GAS CHROMATOGRAPHY AND MASS SPECTROMETRY OF SOME STERICALLY CROWDED TRIALKYLSILYL DERIVATIVES OF MONOSACCHARIDES AND RELATED COMPOUNDS

by

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A dissertation submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements of the degree of

MASTER OF SCIENCE

to my parents

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Abstract

A preliminary study on the gas chromatography and mass spectrometry (Gas Phase Analytical Chemistry) of a series of silyl ether derivatives of monosaccharides and related molecules is described. The silyl groups of interest all contain a bulky alkyl substituent, i.e. t-butyl or i-propyl and collectively are described as sterically crowded trialkylsilyl (SCTASi) groups. They are : tert-butyldimethylsilyl (TBDMSi); cyclo-tetramethylene-iso-propyl-silyl (TMIPSi); and cyclo-tetramethylene-tert-butylsilyl (TMTBSi). Monosaccharides (D-2-deoxyribose, D-ribose, D-xylose, D-glucose, D-galactose, D-mannose and D-fructose) as well as some related molecules (D-1,4 ribono-lactone and β-D-benzylribofuranoside) were reacted with the silyl reagents in various proportions and the products were analyzed by gas chromatography and the peaks studied by electron impact mass spectrometry. By these methods partial and mixed silyl derivatives could be obtained, which yielded information on structure and rearrangement and fragmentation directing behavior of SCTASi-groups in mass spectra.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF SCHEMES

LIST OF FIGURES

Page

ABBREVIATIONS

Ac	acetyl
AcAnh	acetic anhydride
AcIm	acetyl imidazole
AcOH	acetic acid
B	base unit of nucleoside
CI	chemical ionization
DMF	N,N-dimethylformamide
EI	electron impact
Et	ethyl
FI	field ionization
FD	field desorption
GC	gas chromatography
HPLC	high performance liquid chromatograph
Im	imidazole
Im·HCl	imidazole hydrogen chloride
i-Pr	*iso*-propyl
$M^{+\cdot}$	molecular ion
PYR	pyridine
S	sugar unit of nucleoside
SCTASi	sterically crowded trialkylsilyl
TBDMSi	*tert*-butyl dimethysilyl

t-Bu	*tert*-butyl
TFA	trifluoroacetyl
TFAA	trifluoroacetyl anhydride
TFAIm	trifluoroacetyl imidazole
THF	tetrahydrofuran
TMIPSi	*cyclo*-tetramethylene-*iso*-propylsilyl
TMSi	trimethylsilyl
TMTBSi	*cyclo*-tetramethylene-*tert*-butylsilyl

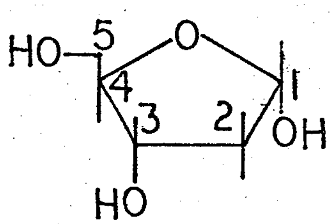
SYMBOLS

α	separation factor
	single electron movement
	double electron movement
	*iso*-propyl
	*tert*-butyl
	*cyclo*-tetramethylene

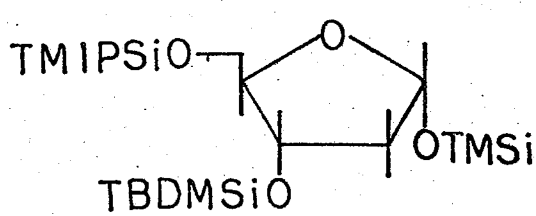
Nomenclature

I	= D-2-deoxyribose	a	= TMSi
II	= D-ribose	b	= TBDMSi
III	= D-xylose	c	= TMIPSi
IV	= D-glucose	d	= TMTBSi
V	= D-galactose	e	= TMHSi
VI	= D-mannose	p	= TFA
VII	= D-fructose	q	= Ac
VIII	= β-D-benzyl ribofuranoside		
IX	= 1,4-ribonolactone		

Each derivative is represented by a Roman numeral with subscripts in small letters. The first subscript denotes a substituent group at the lowest available carbon number on the molecule. The second subscript is for a substituent group at the second lowest available carbon number bearing the hydroxyl, etc.



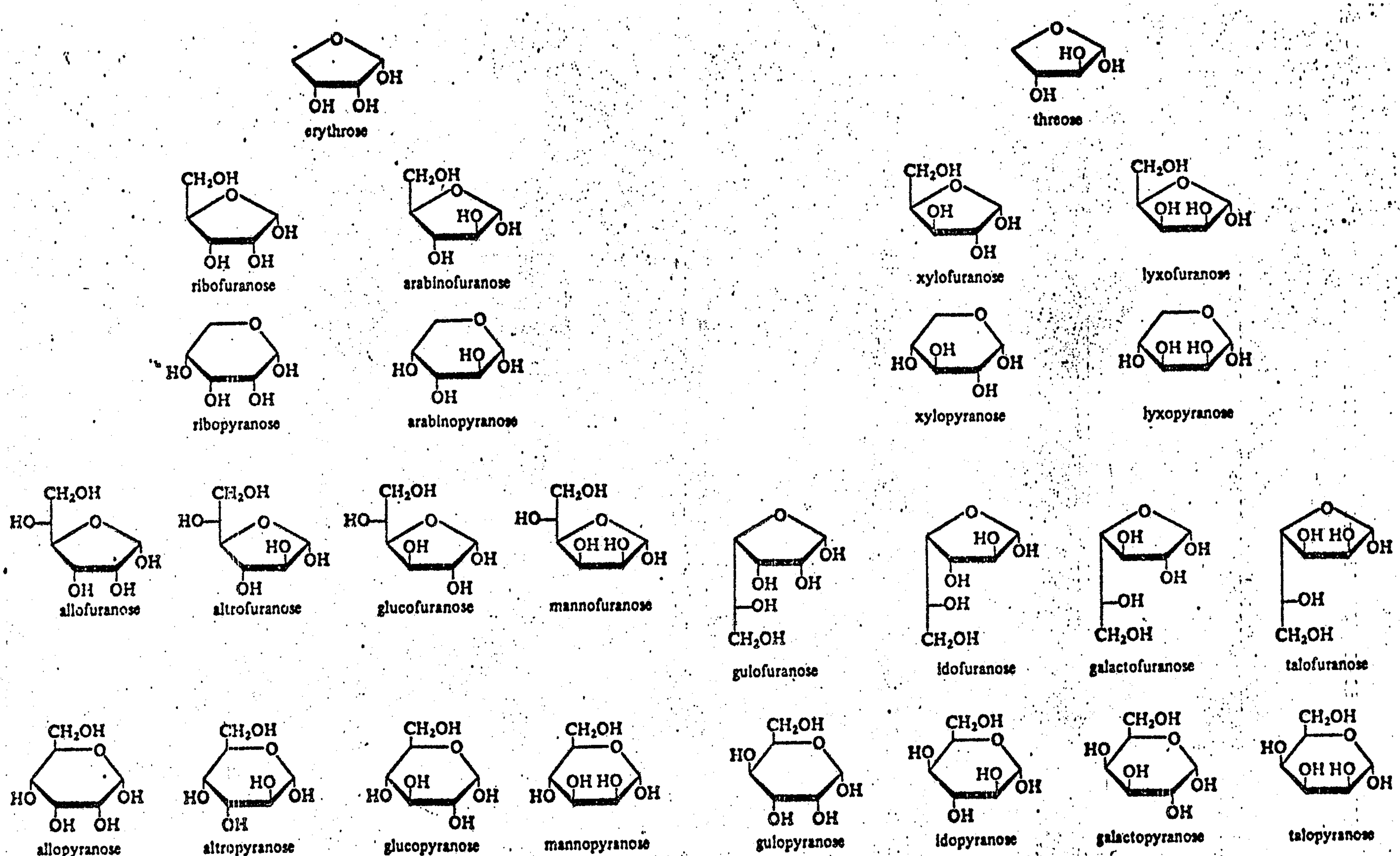
D-2-deoxyribose
with numberings on
each carbon atom



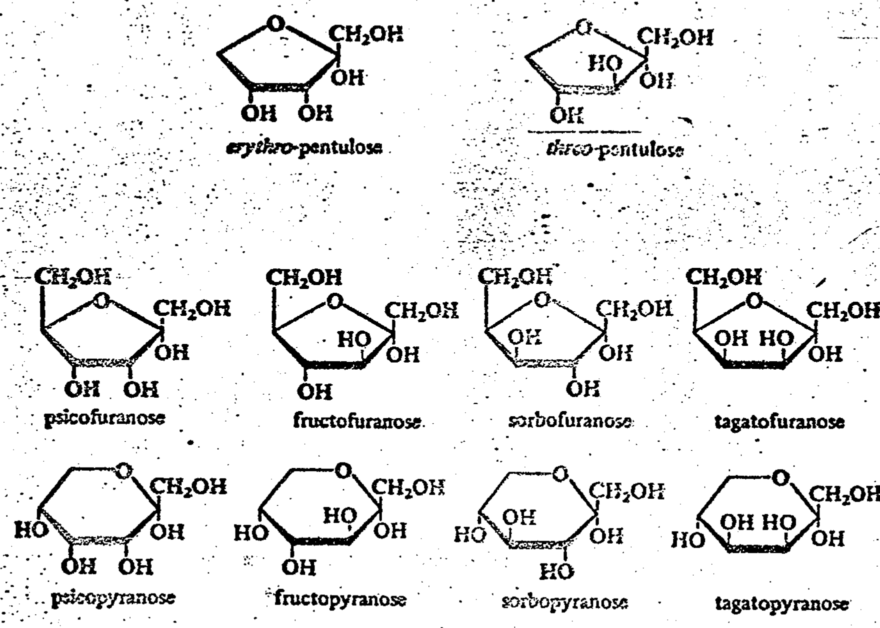
1-O-TMSi-3-O-TBDMSi-5-O-TMIPSi-D-2-deoxyribose or I_{abc}

I_{abc} = D-2-deoxyribose with TMSiO on carbon number 1; TBDMSiO on carbon number 3; and TMIPSiO on carbon number 5.

When the subscripts are bracketed, no specification is make to assign substituent groups to individual carbon atoms.



: Cyclic forms of α-D-aldoses.



: Cyclic forms of α-D-ketoses.

INTRODUCTION

Carbohydrates

Carbohydrates are among the most abundant chemical compounds in biological systems. They can be broadly defined as substances which upon hydrolysis, give polyhydroxy-aldehydes or polyhydroxy-ketones (1)

A brief classification of carbohydrates (2) is given as follows:

Table 1 : Classification of carbohydrates.

- carbohydrates
  - monosaccharides
  - di-saccharides
  - tri-saccharides
  - polysaccharides
    - homopolysaccharides e.g. starch and glycogen
    - heteropolysaccharides e.g. acid muco-saccharides
  - complex carbohydrates
    - glycoproteins
    - glycolipids
    - nucleic acids

Together with lipids and proteins, carbohydrates are considered as the main building units of living organisms. In plants, they are the structural units, in the form of cellulose, hemi-cellulose and lignins, as well as the storage substances, in the form of starch, pectins and sugars. In higher animals, they are found as hyaluronic acid, glycogen, blood group substances, glucose, mucopolysaccharides, adenosine triphosphate (ATP), nucleic acids and hydroxy acids.

The simplest form of carbohydrate is the monosaccharide or "sugar" sub-unit. Monosaccharides can again be differentiated as aldoses and ketoses, depending on the nature of carbonyl group on the molecules. In terms of chemical functional groups, monosaccharides are classified into: 1) neutral sugars; 2) basic sugars (with NH_2 or CH_3-N(H)- groups); and 3) acidic sugars (with carboxyl groups). Each sugar is also named according to the number of carbon atoms it carries. For example, a three "carbon" sugar is a triose. A schematic classification of simple sugars can be represented as follows:-

Table 2: Classification of simple sugars

neutral ketoses	keto-trioses (3 carbons)
acidic ketoses	keto-tetroses (4 carbons)
basic ketoses	⋮
	keto septoses (7 carbons)

neutral aldoses	aldo-trioses (3 carbons)
acidic aldoses	aldo-tetroses (4 carbons)
basic aldoses	⋮
	aldo-septoses (7 carbons)

Isomerism and stereochemistry of monosaccharides

Isomerism and stereochemistry of sugars have been studied since the 19th cnetury. Because of the polyhydroxy nature of monosaccharide molecules, and hence chiral carbon atoms, many stereo-isomers are possible. Take