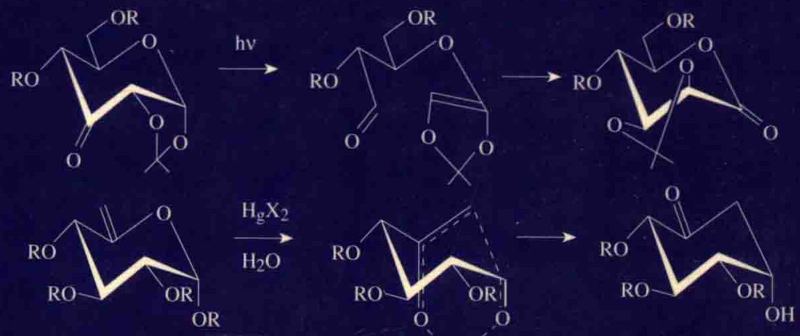
Monosaccharides

Their Chemistry and Their Roles in Natural Products



Peter Collins • Robin Ferrier

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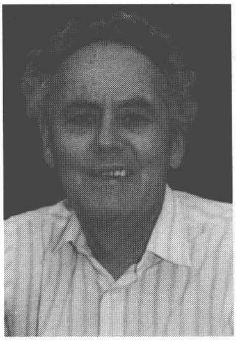

Peter Collins took his BSc degree at Birkbeck College, London University, while employed at Glaxo Laboratories in the team engaged on a synthesis of cortisone. PhD (1963) studies followed, investigating pyranosiduloses in George Overend's monosaccharide group. After a postdoctoral period with Harold Hart at Michigan State University studying cyclohexadiene photochemistry, he took up a teaching post at Birkbeck College, where he has held the Chair of Organic Chemistry since 1987.

His research has centred on monosaccharides, at the forefront being ultraviolet-light-induced transformations of their photo-active derivatives. The syntheses of pseudo-cyclodextrins, oxepan derivatives and carbohydrate ligands for SAP plasma protein have recently featured in his group's activities.

He is Editor of Chapman and Hall's *Carbohydrates—A Source Book* and has published widely in the *Journal of the Chemistry Society, Perkin Transactions 1, Carbohydrate Research* and *Tetrahedron Letters*.

Robin Ferrier did his undergraduate work at the University of Edinburgh and graduate training in the same department under Gerald Aspinall. He was a post-doctoral fellow in Melvin Calvin's group in Berkeley and went from his first teaching position in Birkbeck College, University of London to be Professor of Organic Chemistry in Victoria University of Wellington, New Zealand in 1970.

Research interests have always been near to monosaccharide chemistry with reactions of unsaturated sugars, carbocyclic compounds derived from sugars, free radical reactions and the development of routes to pharmaceutically important products from monosaccharides being the centres of focus for his research students.

He is Senior Reporter for the Royal Society of Chemistry's annual *Specialist Periodical Report on Carbohydrate Chemistry* and has published extensively, mainly in the *Journal of the Chemical Society, Perkin Transactions 1* and *Carbohydrate Research*.

Preface

This book is effectively a second edition of one we wrote for different publishers in 1972.[1] In the interim we have often been questioned about a new edition, but a long sequence of duties has seen our good intentions lead in the inevitable direction. To some degree we now perceive the delay as an advantage because in recent years our subject has altered almost out of recognition, and now we have had the opportunity to portray a greatly extended and invigorated branch of modern chemistry. The book has therefore been substantially restructured, almost entirely rewritten and expanded to accommodate these major changes.

As before, 'we have attempted to present a rationalized account using the concepts of current mechanistic organic chemistry and stereochemistry', but whereas in the preface to the first edition we continued, 'in so doing (we) hope to have depicted our subject as a branch of chemistry which is developing in line with general advances', we now aim to depict our subject as a major component of modern organic chemistry with central significance in biology, in particular in the new science of 'glycobiology'. While up to the 1970s carbohydrate chemistry was rather an isolated component of the subject practised by specialists, this is no longer so and many highlights of the newer developments have been contributed by 'mainstream' organic chemists, the subject having been greatly vitalized in consequence. The range of organic chemistry now described is extensive, and parts of the book can be looked on as portrayals of modern general organic chemistry with monosaccharides as model systems.

In appropriate introductory sections we have retained the pedagogic style adopted previously, and we have been mindful of the student and scientist coming to grips with the subject for the first time. In other sections, where we felt the interests of the practising chemist and research students were paramount, we have provided considerable detail and, following suggestions from many colleagues, have included over 1000 references which will aid direct access to the literature. Our references are unusual in not including names of authors, and while this has allowed some space saving, the main reason for the omission is that we do not necessarily identify seminal papers, often preferring reviews or recent publications with useful bibliographies. We use authors' names sparingly in the text when significant work can be attributed appropriately.

We introduce the subject (Chapter 2) by dealing with matters relating to molecular structure and conformation, and we indicate how sugars are biosynthesized and how they may be obtained synthetically from carbohydrate and non-carbohydrate sources. For those unfamiliar with the basis of monosaccharide chemistry the first part of this chapter is essential, and the treatment of the vitally important issue of molecular shape and its consequences will prove useful for the study of conformational analysis at a level beyond that used in most organic chemistry text books. The heart of the book is in Chapters 3, 4 and 5, in which we describe the fundamental organic chemistry of the monosaccharides, and comparison of these sections with the same chapters in the preceding edition will readily reveal how appreciable has been the recent progress made in the understanding of the panorama of the organic chemistry of the sugars. Free radical, carbene, carbanion and carbocation processes are now, for example, all commonly utilized in synthetic work, whereas for the most part only the last of these were recognized as important in the 1970s.

Chapters 6 and 7 cover other main areas of recent advancement: the use of monosaccharides as starting materials in the synthesis of oligosaccharides of biological importance and in the synthesis of enantiomerically pure non-carbohydrate products. Lastly, in Chapter 8 are described many natural products which contain or are related to sugars, the focus often being on compounds that are of interest in medicinal chemistry and of importance in biology. Parts of this chapter could prove useful to chemists approaching glycobiology for the first time or to biologists wishing to examine chemical features of natural materials.

Five appendices are included on topics that we feel add to the book as a data and reference source: the literature and nomenclature of the subject, n.m.r. chemical shift data, polarimetry and the trivial and systematic names of microbiological sugars. Polarimetry has a special place in carbohydrate chemistry, but unlike the other physical methods treated in the last chapter of the first edition (n.m.r. spectroscopy, mass spectrometry, for example) it has not become an everyday technique to all who practise organic chemistry. For this reason it is singled out for extended treatment in Appendix 4 and our earlier chapter on physical methods has been omitted. Treatment of the biochemistry of the sugars has been severely curtailed (Section 2.5.1).

We thank Professor Alistair Stephen for guidance on aspects of Chapter 8, and Dr Howard Carless for valuable suggestions on many topics. Professor Derek Horton kindly allowed us access to the revised version of the IUPAC-IUB rules *The Nomenclature of Carbohydrates* prior to its publication (see Appendix 2). Excellent secretarial service was provided by Yvonne Cuthbert, Janine Doherty, Alison Hetherington and Katherine Prior, and Keri McCombe assisted with the diagrams. We are most grateful to them all. Parts of the book were written when one of us (R.J.F.) was on sabbatical leave in the Department of Chemistry, University of Edinburgh, and Victoria University is thanked for granting the leave and Professor R. Ramage for making available excellent facilities in Edinburgh. Finally, for their encouragement and support, we thank our wives Shirley and Carolyn who, unlike our subject, have appeared steadfast and unchanging for even longer than the time spanned by our two books.

REFERENCE

1. *Monosaccharide Chemistry*, Penguin Books Ltd, Harmondsworth, Middlesex, 1972.

Abbreviations

The following abbreviations have been used in the text.

Ac	acetyl
Ad	adenin-9-yl
AIBN	2,2′-azobisisobutyronitrile
All	allyl
Ar	aryl
Asn	asparagine
Asp	aspartic acid
ATP	adenosine 5′-triphosphate
BBN	9-borabicyclo[3.3.1]nonane
Bn	benzyl
Boc	*t*-butoxycarbonyl
Bu	butyl
Bz	benzoyl
Cbz	benzyloxycarbonyl
c.d.	circular dichroism
c.i.	chemical ionization
DAST	diethylaminosulphur trifluoride
DBU	1,5-diazabicyclo[5.4.0]undec-5-ene
DCC	dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
DIBALH	diisobutylaluminium hydride
DMAP	4-dimethylaminopyridine
DMF	*N*,*N*-dimethylformamide
DMSO	dimethyl sulphoxide
DMTST	dimethyl (thiomethyl) sulphonium triflate
DNA	deoxyribonucleic acid
ee	enantiomeric excess
Ee	1-ethoxyethyl
e.s.r.	electron spin resonance
Et	ethyl
f.a.b.	fast-atom bombardment
FIAC	1-(2′-deoxy-2′-fluoro-β-D-arabinofuranosyl)-5-iodocytosine
Fru	fructose
Fuc	fucose

Gal	galactose
g.l.c.	gas–liquid chromatography
Glc	glucose
GlcNAc	2-acetamido-2-deoxyglucose
Gly	glycine
HMPIT*	hexamethylphosphoric triamide
h.p.l.c.	high performance liquid chromatography
HSEA	hard sphere *exo*-anomeric effect
IDCP	iodonium dicollidine perchlorate
i.r.	infrared
Kdo	3-deoxy-D-*manno*-2-octulosonic acid
LAH	lithium aluminium hydride
LDA	lithium diisopropylamide
LTBH	lithium triethylborohydride
LUMO	lowest unoccupied molecular orbital
Man	mannose
MCPBA	*m*-chloroperbenzoic acid
Me	methyl
Mem	methoxyethoxymethyl
MNO	4-methylmorpholine *N*-oxide
Mom	methoxymethyl
m.p.	melting point
m.s.	mass spectrometry
Ms	methanesulphonyl
NAD	nicotinamide adenine dinucleotide
NAM	*N*-acetylmuramic acid
NBS	*N*-bromosuccinimide
Neu	neuraminic acid
NIS	*N*-iodosuccinimide
n.m.r.	nuclear magnetic resonance
nOe	nuclear Overhauser effect
Ns	nitrobenzene-*p*-sulphonyl
o.r.d.	optical rotatory dispersion
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PET	positron emission tomography
Ph	phenyl
Phth	phthaloyl
Piv	pivaloyl
p.p.m.	parts per million
Pr	propyl

* This abbreviation indicates that $(Me_2N)_3PO$ is a phosphoric acid derivative. It is commonly abbreviated either to HMPA or to HMPT, with confusing consequences, particularly since $(Me_2N)_3P$, a phosphorous acid derivative, has been similarly shortened.

p.t.c.	phase transfer catalysis
Py	pyridine
Rha	rhamnose
RNA	ribonucleic acid
Ser	serine
s.i.m.s.	secondary-ion mass spectrometry
SOMO	singly occupied molecular orbital
TASF	tris(dimethylamino)sulphur (trimethylsilyl)difluoride
Tbdms	*t*-butyldimethylsilyl
Tbdps	*t*-butyldiphenylsilyl
Tf	trifluoromethanesulphonyl
TFAA	trifluoroacetic anhydride
Th	theophyllyl
THF	tetrahydrofuran
Thp	tetrahydropyranyl
Thr	threonine
Tips	tetraisopropyldisiloxyl
t.l.c.	thin layer chromatography
Tmb	2,4,6-trimethylbenzoyl
Tms	trimethylsilyl
TPAP	tetra-*n*-propylammonium ruthenate (VII)
TPP	triphenylphosphine
Tps	triisopropylbenzenesulphonyl
Tr	triphenylmethyl (trityl)
Ts	*p*-toluenesulphonyl
U	uracil-3-yl
UDP	uridine diphosphate
UDPG	uridine diphosphate glucose
u.v.	ultraviolet

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