galactofuranosyl residues have been identified in bacterial polysaccharides; *e.g.*, in the lipopolysaccharide[20] of *Salmonella typhimurium* 902 (Co1Ib drd2).

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TABLE I

CALCULATED SPECIFIC ROTATIONS FOR S-31 BASED ON DIFFERENT COMBINATIONS OF ANOMERIC LINKAGES

Combination	*Anomeric configuration of sugar*			*Aggregate* $[\alpha]_D$ *calculated (degrees)*	*Mean* $[\alpha]_D$ *(degrees)*
	D-*GlcpA*	D-*Galf*	L-*Rhap*		
i[a]	β	α,α	β,β	+356	+71.2
ii	β	α,α	α,β	+199	+39.8
iii	β	α,α	α,α	+42	+8.4
iv	β	α,β	α,α	−174	−34.8
v	β	α,β	α,β	−17	−3.4
vi	β	α,β	β,β	+140	+28.0
vii	β	β,β	α,α	−390	−78 0
viii	β	β,β	α,β	−233	−46.6
ix	β	β,β	β,β	−76	−15.2

[a]Structure **1**.

The specific rotation of a linear polysaccharide such as S-31 may be considered to be the mean of the sum of the specific rotations of the constituent sugars in the anomeric configuration they possess in the polymer. Nine possible combinations of anomeric linkages exist for one β-D-glucuronic acid unit with two α- and/or β-L-rhamnopyranosyl and two α- and/or β-D-galactofuranosyl residues. We have calculated the specific rotation for each of these combinations by using the literature values for the methyl glycosides of the component sugars as follows: β-D-glucopyranosyluronic acid[21], −40°, α- and β-L-rhamnopyranosyl[22], −63 and +94°, respectively; and α- and β-D-galactofuranosyl[23], +104 and −112°, respectively. The calculations are listed in Table I.

The calculated rotation (i) for the repeating unit **1** proposed by Roy[10] is highly positive, +71°, whereas the observed value was $[\alpha]_D$ −19°. The calculated values (ii and iii) for the combinations having two α-D-galactofuranosyl residues are also dextrorotatory. On the other hand, the calculated value for the combination (ix) of two β-D-galactofuranosyl and two β-L-rhamnosyl units, namely, $[\alpha]_D$ −15°, agrees with the rotation observed, and this structure for S-31 is supported by the chemical evidence[10] for L-rhamnosyl units having the β configuration. It therefore seems very probable that the D-galactofuranosyl residues present in S-31 have the β configuration.

We have been engaged in structural studies on S-10, which is immunologically related to S-31, and have deduced that one of the four D-galactose residues present in its oligosaccharide-ribitol phosphate repeating-unit is present as a (1→2)-, (1→3)-, or (1→2,3)-galactofuranosyl group, because arabinose was produced when S-10 was subjected to complete periodate oxidation, reduction with sodium borohydride, and acid hydrolysis[7]. It may now be inferred that this particular D-galactofuranosyl

residue is likely to be linked at O-3 rather than O-2, and to have the β-anomeric configuration.

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