

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

by

Peter K. T. Ng

A Thesis

**Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements for the
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**Department of Chemistry
The University of Manitoba
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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

	Page
ACKNOWLEDGEMENTS	ii
ABSTRACT	iii
TABLE OF CONTENTS	iv
LIST OF TABLES	vii
LIST OF SCHEMES	viii
LIST OF FIGURES	ix
ABBREVIATIONS	xiv
NOMENCLATURE	xvi
I. INTRODUCTION	1
Carbohydrates	1
Isomerism and stereochemistry of monosaccharides	2
Analytical chemistry of carbohydrates	6
Gas phase analytical chemistry	9
Chemical derivatization	10
Silylation	10
Gas phase analytical chemistry of carbohydrates	15
Gas phase analysis in carbohydrate structure determination	15
II. EXPERIMENTAL	20
Reagents	20
Synthesis of β -D-benzylribofuranoside	21
Preparation of analytical derivatives	22
Persilylation	22
Partial silylation	23

	Page
Mixed derivatization	23
Gas chromatography	24
Quantitative GC	25
Mass spectrometry	28
III. GAS CHROMATOGRAPHY	29
Introduction	29
Retention indices	30
GC system	31
Solvent systems	32
Silylated monosaccharides	36
Silylated 1,4-ribonolactones	48
Silylated β -D-benzylribofuranosides	55
Quantitative GC	65
Mutarotation of sugars	69
IV. MASS SPECTROMETRY	74
Introduction	74
Electron impact mass spectrometry	75
Electron impact behavior of trialkylsilyl ethers of carbohydrates	77
a) Mass spectra of TBDMSi-D-hexopyranose systems	83
1) Pentakis-O-TBDMSi-D-glucoses	83
2) Pentakis-O-TBDMSi-D-mannoses	91
3) Pentakis-O-TBDMSi-D-fructoses	91

	Page
b) Mass spectra of SCTASi-O-D-2-deoxyriboses	96
1) Per SCTASi-D-2-deoxyriboses	96
2) Partial SCTASi-D-2-deoxyriboses	104
c) Mass spectra of SCTASi- β -D-ribofuranosides	109
1) Per SCTASi- β -D-benzylribofuranosides	109
2) Partial SCTASi-O- β -D-benzylribofuranosides	117
3) Mixed Ac/TBDMSi derivatives of β -D-benzyl- ribofuranosides	129
4) Mass spectra of SCTASi-D-riboses	137
5) Mass spectra of SCTASi-D-xyloses	137
d) Mass spectra of SCTASi-1,4-ribonolactones	
1) Per SCTASi-1,4-ribonolactones	117
2) Partial SCTASi-1,4-ribonolactones	152
V. CONCLUSION	164
VI. BIBLIOGRAPHY	166

LIST OF TABLES

	Page
1) Classification of carbohydrates.	1
2) Classification of sugars.	2
3) Number of stereo-isomers for monosaccharides.	4
4) Analytical capabilities of a variety of instrumental techniques.	7 8
5) Derivatives from different protecting groups.	18
6) GC retention data of per-O-TMSi-sugars.	38
7) GC retention data of partial-O-TBDBSi-sugars.	43
8) GC retention data of per-O-TBDMSi-sugars.	46
9) Comparison of different studies of silylated sugars.	47
10) GC retention data of silylated 1,4-ribonolactones.	50
11) GC retention data of β -D-benzylribofuranoside derivatives.	56
12) Comparison of mutarotation studies in pyridine.	71

LIST OF SCHEMES

	Page
1) Cyclization of D-ribose in H ₂ O.	4
2) Formation of external acetals.	5
3) General outline for carbohydrate structure determination.	16
4) Formation of 1,4-lactones from aldoses.	48
5) TMSilylation of lactones.	48
6) Possible fissions of a trimethylsilyl ether.	79
7) Geneses of m/z 693, m/z 561, m/z 429, m/z 519 and m/z 445.	86
8) Formation of m/z 487, m/z 519 and m/z 445 from m/z 693.	87
9) Formation of m/z 231, m/z 245, and m/z 375 from M ⁺ ion.	88
10) Formation of m/z 288 from M ⁺ ion.	89
11) Formation of m/z 301 from pentakis-O-TBDMSi-glucofuranose.	70
12) Formation of (M-145) ⁺ ion from M ⁺ of pentakis-O-TBDMSi-D-fructose.	91
13) Mass spectral fragmentation of SCTASi-D-2-deoxyriboses.	102
14) Mass spectral fragmentation patterns of SCTASi-β-D-benzyl-ribofuranosides.	114
15) Mass spectral fragmentation patterns of SCTASi-D-ribofuranoses.	142

LIST OF FIGURES

	Page
1) Diagram of an aldo-pentose showing three chiral centres.	3
2) Diagram showing the number of chiral centres on an aldo-pentose if D- and L- configurations are distinguished.	3
3) Common SCTASi groups	14
4a) Gas chromatogram of the upper layer of a silylated sugar reaction mixture when DMF was used as a solvent.	37
4b) Mass spectrum of di- <u>tert</u> -butyltetramethyldisiloxane.	35
5) Gas chromatogram of silylated D-ribose.	39
6) Gas chromatogram of TBDMSi-D-2-deoxyribose.	40
7) Gas chromatogram of silylated D-ribose.	41
8) Gas chromatogram of TBDMSi-D-galactose.	42
9) Possible structures of bis-O-TBDMSi-D-2-deoxyribose.	44
10) Gas chromatogram of silylated 1,4-ribonolactones.	51
11) Gas chromatogram of partially silylated 1,4-ribonolactones.	52
12) Gas chromatogram of O-TMTBSi-1,4-ribonolactones.	53
13) Gas chromatogram of mixed TMSi/TBDMSi derivatives of 1,4-ribonolactones.	54
14) Gas chromatogram of O-silylated β -D-benzylribofuranosides.	58
15) Gas chromatogram of mono-O-TMTBSi- β -D-benzylribofuranosides.	59
16) Gas chromatogram of O-TMTBSi- β -D-ribofuranosides.	60
17) Gas chromatogram of TMIPSi ₃ - β -D-benzylribofuranoside.	61
18) Gas chromatogram of mixed TMSi/TBDMSi derivatives of β -D-benzylribofuranoside.	62

	Page
19) Gas chromatogram of TFA/TBDMSi mixed derivatives of β -D-benzylribofuranosides.	63
20) Gas chromatogram of mixed derivatives of β -D-benzylribofuranosides.	64
21) FID response curves for silylated β -D-benzylribofuranosides and 1,4-ribonolactones.	67
22) FID response curves of silylated hexose, pentose and D-2-deoxyribose.	68
23) Equilibrium processes in mutarotation of sugars.	70
24) Formation of different ions from the molecular ion.	76
25) Mass spectrum of decafluorophenylphosphine.	78
26) Loss of trimethylsilanol from M-15 ⁺ .	81
27) Mass spectrum of pentakis-O-TBDMSi-D-glucose.	84
28) Mass spectrum of pentakis-O-TBDMSi-D-glucose.	85
29) Mass spectrum of pentakis-O-TBDMSi-D-mannose.	92
30) Mass spectrum of pentakis-O-TBDMSi-D-mannose.	93
31) Mass spectrum of pentakis-O-TBDMSi-D-fructose.	94
32) Mass spectrum of pentakis-O-TBDMSi-D-fructose.	95
33) Comparison between SCTASi-deoxyribonucleosides and SCTASi-D-2-deoxyriboses.	96
34) Major fragments of SCTASi-2-deoxyribose.	97
35) Mass spectrum of tris-O-TBDMSi-D-2-deoxyribose.	98
36) Mass spectrum of tris-O-TBDMSi-D-2-deoxyribose.	99

	Page
37) Mass spectrum of tris-O-TMTBSi-D-2-deoxyribose.	100
38) Mass spectrum of tris-O-TMTBSi-D-2-deoxyribose.	101
39) Mass spectrum of bis-O-TBDMSi-D-2-deoxyribose.	105
40) Mass spectrum of bis-O-TBDMSi-D-2-deoxyribose.	106
41) Mass spectrum of mono-O-TMSi-bis-O-TBDMSi-D-2-deoxyribose.	107
42) Mass spectrum of mono-O-TBDMSi-bis-O-TMSi-D-2-deoxyribose.	108
43) a) Comparison of SCTASi-ribonucleoside, SCTASi- β -D-benzylribofuranoside and SCTASi-D-ribofuranoside.	109
b) Major fragments of SCTASi- β -D-benzylribofuranosides.	109
44) Mass spectrum of tris-O-TMSi- β -D-benzylribofuranoside.	110
45) Mass spectrum of tris-O-TBDMSi- β -D-benzylribofuranoside.	111
46) Mass spectrum of tris-O-TMIPSi- β -D-benzylribofuranoside.	112
47) Mass spectrum of tris-O-TMTBSi- β -D-benzylribofuranoside.	113
48) Mass spectrum of mono-O-TBDMSi- β -D-benzylribofuranoside.	118
49) Mass spectrum of mono-O-TBDMSi- β -D-benzylribofuranoside.	119
50) Mass spectrum of mono-O-TBDMSi- β -D-benzylribofuranoside.	120
51) Mass spectrum of mono-O-TMTBSi- β -D-benzylribofuranoside.	121
52) Mass spectrum of mono-O-TMTBSi- β -D-benzylribofuranoside.	122
53) Mass spectrum of mono-O-TMTBSi- β -D-benzylribofuranoside.	123
54) Mass spectrum of bis-O-TBDMSi- β -D-benzylribofuranoside.	124
55) Mass spectrum of bis-O-TBDMSi- β -D-benzylribofuranoside.	125
56) Mass spectrum of bis-O-TBDMSi- β -D-benzylribofuranoside.	126
57) Mass spectrum of bis-O-TMTBSi- β -D-benzylribofuranoside.	127
58) Mass spectrum of bis-O-TMTBSi- β -D-benzylribofuranoside.	128

	Page
59) Mass spectrum of mono-O-TBDMSi-bis-O-Ac- β -D-benzylribofuranoside.	130
60) Mass spectrum of mono-O-TBDMSi-bis-O-Ac- β -D-benzylribofuranoside.	131
61) Mass spectrum of mono-O-TBDMSi-bis-O-Ac- β -D-benzylribofuranoside.	132
62) Mass spectrum of mono-O-Ac-bis-O-TBDMSi- β -D-benzylribofuranoside.	133
63) Mass spectrum of mono-O-Ac-bis-O-TBDMSi- β -D-benzylribofuranoside.	134
64) Mass spectrum of mono-O-Ac-bis-O-TBDMSi- β -D-benzylribofuranoside.	135
65) Mass spectrum of tris-O-Ac- β -D-benzylribofuranoside.	136
66) Mass spectrum of tetrakis-O-TBDMSi-D-ribose.	138
67) Mass spectrum of tetrakis-O-TBDMSi-D-ribose.	139
68) Mass spectrum of tetrakis-O-TBDMSi-D-ribose.	140
69) Mass spectrum of tetrakis-O-TBDMSi-D-ribose.	141
70) Mass spectrum of tetrakis-O-TMTBSi-D-ribose.	144
71) Mass spectrum of tetrakis-O-TBDMSi-D-xylose.	145
72) Mass spectrum of tetrakis-O-TBDMSi-D-xylose.	146
73) Mass spectrum of tris-O-TMSi-1,4-ribonolactone.	148
74) Mass spectrum of tris-O-TBDMSi-1,4-ribonolactone.	149
75) Mass spectrum of tris-O-TMIPSi-1,4-ribonolactone.	150
76) Mass spectrum of tris-O-TMTBSi-1,4-ribonolactone.	151

	Page
77) Mass spectrum of mono-O-TBDMSi-1,4-ribonolactone.	153
78) Mass spectrum of mono-O-TBDMSi-1,4-ribonolactone.	154
79) Mass spectrum of mono-O-TBDMSi-1,4-ribonolactone.	155
80) Mass spectrum of mono-O-TMTBSi-1,4-ribonolactone.	156
81) Mass spectrum of mono-O-TMTBSi-1,4-ribonolactone.	157
82) Mass spectrum of bis-O-TBDMSi-1,4-ribonolactone.	158
83) Mass spectrum of bis-O-TBDMSi-1,4-ribonolactone.	159
84) Mass spectrum of bis-O-TBDMSi-1,4-ribonolactone.	160
85) Mass spectrum of bis-O-TMTBSi-1,4-ribonolactone.	161
86) Mass spectrum of bis-O-TMTBSi-1,4-ribonolactone.	162
87) Mass spectrum of bis-O-TMTBSi-1,4-ribonolactone.	163

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
<u>i</u> -Pr	<u>iso</u> -propyl
M ⁺	molecular ion
PYR	pyridine
S	sugar unit of nucleoside
SCTASi	sterically crowded trialkylsilyl
TBDMSi	<u>tert</u> -butyl dimethylsilyl

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

SYMBOLS

α

separation factor

single electron movement

double electron movement

iso-propyl

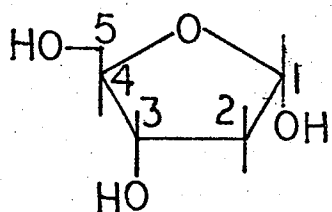
tert-butyl

cyclo-tetramethylene

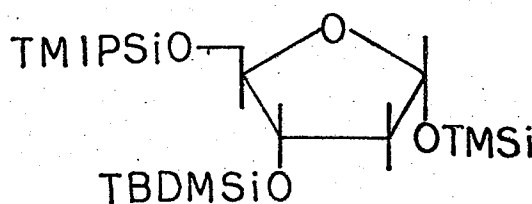
Nomenclature

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.



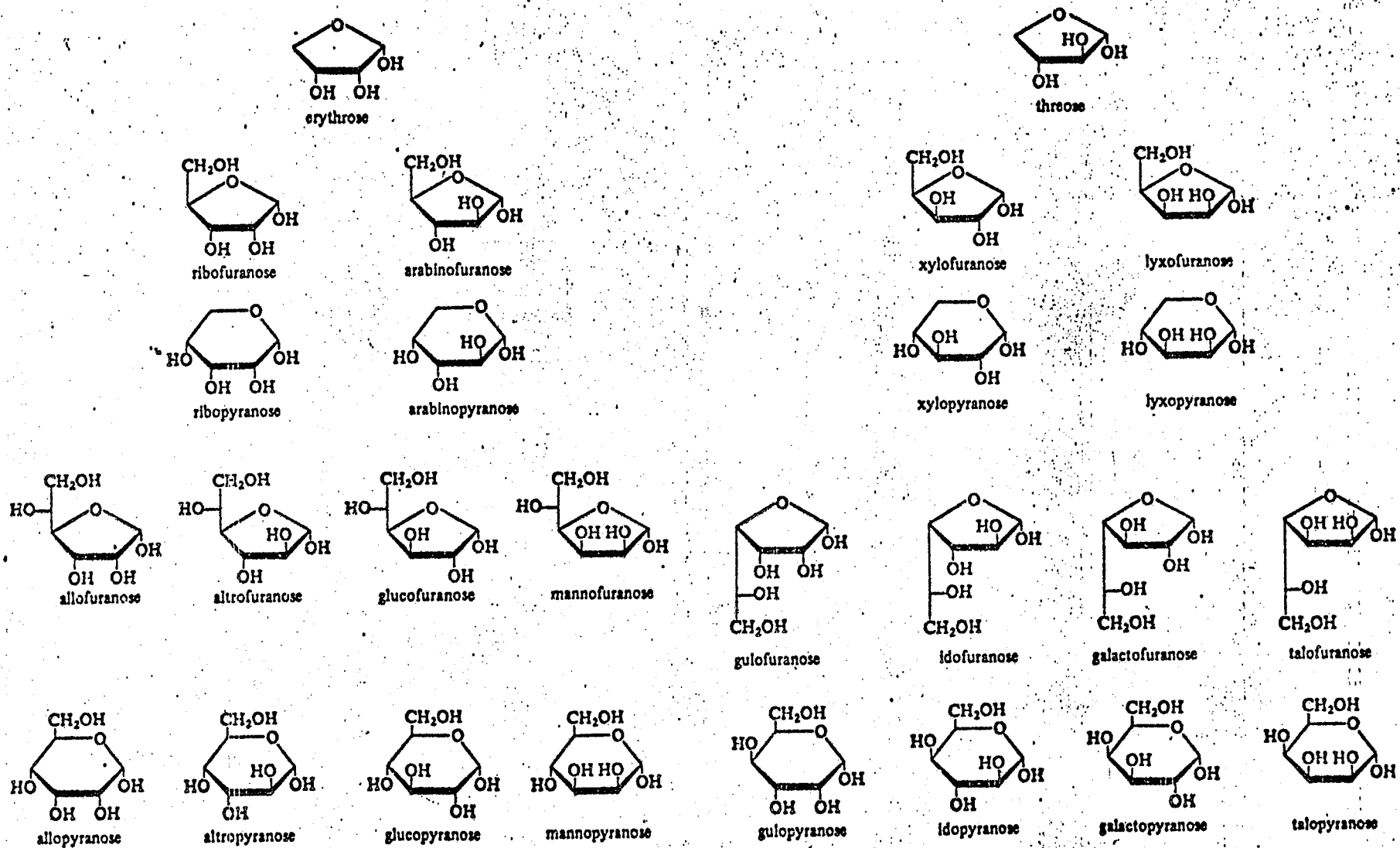
D-2-deoxyribose
with numberings on
each carbon atom



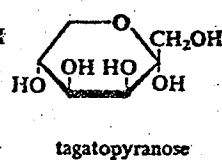
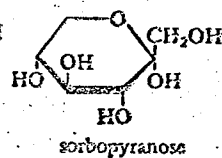
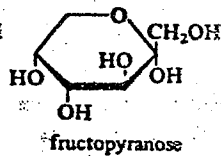
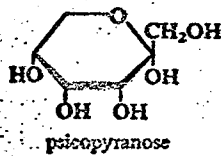
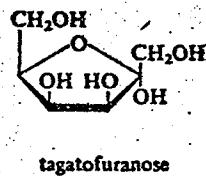
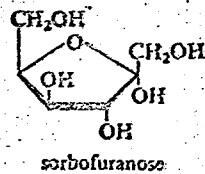
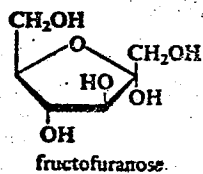
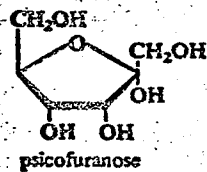
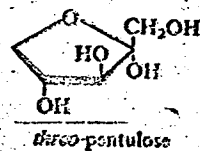
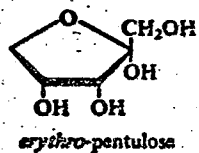
1-0-TMSi-3-0-TBDMSi-5-0-TMIPSi-D-2-deoxy-
ribose or I_{abc}

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 made to assign substituent groups to individual carbon atoms.



: Cyclic forms of α -D-aldoses.



: Cyclic forms of α -D-ketoses.

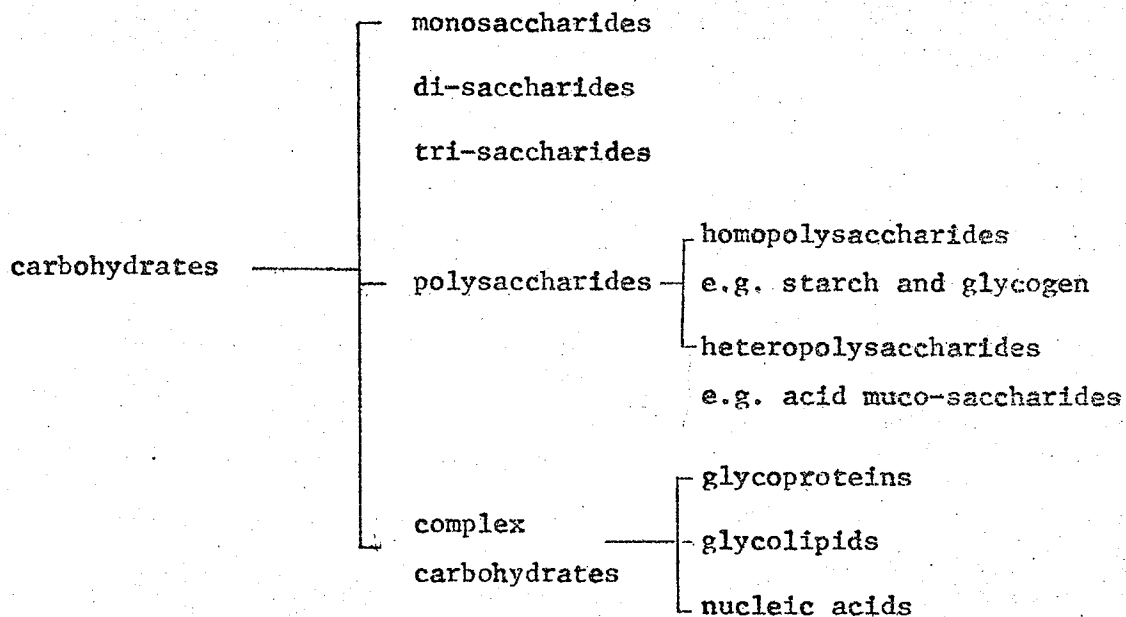
INTRODUCTION

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:

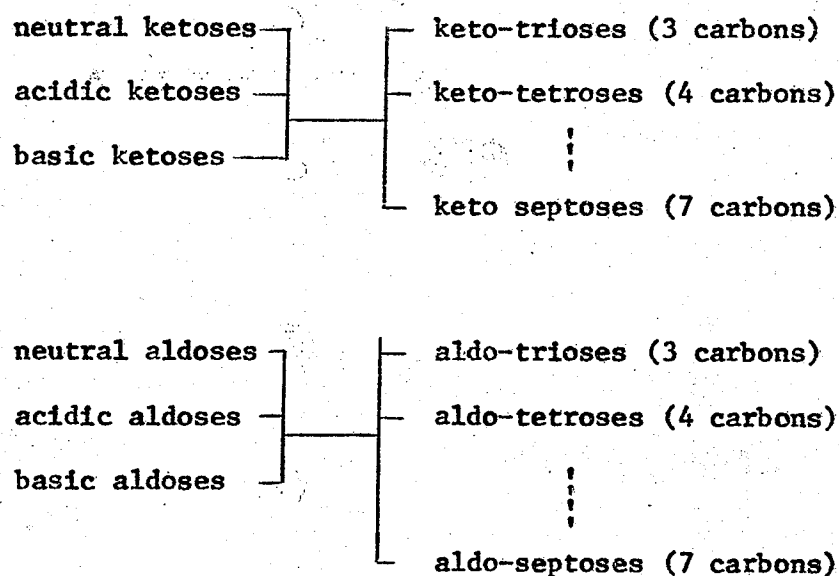
Table 1 : Classification of carbohydrates.



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, hemicellulose 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 $\text{CH}_3\text{-N(H)-}$ 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



Isomerism and stereochemistry of monosaccharides

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