

SPRINGER LABORATORY

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# Esterification of Polysaccharides



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# Table of Contents

|          |                                                                 |           |
|----------|-----------------------------------------------------------------|-----------|
| <b>1</b> | <b>INTRODUCTION AND OBJECTIVES</b>                              | <b>1</b>  |
| <b>2</b> | <b>STRUCTURE OF POLYSACCHARIDES</b>                             | <b>5</b>  |
| 2.1      | Structural Features                                             | 5         |
| 2.1.1    | Cellulose                                                       | 6         |
| 2.1.2    | $\beta$ -(1 $\rightarrow$ 3)-Glucans                            | 7         |
| 2.1.3    | Dextran                                                         | 8         |
| 2.1.4    | Pullulan                                                        | 8         |
| 2.1.5    | Starch                                                          | 9         |
| 2.1.6    | Hemicelluloses                                                  | 9         |
| 2.1.7    | Guar                                                            | 12        |
| 2.1.8    | Inulin                                                          | 12        |
| 2.1.9    | Chitin and Chitosan                                             | 12        |
| 2.1.10   | Alginates                                                       | 14        |
| <b>3</b> | <b>ANALYSIS OF POLYSACCHARIDE STRUCTURES</b>                    | <b>15</b> |
| 3.1      | Optical Spectroscopy                                            | 16        |
| 3.2      | NMR Spectroscopy                                                | 18        |
| 3.2.1    | $^{13}\text{C}$ NMR Spectroscopy                                | 19        |
| 3.2.2    | $^1\text{H}$ NMR Spectroscopy                                   | 26        |
| 3.2.3    | Two-dimensional NMR Techniques                                  | 31        |
| 3.2.4    | Chromatography and Mass Spectrometry                            | 34        |
| <b>4</b> | <b>ESTERS OF CARBOXYLIC ACIDS – CONVENTIONAL METHODS</b>        | <b>41</b> |
| 4.1      | Acylation with Carboxylic Acid Chlorides and Anhydrides         | 41        |
| 4.1.1    | Heterogeneous Acylation – Industrial Processes                  | 41        |
| 4.1.2    | Heterogeneous Conversion in the Presence of a Base              | 46        |
| <b>5</b> | <b>NEW PATHS FOR THE INTRODUCTION OF ORGANIC ESTER MOIETIES</b> | <b>53</b> |
| 5.1      | Media for Homogeneous Reactions                                 | 53        |
| 5.1.1    | Aqueous Media                                                   | 54        |
| 5.1.2    | Non-aqueous Solvents                                            | 57        |
| 5.1.3    | Multicomponent Solvents                                         | 62        |
| 5.1.4    | Soluble Polysaccharide Intermediates                            | 70        |

|        |                                                                               |     |
|--------|-------------------------------------------------------------------------------|-----|
| 5.2    | In Situ Activation of Carboxylic Acids .....                                  | 75  |
| 5.2.1  | Sulphonic Acid Chlorides .....                                                | 76  |
| 5.2.2  | Dialkylcarbodiimide .....                                                     | 82  |
| 5.2.3  | <i>N,N'</i> -Carbonyldiimidazole .....                                        | 86  |
| 5.2.4  | Iminium Chlorides .....                                                       | 103 |
| 5.3    | Miscellaneous New Ways for Polysaccharide Esterification .....                | 106 |
| 5.3.1  | Transesterification .....                                                     | 106 |
| 5.3.2  | Esterification by Ring Opening Reactions .....                                | 112 |
| 6      | <b>SULPHONIC ACID ESTERS</b> .....                                            | 117 |
| 6.1    | Mesylates .....                                                               | 117 |
| 6.2    | Tosylates .....                                                               | 120 |
| 6.3    | Miscellaneous Sulphonic Acid Esters .....                                     | 128 |
| 7      | <b>INORGANIC POLYSACCHARIDE ESTERS</b> .....                                  | 129 |
| 7.1    | Sulphuric Acid Half Esters .....                                              | 129 |
| 7.2    | Phosphates .....                                                              | 136 |
| 7.3    | Nitrates .....                                                                | 140 |
| 8      | <b>STRUCTURE ANALYSIS OF POLYSACCHARIDE ESTERS</b> .....                      | 143 |
| 8.1    | Chemical Characterisation – Standard Methods .....                            | 145 |
| 8.2    | Optical Spectroscopy .....                                                    | 145 |
| 8.3    | NMR Measurements .....                                                        | 149 |
| 8.4    | Subsequent Functionalisation .....                                            | 155 |
| 8.4.1  | NMR Spectroscopy<br>on Completely Functionalised Derivatives .....            | 155 |
| 8.4.2  | Chromatographic Techniques .....                                              | 162 |
| 9      | <b>POLYSACCHARIDE ESTERS<br/>WITH DEFINED FUNCTIONALISATION PATTERN</b> ..... | 169 |
| 9.1    | Selective Deacylation .....                                                   | 170 |
| 9.2    | Protective Group Technique .....                                              | 172 |
| 9.2.1  | Tritylation .....                                                             | 173 |
| 9.2.2  | Bulky Organosilyl Groups .....                                                | 176 |
| 9.3    | Medium Controlled Selectivity .....                                           | 180 |
| 10     | <b>SELECTED EXAMPLES OF NEW APPLICATIONS</b> .....                            | 181 |
| 10.1   | Materials for Selective Separation .....                                      | 182 |
| 10.1.1 | Stationary Phases for Chromatography .....                                    | 184 |
| 10.1.2 | Selective Membranes .....                                                     | 184 |
| 10.2   | Biological Activity .....                                                     | 186 |
| 10.3   | Carrier Materials .....                                                       | 187 |
| 10.3.1 | Prodrugs on the Basis of Polysaccharides .....                                | 188 |
| 10.3.2 | Nanoparticles and Hydrogels .....                                             | 190 |
| 10.3.3 | Plasma Substitute .....                                                       | 192 |

|                                 |     |
|---------------------------------|-----|
| 11 OUTLOOK .....                | 195 |
| 12 EXPERIMENTAL PROTOCOLS ..... | 197 |
| REFERENCES .....                | 217 |
| SUBJECT INDEX .....             | 229 |

Polysaccharides are unique biopolymers with an enormous structural diversity. Huge amounts of polysaccharides are formed biologically by many organisms including plants, animals, fungi, algae, and microorganisms as storage polymers and structure-forming macromolecules due to their extraordinary ability for strong formation by supramolecular interactions of variable types. In addition, polysaccharides are increasingly recognized as key substrates for biotransformation processes regarding, e.g., activity and selectivity. Although the naturally occurring polysaccharides are already out-forming, chemical modification can improve the given features and can even be used to tailor advanced materials.

Chemical modification of polysaccharides represents the most versatile transformation as they provide easy access to a variety of functional materials with reliable properties. In particular, state-of-the-art esterification can yield a broad spectrum of polysaccharide derivatives, as discussed in the frame of this book from a practical point of view but are currently only used under lab-scale conditions. In contrast, simple esterification of the most abundant polysaccharide cellulose and starch are commercially accepted procedures. Nevertheless, it is the author's intention to review chemical concepts of esterification, such as conversion of cellulose to carboxylic acid esters of  $C_1$  to  $C_6$  acids including mixed derivatives of glycolic acid and cellulose nitrate, which are produced in large quantities. These commercial pathways of polysaccharide esterification are carried out exclusively under heterogeneous conditions at least at the beginning of the conversion. The majority of cellulose acetate (about 80–90% per year) is based on a route that includes the dissolution of the products formed [1–3].

Research and development offers new opportunities for the synthesis of polysaccharide esters resulting from:

- New reagents (ring opening transesterification), enzymatic acylation and *in situ* activation of carboxylic acids
- Homogeneous reaction paths, i.e., starting with a dissolved polysaccharide and new reaction media
- Regioselective esterification applying protecting-group techniques and protecting-group-free methods exploiting the superstructural features of the polysaccharides as well as enzymatically catalyzed procedures

With regard to structure characterization on the molecular level most important are NMR spectroscopic techniques including specific sample preparation. Having