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Note

The structure of the *Streptococcus pneumoniae* type 29 polysaccharide: a re-examination

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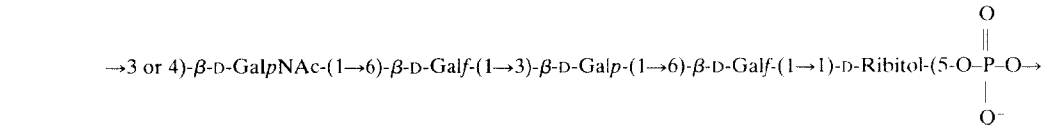
The structure of the capsular polysaccharide elaborated by *Streptococcus pneumoniae* type 29 (S-29) was investigated by Baddiley and co-workers[1]. It is of the teichoic acid type and was proved to be composed of repeating units having the structure **1**. The only uncertainity in this structure was whether the phosphate was linked to O-3 or O-4 of the β-D-Gal*p*NAc residue. We have now re-investigated this structure, using n.m.r. spectroscopy.



1

In the capsular polysaccharide elaborated by *Haemophilus influenzae* type f[2], also of the teichoic acid type, phosphate is linked to O-3 of a β-D-Gal*p*NAc residue. The ^{13}C-n.m.r. spectrum contained signals for C-2, C-3, and C-4 of this residue at δ 53.6 ($J_{C,P}$ 5.8 Hz), 77.0 ($J_{C,P}$ 5.5 Hz), and 69.2 ($J_{C,P}$ <1 Hz). The corresponding values for β-D-Gal*p*NAc are δ 54.80, 72.01, and 68.65. In the ^{13}C-n.m.r. spectrum of S-29 (Fig. 1), the signal for C-2 in the β-D-Gal*p*NAc residue appears at δ 53.56 (not coupled), and no coupled signals corresponding to those observed for the *H.i.* type f polysaccharide were observed. This finding clearly demonstrates that the phosphate group in S-29 cannot be linked to O-3 of the β-D-Gal*p*NAc residue but has to be linked to its 4-position.

The ^{31}P-n.m.r. spectrum of S-29 contained only one signal, at δ 1.27, demonstrating that all phosphate is present as di-esters. The two-dimensional P–H correlation spectrum (Fig. 2) showed two correlations, at δ ~4.1 and 4.55. The former could be assigned to H-5 and H-5′ of the ribitol moiety (dd, large geminal and vicinal coupling constants) and the latter to H-4 of the β-D-Gal*p*NAc residue

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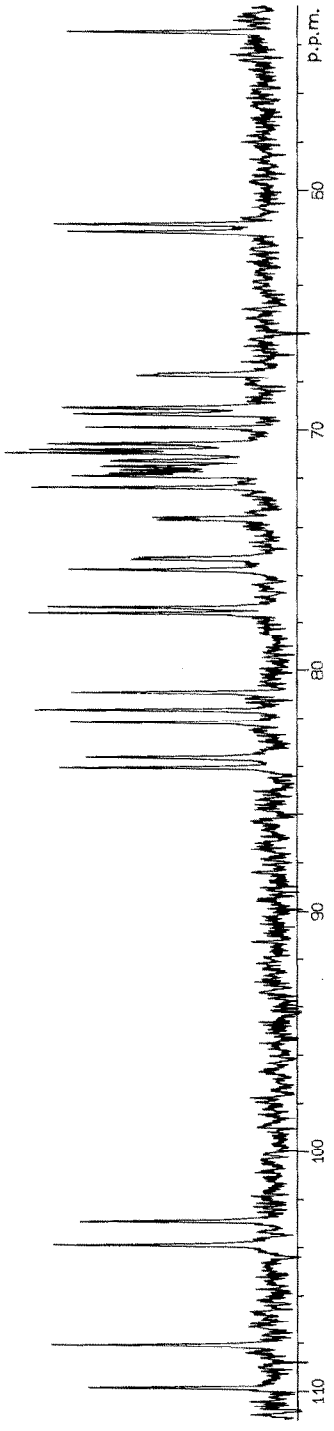
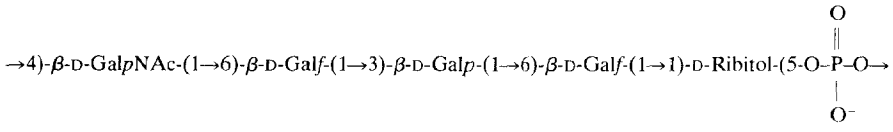


Fig. 1. ^{13}C-N.m.r. spectrum of S-29. The extremities of the spectrum have been omitted.

(small coupling constants). The corresponding values for ribitol and β-D-Gal*p*NAc are δ 3.81 and 3.98.

These complementary studies therefore demonstrate that S-29 is composed of repeating units having the structure **2**. The n.m.r. spectra were, also in other respects, consistent with the proposed structure, and need not be discussed.



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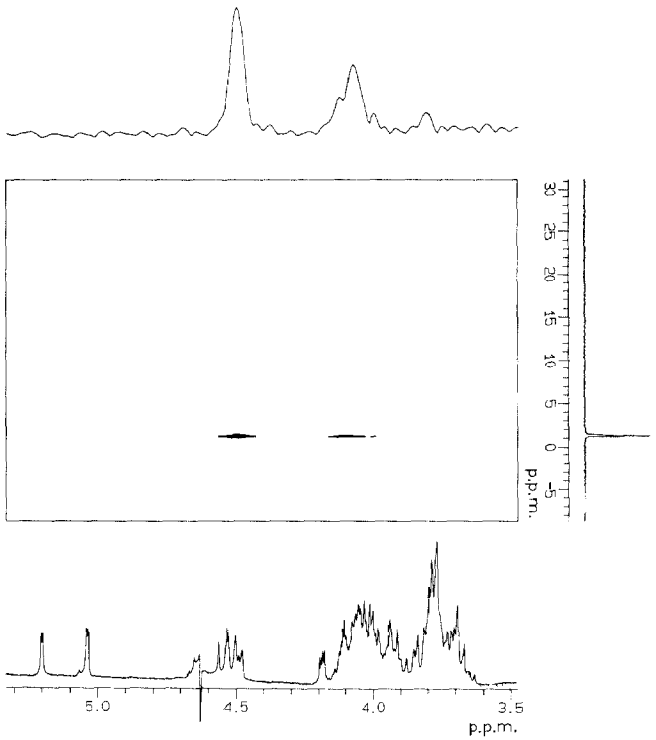

Fig. 2. Two-dimensional P–H correlation spectrum of S-29.

EXPERIMENTAL

N.m.r. spectra were obtained at 270 (^{1}H), 67.8 (^{13}C), and 109.3 MHz (^{31}P) with a JEOL GSX-270 instrument for solutions in D_2O. All spectra were recorded at 40°, using internal sodium 3-(trimethylsilyl)propanoate-d_4 (TSP, δ 0.00, ^{1}H), internal 1,4-dioxane (δ 67.40, ^{13}C), and external aqueous 2% phosphoric acid (δ 0.00, ^{31}P) as references.

ACKNOWLEDGMENTS

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