# Microbial Polysaccharides and Polysaccharases

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#### PREFACE

Polysaccharides are ubiquitous - they are by far the most abundant biopolymers on earth. They show a wide variety of chemical composition, and we can now begin to understand how these give rise to the wide variety of physical and

biochemical properties shown by polysaccharides.

Polysaccharides are renewable resources, and present a wide range of potential products of use to man. Some, such as cellulose, have been prepared and used by man for centuries; others, such as the bacterial xanthans, are recent products of microbial technology. It is amongst the microbial polysaccharides that we can look for the greatest potential production of useful polysaccharides. The techniques and equipment for the selection and industrial mass culture of microbes are at our disposal.

Hand in hand with the production of polysaccharides must go an understanding of their degradation. Microbes are of paramount importance in the enzymic breakdown of polysaccharides. For man this is doubled-edged, with properties such as cellulolysis and amylolysis leading to great commercial benefit or great commercial loss according to

circumstances.

This book is an outcome of the 83rd Ordinary Meeting of the Society for General Microbiology, at the University of Aberdeen, September 1978. It combines the Society Symposium, 'The Microbial Degradation of Polysaccharides' and the Microbial Cell Surfaces and Membranes Group Symposium 'Microbial Extracellular Polysaccharides'. Our intention has been to provide a timely compilation of the current academic and industrial achievements in these topics, and to point to future developments.

#### ACKNOWLEDGEMENTS

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#### Chapter 1

#### MICROBIAL EXOPOLYSACCHARIDES: CONTROL OF SYNTHESIS AND ACYLATION

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#### Introduction

Microbial extracellular polysaccharides (exopolysaccharides) range in the complexity of their chemical structures from homopolysaccharides with one or more type of linkage to heteropolysaccharides containing several different monosaccharides, some of which may be present in more than one molar equivalent. In addition, various acyl groups may be present, the most common being acetate as 0-acetyl groups and pyruvate in the form of ketals attached to the 3 and 4 or 4 and 6 positions of one of the neutral sugar residues, or more rarely, to a uronic acid (Figure 1). Although the gross structure of a number of exopolysaccharides has now been determined, only two of these can currently be considered to be of industrial importance - alginates [see Jarman, Chapter 2] and the exopolysaccharide of the plant pathogen Xanthomonas campestris [Jansson et al., 1975; Melton et al., 1976; Evans et al., Chapter 3; Gabriel, Chapter 8]. Detailed structures of several other polysaccharides produced industrially have not yet been reported. Alginates can be considered essentially as homopolymers of D-mannuronic acid subsequently modified by an extracellular epimerase converting some of the D-mannuronic acid residues to L-guluronic acid [Deavin et al., 1977]. Most heteropolysaccharides are however, composed of repeating units varying in size from disaccharides to hexasaccharides or even larger oligosaccharides. In this respect, Xanthomonas campestris polysaccharide (Figure 2) resembles a number of other exopolysaccharides, the structures of which have been elucidated and examples of which are shown in Table 1. Where it differs from these other polymers is that the backbone is a cellulose molecule substituted on alternating glucose units by an acylated trisaccharide (or possibly occasionally smaller oligosaccharide) which may also be pyruvylated.

Fig. 1 Ketals attached to the terminal reducing galactose residues of colanic acids from different strains of *Escherichia coli* and *Salmonella typhimurium*. From Garegg et al. [1971a, b].

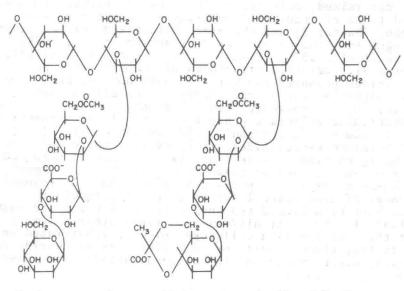


Fig. 2 Structure of extracellular polysaccharide of *Kanthomonas* campestris, according to Jansson et al. [1975].

TABLE 1

Repeating unit structures of Klebsiella exopolysaccharides

Туре	Components	Structure	Reference
1	Fucose, glucose, glucuronic acid, pyruvate	$+3)$ G1c(1 $\frac{8}{4}$ +3)G1cA(1 $\frac{6}{4}$ +4)Fuc(1 $\frac{\alpha}{2}$   $\frac{2}{8}$ Pyr	Erbing <i>et al.</i> [1976]
2	Mannose, glucose, glucuronic acid (various acyl groups)	$\rightarrow 4)$ Glc( $1^{-\alpha}\rightarrow 3$ )Glc( $1^{-\alpha}\rightarrow 4$ )Man( $1^{-\alpha}\rightarrow 4$ )Clc( $1^{-\alpha}\rightarrow 4$ )Man( $1^{-\alpha}\rightarrow 4$ )Glc( $1^{-\alpha}\rightarrow 4$ )Man( $1^{-\alpha}\rightarrow 4$ )	Gahan <i>et al.</i> [1967] Sutherland [1972]
rv.	Mannose, glucose, glucuronic acid, pyruvate, acetate	$\rightarrow$ 4)G1cA(1 $\frac{\beta}{\rightarrow}$ 4)G1c(1 $\frac{\beta}{\rightarrow}$ 5)Man(1 $\frac{\beta}{\mid}$ 6 Ac Pyr	Dutton and Yang [1973]
7	Mannose, glucose, galactose, glucuronic acid, pyruvate	$+3)G_{1}^{1}CA(1 \xrightarrow{\beta} +2)Man(1 + 3)G_{1}^{1}C(1 \xrightarrow{1} + 1)G_{1}^{1}G_{1}$ $G_{1}$ $G_{2}$ $G_{3}$ $G_{3}$ $G_{2}$ $G_{3}$	Dutton <i>et al.</i> [1974]
00	Glucose, galactose, glucuronic acid (acetate, pyruvate)	$+3)$ Ga1(1 $\frac{\beta}{+3}$ )G1c(1 $\frac{\alpha}{+3}$ )G1c(1 $\frac{\beta}{+3}$	Sutherland [1970]
11	Galactose, glucose, glucuronic acid, pyruvate	$+3)G1c(1^{\frac{\beta}{4}})G_1cA(1^{\frac{\beta}{4}})Ga1(1^{\frac{\alpha}{4}})Ga1(1^{$	Thurow et al. [1975]
16	Fucose, glucose, glucuronic acid, galactose	+3)- $\alpha$ -D-G]c - (1+4)- $\beta$ -D-G1cA - (1+4)- $\alpha$ -L-Fuc - (1+8) - $\alpha$ -D-Gab g-D- Gal	Chakraborty et al.