The investigation forms part of a research programme supported by the *Swedish Natural Science Research Council.*

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Received January 4, 1971.

NMR Spectra of Trimethylsilylated Oligosaccharides and their Alditols

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NMR spectrometry of trimethylsilylated oligosaccharides has been used to establish the anomeric nature of the sugar residues.[1,2] An advantage of the trimethylsilylation is that the signals from the anomeric protons become well separated from other protons in the sugar residues, which are shifted upfield. Reduction of the oligosaccharide to the corresponding alditol eliminates the anomeric proton of the reducing sugar residue and NMR of trimethylsilylated oligosaccharide alditols has recently been used in connection with structural studies on *Salmonella* lipopolysaccharides.[3–6]

In the present investigation, chemical shifts and coupling constants for the anomeric protons of some trimethylsilylated oligosaccharides and their alditols have been determined (Table 1). For all the substances listed in the table, except the gentiobiitol derivative, the signal from the anomeric proton was well separated from the other signals. As the disaccharides occurred as α/β-mixtures, the signals given by the different anomeric protons were readily identified.

As expected all the β-D-glucosides and the β-D-galactosides showed high coupling constant, 6.5 – 7.0 Hz, and the correspond-

Table 1. NMR parameters for the anomeric proton of the glycosidic linkage in some trimethylsilylated oligosaccharides and their alditols.

Oligosaccharide	Chemical shift ppm (τ values)	Coupling constant Hz
O-β-DGp(1→2)DG[a]	5.49	6.5
O-β-DGp(1→2)DG-ol	5.63	6.5
O-α-DGp(1→4)DG	5.13	3.4
O-α-DGp(1→4)DG-ol	4.74	3.0
O-β-DGp(1→4)DG	5.57	6.5
O-β-DGp(1→4)DG-ol	5.20	6.5
O-α-DGp(1→6)DG	5.02	3.0
O-α-DGp(1→6)DG-ol	5.40	3.0
O-β-DGp(1→6)DG	5.78	7.0
O-β-DGp(1→6)DG-ol	5.82	7.0
O-β-DGalp(1→4)DG	5.65	6.5
O-β-DGalp(1→4)DG-ol	5.38	6.5
O-α-DGalp(1→6)DG	5.10	3.0
O-α-DGalp(1→6)DG-ol	5.45	1.0
O-β-DGalp(1→6)DGal	5.52	6.5
O-β-DGalp(1→6)DGal-ol	5.81	6.5
MeO-α-DManp	5.61	1.5
MeO-β-DManp	5.80	1.5
O-β-DGp(1→1)-DMan-ol	5.74	7.0
O-β-DGp(1→3)-DMan-ol	5.40	6.5
O-β-DGalp(1→2)-glycerol	5.18	1.5

[a] DG = D-glucose, DG-ol = D-glucitol *etc.*

ing α-glycosides low coupling constants (1.5 – 3.0 Hz). The latter values are not very accurate, as, instead of a distinct doublet a single broadened peak was generally observed.

Also in agreement with earlier results, the equatorially oriented anomeric protons gave signals at lower fields than the axially oriented anomeric protons.

The chemical shifts are less predictable. For the substances studied, reduction of a disaccharide to the alditol produces an upfield shift for the (1→2) and (1→6) linked disaccharides but a downfield shift for the (1→4) linked disaccharides.

No anomeric pair of disaccharides containing D-mannopyranosidic linkages was available, and the methyl α- and β-D-mannopyranoside derivatives were therefore investigated. In agreement with previous results, no significant differences in chemical shifts or coupling constants between the isomers were observed.

Experimental. The disaccharides were either commercial samples or were available in this laboratory. Reduction of the disaccharides with sodium borohydride yielded the alditols. Trimethylsilylation was performed as described by Sweeley *et al.*[7] NMR spectra, in carbon tetrachloride, were recorded with a Varian A-60 A instrument, using TMS as internal standard.

Acknowledgement. This work was supported by a grant from the *Swedish Natural Science Research Council.*

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Received January 8, 1970.

Structure of an Oligosaccharide Obtained on Degradation of the Lipopolysaccharide from *Salmonella typhimurium* LT2

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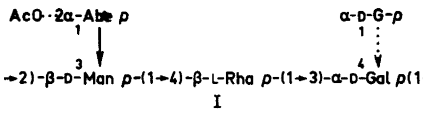
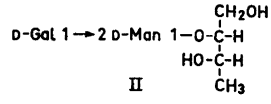
In the structure (I) proposed for the oligosaccharide repeating unit of the O-specific side-chains of the *Salmonella typhimurium* lipopolysaccharide (LPS),[1]



I

the anomeric configuration of the β-D-mannopyranose and α-D-galactopyranose residues was tentative and based upon earlier results.[2] Recently, however, Nikaido[3] has proposed, from enzymatic evidence, that the D-mannopyranose residue is α-linked. The anomeric natures of the sugar residues in the repeating units of LPS from different *Salmonella* serogroups have been determined by polarimetry and NMR studies on the oligosaccharides obtained after graded hydrolysis.[4–6] In the present paper, similar studies on an oligosaccharide obtained by Smith degradation of the *S. typhimurium* LT2 LPS are reported.

On periodate oxidation of the *S. typhimurium* LPS, the α-L-rhamnopyranose residues and the terminal D-glucopyranose residues but not other sugar residues in the O-specific side-chains should be oxidised. Subsequent borohydride reduction and mild acid hydrolysis (Smith degradation), which should also result in cleavage of the abequosidic linkage, would therefore yield the trisaccharide alditol II, containing the



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