

FOREWORD

Carbohydrate chemists are very lucky. They work in a science which is intellectually and experimentally challenging but nonetheless highly applied; such studies are more likely to give answers to interesting biological problems of real consequence than any other set of current investigations that are presently being undertaken. The 550 or so pages of this special issue devoted to Carbohydrates has been divided into the November and December issues of *Tetrahedron Asymmetry*. One of the objectives of these issues is to bring the breadth of the science currently studied in carbohydrate chemistry to the attention of a wider group of chemists who do not usually read more specialist carbohydrate journals. These issues give some illustration of the breadth of interests and expertise of glycoscientists today.

Although significant advances have been made in the formation of glycosidic bonds, the continuing effort in this area is represented by the synthesis of (a) hyaluronic acid related oligosaccharides with a glucuronic acid at the reducing end; (b) of tetrasaccharides corresponding to biological repeat units of the *Serratia marcescens* O18 polysaccharide; (c) 2-azido-2-deoxyhexopyranosyl building blocks as glycosyl donors for the synthesis of oligosaccharides; (d) use of O-glycosyl trichloroacetimidates in the synthesis of unsymmetrical trehalose analogues; (e) the use of thioglycosides as active and latent glycosyl donors; and (f) synthesis of sulphur linked fucopyranosyl disaccharides.

The synthesis of carbohydrate mimics is illustrated by approaches to C-glycosides including the synthesis (a) of difluoromethylene-linked C-glycosides and C-disaccharides by radical methodology; (b) of novel fused ring C-glycosides; (c) of the use of selenophenyl galactopyranosides for the synthesis of α - and β -(1,4)-C-disaccharides; and (d) the synthesis and conformational studies of α -C-galactosides of D-mannose derivatives.

Studies on the recognition by enzymes or receptors of carbohydrates, and of assays of carbohydrates include (a) acceptor substrate recognition by N-acetyl-glucosaminyltransferase-V; (b) 2,5-dideoxy-2,5-imino-D-mannitol as a pyrophosphate fructose-6-phosphate-1-phosphotransferase inhibitor; (c) potential epitopes for the preparation of antibodies with saccharidase activity; (d) synthesis of a bio-fluorescence-labelled lactoside as a substrate for the continual assay of ceramide glycanase; and (e) an evaluation of methods used for the determination of starch. Applications of the use of enzymes in synthesis are shown by (a) the synthesis of 7-deoxy-N-acetylneuraminic acids; (b) the preparation of glycosides using glycosidases; and (c) the diastereoselective cleavage of β -glucosyl sulphoxides by β -glucosidase. A study in the use of carbohydrate-based liquid crystals reports the sign inversion of the helical pitch in carbohydrate-based liquid crystals.

Conformational studies reported in this issue include: (a) a comparative and colourful assessment of the conformations and hydrophobicity potential profiles of cyclodextrins, cyclomannins and cyclogalactins; (b) the preference for twist-boat structures in α -L-sorbypyranose; (c) the conformation of sugar amides,

thioamides and thioureas; and (d) the synthesis of sulphur analogues and conformational studies of kojibiosides.

Examples of the development of synthetic methodology applied to carbohydrate targets are: (a) the use of dibutylstannylene acetals as useful intermediates for the regioselective sulphation of glycosides; (b) iron acyl complexes in the opening of sugar epoxides; (c) stereocontrolled hydroxymethylation of carbohydrate imines applied to the formal synthesis of destomic acid and lincosamine; (d) studies on nucleophilic induction of rearrangement of thioglycoside (e) formation of seven membered carbocycles from sugars; (f) stereoselective and enantiomeric access to an A/B ring equivalent of the trichothecene family; and (g) stereocontrolled synthesis of spirodihydrouracil nucleosides

Total syntheses of materials using carbohydrates as starting materials are exemplified by the synthesis of (a) sphingosine and phytosphingosine from D-threose; (b) ganglioside GQ1b and related polysialogangliosides (c) novel mimics of the sialyl Lewis X determinants; (c) muramic acid analogues by the use of nucleophilic carbohydrate derivatives; (d) analogues of sialic acid with an acetamido group at C-4; and (e) 3-deoxy-D-glucosidic acid (f)

Radical reactions may be used in which the protection of hydroxyl groups is minimised and some examples of the radical methodology applied to the chemistry of carbohydrates are: (a) stereocontrolled radical reactions in carbohydrate and nucleoside chemistry; (b) radical decarboxylation in the preparation of 1-methylcarbapenem antibiotic precursors from D-glucosamine; (c) radical cyclisations on sugar templates to provide stereoselective syntheses of γ -butyrolactones to carbohydrates; and (d) the synthesis of cyclopentanes by radicals towards the synthesis of mannostatin.

The range of useful and readily available sugar starting materials include (a) methyl α -D-fructopyranoside in the synthesis of carboxylates; (b) difructose dianhydrides as synthetic intermediates; (c) the formation and isomerisation of cyclic acetals and ketals of pentonolactones; and (d) rhamnoheptonolactones as starting materials for the synthesis of rhamnose analogues. Carbohydrates are used as templates for asymmetric synthesis in (a) carbohydrate based 1,3-oxazin-2-ones controlling both asymmetric aldol and Diels Alder reactions and (b) asymmetric induction in the 2+2 cycloaddition of chlorosulphonyl isocyanate to 3-O-vinyl glycosides.

As can be seen from the list of authors contributing to these issues, the study of carbohydrates is a truly international science. Contributions are published from industrial and academic laboratories in Canada, China, France, Germany, India, Italy, Japan, Netherlands, Poland, Spain, Sweden, Switzerland, United Kingdom, and USA. Sugar chemistry is at a stage when the rewards and opportunities open to investigators in the area are great; if the range of science described here attracts new workers to this field, this special issue will have fulfilled its major objective.

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