Capsular polysaccharides (CPS) are crucial virulence factors of Streptococcus pneumoniae. The previously unknown CPS structures of the pneumococcal serogroup 16 (serotype 16F and 16A) were thoroughly elucidated by nuclear magnetic resonance (NMR) spectroscopy and verified by chemical analysis. The following repeat unit structures were determined: 16F: (1-3)-α-L-Rhap-[4-P-1-Gro]-(1-3)-α-D-Glcp-[6-P-1-Gro]-(1-3)-β-L-Rhap-[2-OAc]-(1-4)-β-D-Glcp-(1-16A: (1-3)-β-D-Galf-[2-OAc]-(1-3)-α-L-Rhap-(1-2)-α-L-Rhap-(1-3)-α-D-Galp-[6-P-1-Gro]-(1-3)-β-D-Galp-(1-4)-β-D-Glcp-(1-70% OAc: O-acetyl substitution; P-1-Gro: glycerol-1-phosphate substitution.

A further analysis of CPS biosynthesis of serotype 16F and 16A, in conjunction with published cps gene bioinformatics analysis and structures of related serotypes, revealed presumable specific function of glycosyltransferase, acetyl transferase, phosphotransferase and polymerase. The functions of glycosyltransferase WcxN and WcxT were proposed for the first time, which were assigned to catalyze linkage of α-L-Rhap- (1-3)-α-D-Glcp and α-L-Rhap- (1, 2)-α-L-Rhap, respectively. Furthermore, since serotype 16F was genetically close to serogroup 28, cross-reactions between serogroup 16 and serogroup 28 were studied using diagnostic antisera, which provided further understanding of antigenic properties of CPS and diagnostic antisera. Interestingly, serotype 16F cross-reacted with factor antisera 28b and 11c. Meanwhile, serotype 16A cross-reacted with factor antiserum 11c.

Importance: The vaccine pressure against Streptococcus pneumoniae could result in the change of prevalence in carriage and invasive serotypes. As such, it is necessary to monitor the distribution to achieve successful vaccination of the population, and similarly, it is important to increase the knowledge of even the currently less prevalent serotypes. The CPS are vital for the virulence of the pathogen and antigenic properties of CPS are based on the structure. Consequently, a better understanding of the structure, biosynthesis and serology of the capsular polysaccharides can be of great importance towards developing future diagnostic tools and vaccines.