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RESEARCH FRONT: Carbohydrates and Other Sticky Topics

Forewords

Carbohydrate Research in the 20th Century

Stephen J. Angyal

Aust. J. Chem. **2009**, 62, 501–502.

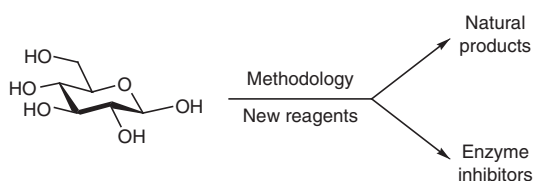
In the second half of the 20th century carbohydrate chemistry has changed a lot, particularly in the past 50 years: new chemical and physical methods have been introduced to handle them and new theories to explain their properties and behaviour. Robert Stick has made good use of these methods to explain and extend the chemistry of carbohydrates and correlate it with their biochemistry.

Robert Vyent Stick: A Colourful Character

Spencer J. Williams

Aust. J. Chem. **2009**, 62, 503–509.

The present issue is inspired by a recent symposium held to honour the career of Robert Stick (The University of Western Australia). This essay is in two parts: the first part covers highlights of Robert Stick's career in organic (carbohydrate) chemistry, and the second part is an interview with Robert on his teaching and research career in academia.



Reviews

Recent Developments in Glycoside Synthesis with Glycosynthases and Thioglycoligases

Bojana Rakić, Stephen G. Withers

Aust. J. Chem. **2009**, 62, 510–520.

Glycoconjugates and oligo- and polysaccharides continue to be of great interest for the therapeutics and biotechnology industries but their production remains challenging. Enzymes can provide relatively simple and scalable syntheses of these complex compounds compared with traditional synthetic chemistry approaches. This review highlights recent developments in the engineering of glycosynthases and thioglycoligases from retaining and inverting glycosidases for the synthesis of glycosides, and addresses the advances in screening methods and directed evolution techniques that will continue to drive new discoveries in this field.

Affinity-Based Proteomics Probes; Tools for Studying Carbohydrate-Processing Enzymes

Keith A. Stubbs, David J. Vocadlo

Aust. J. Chem. **2009**, 62, 521–527.

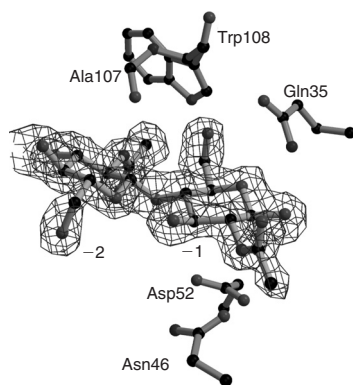
Activity-based proteomic profiling has been developed as a strategy to characterize enzyme activities in biological systems. This strategy has the potential to aid annotation of putative proteins from genomic analyses, and identify enzymes from unsequenced genomes, which should facilitate more detailed studies of enzymes having properties of interest. In this review we describe, with a focus on bacterial carbohydrate-processing enzymes, how gaining a functional understanding of biochemical pathways is important and how activity-based proteomic profiling can play a useful role.

Rapid Communication

The Chitopentaose Complex of a Mutant Hen Egg-White Lysozyme Displays No Distortion of the -1 Sugar Away from a 4C_1 Chair Conformation

Gideon J. Davies, Stephen G. Withers,
David J. Vocadlo

Aust. J. Chem. **2009**, 62, 528–532.



Inspiration for the design of clinically-relevant glycosidase inhibitors comes from the distortions of the substrates at the transition state. We show that, in contrast to some historical work, enzyme-product complexes of lysozyme need not be distorted. That the substrate is distorted at the Michaelis complex and transition state, however, remains at the forefront of current thinking in the field.

Highlight

A Brief and Informationally Rich Naming System for Oligosaccharide Motifs of Heteroxylans Found in Plant Cell Walls

Régis Fauré, Christophe M. Courtin,
Jan A. Delcour, Claire Dumon,
Craig B. Faulds, Geoffrey B. Fincher,
Sébastien Fort, Stephen C. Fry,
Sami Halila, Mirjam A. Kabel,
Laurice Pouvreau, Bernard Quemener,
Alain Rivet, Luc Saulnier,
Henk A. Schols, Hugues Driguez,
Michael J. O'Donohue

Aust. J. Chem. **2009**, 62, 533–537.

This article describes a convenient and information-rich method to name heteroxylans. IUPAC rules do not provide simple nomenclature for heteroxylans, but current short names are informationally poor. The naming system described provides a single letter-based system that should radically improve the published descriptions of heteroxylan structures, while remaining accessible to most researchers.

5-*O*-Feruloyl- α -L-Araf

1

↓

3

β -D-Xylp-(1 \rightarrow 4)-D-Xylp

New abbreviation: A^{5f3}X

Nomenclature from IUPAC carbohydrate rules:

O-[5-*O*-(*trans*-feruloyl)- α -L-Araf]-(1,3)-*O*- β -D-Xylp-(1,4)-D-Xylp

Short form from IUPAC carbohydrate rules: Fe5Ara α 3Xyl β 4Xyl

Old abbreviation: FAXX

Full Papers

Synthesis of Naturally Occurring Arsenic-Containing Carbohydrates

Pedro Traar, Alice Rumpler,
Tobias Madl, Gerald Saischek,
Kevin A. Francesconi

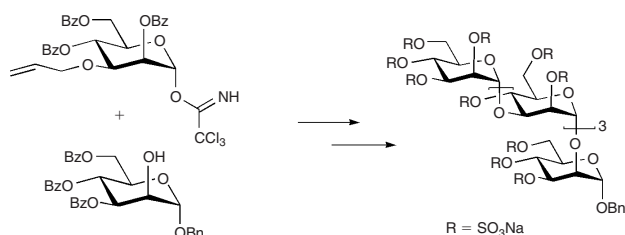
Aust. J. Chem. **2009**, 62, 538–545.

Arsenic-containing carbohydrates (arsenosugars) are natural constituents of marine organisms, which are of toxicological interest because they occur in common seafood. The first synthesis of two major arsenosugars that occur widely in seafood is reported. A full toxicological assessment of these compounds is now possible.

An Improved Synthetic Route to the Potent Angiogenesis Inhibitor Benzyl Man α (1 \rightarrow 3)-Man α (1 \rightarrow 3)-Man α (1 \rightarrow 3)-Man α (1 \rightarrow 2)-Man Hexadecasulfate

Ligong Liu, Ken D. Johnstone,
Jon K. Fairweather, Keith Dredge,
Vito Ferro

Aust. J. Chem. **2009**, 62, 546–552.



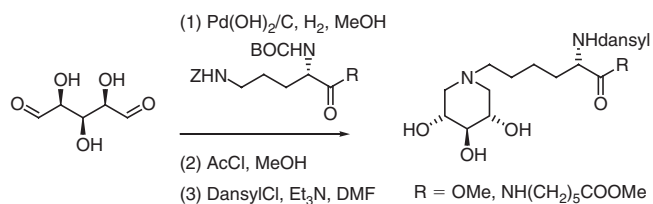
The illustrated sulfated pentasaccharide glycoside is a potent inhibitor of angiogenesis, i.e., the growth of new blood vessels from pre-existing ones surrounding a tumour. An efficient synthetic route to this pentasaccharide and its analogues has been developed which utilizes only two monosaccharide building blocks and minimizes the use of toxic reagents.

Synthesis and Biological Evaluation of 1,5-Dideoxy-1,5-iminoxylitol–Amino Acid Hybrids as Xylosidase Inhibitors

Andreas J. Steiner, Arnold E. Stütz, Chris A. Tarling, Stephen G. Withers, Tanja M. Wrodnigg

Aust. J. Chem. **2009**, 62, 553–557.

Iminoalditols are powerful competitive inhibitors of many glycosidases. They have found important roles as biological probes, for example in the investigation of glycoprotein trimming glycosidases, and have become valuable diagnostic tools for studies of enzyme active sites and catalytic mechanisms. 1,5-Dideoxy-1,5-iminoxylitol–amino acid hybrids have been synthesized by cyclisation via a double reductive amination of *xylo*-pentodialdose, further modification with aromatic substituents gave access to fluorescent lipophilic derivatives. Kinetic studies revealed that all compounds exhibited better inhibitory properties against β -xylosidase from *Thermoanaerobacterium saccharolyticum* than the parent iminosugar. By further functionalisation with other reporter groups or attachment to suitable surfaces such compounds could be useful tools for studying xylanases and β -xylosidases.

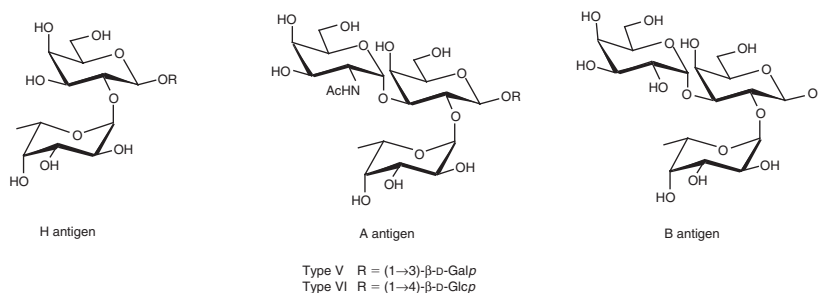


Synthesis of ABO Histo-Blood Group Type V and VI Antigens

Peter J. Meloncelli, Todd L. Lowary

Aust. J. Chem. **2009**, 62, 558–574.

The ABO histo-blood group oligosaccharides form part of one of the most important carbohydrate-based antigen groups, and they must be considered when conducting both blood transfusions and organ transplants. Here we report the synthesis of the ABO type V and VI antigens via a linear chemical synthesis in multimilligramme quantities. These targets will play an important role in a range of biochemical studies including the development of tolerogens for ABO-incompatible heart transplants.

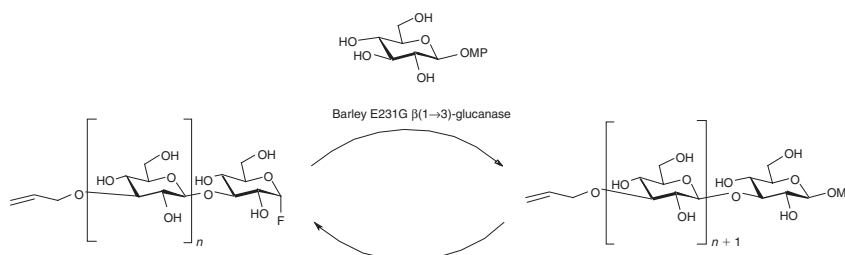


A Chemoenzymatic Route to Conjugatable $\beta(1\rightarrow3)$ -Glucan Oligosaccharides

Emilie Montel, Maria Hrmova, Geoffrey B. Fincher, Hugues Driguez, Sylvain Cottaz

Aust. J. Chem. **2009**, 62, 575–584.

A methodology employing glycosynthase technology gives access to $\beta(1\rightarrow3)$ -glucan oligosaccharides conjugatable on both reducing and non-reducing ends. These oligosaccharide derivatives constitute valuable tools for the design of probes useful for the studies of receptors and enzymes associated with $\beta(1\rightarrow3)$ -glucans.



Activation of Sugar Hydroxyl Groups Prior to Glycosylation

Robert J. Ferrier,
Richard H. Furneaux

Aust. J. Chem. **2009**, 62, 585–589.

The chemical bonding of sugars to other sugars or non-sugars remains of the greatest importance in organic chemistry, biochemistry, and medicinal chemistry after its inception a century ago, and methodology for the available processes continues to attract much attention. General requirements are for suitable glycosyl donors and glycosyl acceptors, the chemistry of the former being well advanced while that of the latter has been relatively neglected, and is therefore given preferential attention here. Familiar and novel methods of activating glycosyl donors are described and illustrated.

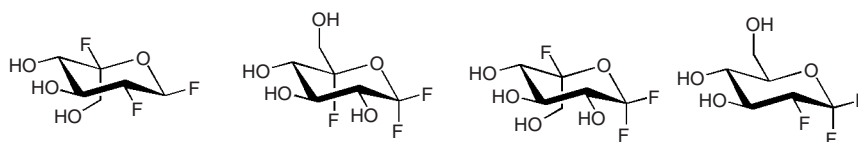


Non-Stick Sugars: Synthesis of Difluorosugar Fluorides as Potential Glycosidase Inactivators

Brian P. Rempel, Stephen G. Withers

Aust. J. Chem. **2009**, 62, 590–599.

Four new difluorosugar fluorides, 2-deoxy-2,5-difluoro- α -L-idopyranosyl fluoride, 1,5-difluoro-D-glucopyranosyl fluoride, 1,5-difluoro-L-idopyranosyl fluoride, and 2-deoxy-1,2-difluoro-D-glucopyranosyl fluoride were synthesized by a radical bromination/fluoride displacement sequence, followed by deprotection. Testing these as inactivators of the β -glucosidase from *Agrobacterium* sp. showed binding to the active site as reversible competitive inhibitors, but the only time-dependent inactivation observed was found to be due to an extremely small amount of a highly reactive impurity.



Book Review

Carbohydrates: the Essential Molecules of Life

Richard J. Payne

Aust. J. Chem. **2009**, 62, 600–601.