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DETERMINATION OF THE STRUCTURES OF TRISACCHARIDES BY ^{13}C-N.M.R. SPECTROSCOPY

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ABSTRACT

A literature survey of the ^{13}C-n.m.r. chemical-shift data for aqueous solutions of monosaccharides, disaccharides, oligosaccharides, and their methyl derivatives is reported. Analysis of these data reveals a set of empirical rules which may be used in the elucidation of the structure of trisaccharides of known monosaccharide composition, and an example is reported. However, it is not possible to extend the rules to tetrasaccharides and higher saccharides without additional chemical-shift data for related model compounds.

INTRODUCTION

We have used ^{13}C-n.m.r. spectroscopy to determine the structures of various neutral tri- to hepta-saccharides obtained from the milk of marsupials and monotremes[1–5]. The method depends on the observation of a resolved resonance for each carbon atom in the oligosaccharide, and subsequent assignment. The assignment procedure was based initially on the assigned spectra of model compounds[1], but generalisations and empirical rules were observed which allowed the analysis of more-complex branched chains[5] without the need for detailed chemical-shift data for model compounds.

Analysis of the ^{13}C-n.m.r. chemical-shift data in the literature on monosaccharides, disaccharides, and oligosaccharides enabled these empirical rules to be refined. We now report the ^{13}C-n.m.r. data for small oligosaccharides, state the empirical rules, and apply them to determine the structure of a trisaccharide of known monosaccharide composition.

The data in Table I for monosaccharides, disaccharides, oligosaccharides, their methyl and 2-acetamido-2-deoxy derivatives, and *N*-acetylneuraminic acid were obtained for solutions in H_2O, D_2O, or H_2O–D_2O. Chemical-shift data for D and L isomers are the same (see L-fucopyranose in Table I). Some data (not included in Table I) are available for solutions in dimethyl sulphoxide and, in general, the observed chemical shifts are close to those obtained for aqueous solutions[6,7]. Internal standards (1,4-dioxane, methanol, and others) were used generally, but external Me_4Si or 1,4-dioxane was used occasionally. All chemical shifts

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TABLE I

^{13}C-CHEMICAL SHIFTS OF MONOSACCHARIDES, DISACCHARIDES, OLIGOSACCHARIDES, AND THEIR METHYL DERIVATIVES

The chemical shifts (recorded in p.p.m. from the signal for Me_4Si) for each residue of an oligosaccharide are given under the heading for the relevant monosaccharides, which are arranged alphabetically. For example, in lactose [β-D-Gal-(1→4)-D-Glc] the 4-substituted glucose unit is listed with other substituted glucoses under glucose itself, while the shifts for the galactose ring are included under the heading for galactose.

The letter A is used to indicate the α anomer and B the β anomer, with the adjacent residues written in their abbreviated form. A residue or residues further away have negligible effect on the chemical shifts of A or B (see rule *1*) and are therefore only denoted by the symbol R, which may also represent CH_3. The chemical shift values have been averaged, when the substituents on either side of the residue under consideration are the same; averaged data are indicated by *. The symbol † is used where reassignment of the original data is proposed (see text). Chemical shifts of methyl groups of methyl glycosides have not been included. All spectra were recorded for solutions in D_2O, H_2O, or mixtures thereof.

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*HNC=O*	*COCH$_3$*	*C-7*	*C-8*	*C-9*	*Ref.*
2-Acetamido-2-deoxy-D-galactopyranose (GalpNAc)												
A = α-GalpNAc												
A	92.2	51.4	68.6	69.7	71.6	62.4	176.1	23.2				8
β-GalNAc-(1→6)-A	92.2	51.5	68.5	69.7	70.3	69.0	176.1	23.2				9
B = β-GalpNAc												
B	96.5	54.9	72.3	69.0	76.3	62.2	175.8	23.4				8
B-(1→6)-GalNAc	103.3	53.6	72.2	69.0	76.3	62.2	175.9	23.5				9
β-GalNAc-(1→6)-B	96.6	55.0	72.2	69.0	75.1	69.0	175.9	23.5				9
2-Acetamido-2-deoxy-D-glucopyranose (GlcpNAc)												
A = α-GlcpNAc												
A	92.1	55.3	72.0	71.4	72.8	61.9	175.7	23.3				8
A-(1→CH$_3$*	98.9	54.4	72.2	70.6	72.1	61.4	175.1	22.8				10,11
A-(1→4)-Gal-R*	98.7	54.7	71.5	71.1	72.7	60.9	175.2	22.7				12
β-Gal-(1→3)-A	91.7	53.5	80.9	69.4	71.8	61.0	175.2	22.7				13
α-L-Fuc-(1→4)-A	91.9	55.6	70.7	78.9	72.1	61.2	175.7	23.1				14
R-β-GlcNAc-(1→4)-A*	91.9	55.0	70.6	81.1	71.5	61.4	175.9	23.2				9,15
β-Gal-(1→4)-A	91.6	55.1	70.6	80.1	71.5	61.3	176.0	23.3				15
CH$_3$→3)-A-(1→CH$_3$	98.7	52.6	81.1	69.6	72.2	61.2						10
CH$_3$→4)-A-(1→CH$_3$	98.4	54.2	71.3	80.2	71.3	61.1						10
CH$_3$→6)-A-(1→CH$_3$	98.5	54.0	71.7	70.8	71.7	70.8						10
α-L-Fuc-(1→4) β-Gal-(1→3)>A	91.5	54.6	75.3/ 74.8	74.8/ 75.3	72.1	60.4	174.9	22.8				13

α-L-Fuc-(1→6) β-Gal-(1→3)>A	91.9	53.3	80.5	69.0	71.2	69.0	175.0	22.8	13
CH_3→3) CH_3→4)>A-(1→CH_3	98.6	52.9	81.0	79.4	71.4	60.9			10
CH_3→3) CH_3→6)>A-(1→CH_3	98.6	54.2	81.0	69.7	71.4	70.8			10
CH_3→4) CH_3→6)>A-(1→CH_3	98.4	54.2	71.4	80.4	71.3	69.9			10
B = β-Glc*p*NAc									
B	96.2	58.0	75.2	71.2	77.2	62.0	175.9	23.5	8
B-(1→CH_3*	102.5	57.0	74.7	70.8	76.5	61.6	175.3	23.1	10,11
B-(1→4)-GlcNAc	102.7	56.9	74.7	71.0	77.2	61.8	175.8	23.4	9
B-(1→3)-Gal-R	104.3	57.7	75.9	72.2/ 72.0	77.9	62.6			16
B-(1→6)-Gal-R*	102.8	57.5	75.8	72.1	77.9	62.8			16
B-(1→3)-L-Rha	103.9	57.0	74.9	71.0	76.9	61.8	176.1	23.5	9
β-Gal-(1→3)-B	95.3	56.3	83.3	69.2	75.0	61.0	175.2	22.9	13
α-L-Fuc-(1→4)-B	96.1	58.4	73.9	78.6	76.6	61.2	175.7	23.4	14
R-β-GlcNAc-(1→4)-B*	96.2	57.5	73.7	80.7	75.9	61.4	175.9	23.5	9,15
β-Gal-(1→4)-B	96.2	57.6	74.9	79.7	76.1	61.3	176.0	23.5	15
CH_3→3)-B-(1→CH_3	102.2	54.4	83.6	69.4	76.2	61.4			10
CH_3→4)-B-(1→CH_3	102.3	56.1	74.1	80.3	75.5	61.3			10
β-Gal-(1→4)-B-(1→4)-GlcNAc	102.8	56.6	74.0	79.7	76.8	62.0	176.1	23.6	15
R-β-Gal-(1→4)-B-(1→6)-GalNAcol-R*	102.0	55.9	73.8	78.3	75.7	60.9	175.2	23.0	12
R-β-Man-(1→4)-B-(1→4)-GlcNAc	102.6	56.4	73.4	80.0	75.8	61.4			17
CH_3→6)-B-(1→CH_3	102.3	55.9	74.4	70.8	75.0	71.7			10
α-L-Fuc-(1→4) β-Gal-(1→3)>B	95.4	57.5	76.8	76.1	75.3	60.4	174.9	22.8	13
α-L-Fuc-(1→6) β-Gal-(1→3)>B	95.2	56.1	83.0	68.7	75.0	68.7	175.2	22.5	13
CH_3→3) CH_3→4)>B-(1→CH_3	102.2	54.9	83.5	79.3	75.4	61.1			10
CH_3→3) CH_3→6)>B-(1→CH_3	102.2	54.5	83.5	69.6	75.0	71.7			10

TABLE I *(continued)*

		C-1	C-2	C-3	C-4	C-5	C-6	HNC=O	$COCH_3$	C-7	C-8	C-9	Ref.
$CH_3 \rightarrow 4)$ / $CH_3 \rightarrow 6)$ B-(1→CH_3		102.2	56.0	74.0	80.4	74.2	71.5						10
*2-Acetamido-2-deoxy-*D*-mannopyranose (Man*p*NAc)*													
A = α-Man*p*NAc	A	94.3	54.4	70.1	68.0	73.2	61.7	175.9	23.2				8
B = β-Man*p*NAc	B	94.3	55.3	73.2	67.8	77.5	61.7	176.8	23.2				8
N-*Acetylneuraminic acid* [a]													
A = α anomer	A Sialic acid	—	98.4	41.9	69.4	53.1	72.8			69.4	73.8	64.1	18
B = β anomer		177.9	97.6	40.6	68.5	53.5	71.5	176.0	23.3	69.8	71.6	64.6	18

		C-1	C-2	C-3	C-4	C-5	C-6	Ref.
D-*Allopyranose (All*p*)*								
A = α-All*p*	A-(1→CH_3	100.4	68.1/ 68.3	72.3	67.3	68.3/ 68.1	62.0	21
	A-(1→1)-α-Glc	94.7	68.1/ 68.6	72.0	67.2	68.6/ 68.1	61.9	21
B = β-All*p*	B	94.3	72.2	72.0	67.7	74.4	62.1	22
D-*Allofuranose (All*f*)*								
A = α-All*f*	A-(1→CH_3	103.8	72.3	69.9	85.9	72.7	63.5	23
B=β-All*f*	B-(1→CH_3	109.0	75.6	72.7	83.4	73.8	63.9	23
D-*Altropyranose (Alt*p*)*								
A = α-Alt*p*	A	94.7	71.2	71.1	66.0	72.0	61.6	24
	A-(1→CH_3	101.1	70.0	70.0	64.8	70.0	61.3	25
B = β-Alt*p*	B	92.6	71.6	71.3	65.2	75.0	62.5	24

[a] These values were determined at neutrality and they change with pH; related derivatives have been studied[18–20].

D-*Altrofuranose (Altf)*								
A = α-Alt*f*								
	A	102.2	82.4	76.9	84.3	72.5	63.3	24
B = β-Alt*f*								
	B	96.2	77.5	76.0	82.1	73.4	63.3	24
D-*Arabinopyranose (Arap)*								
A = α-Ara*p*								
	A	97.6	72.9	73.5	69.6	67.2		26
	A-(1→CH_3	107.0	73.9	75.6	71.5	69.3		26
B = β-Ara*p*								
	B	93.4	69.5	69.5	69.5	63.4		26
	B-(1→CH_3	101.0	69.4	69.9	70.0	63.8		27
D-*Arabinofuranose (Araf)*								
A = α-Ara*f*								
	A	101.2	70.3	70.3	81.5	61.3		28
	A-(1→CH_3	109.3	81.9	77.5	84.9	62.4		27
B = β-Ara*f*								
	B	95.2	74.3/ 75.8	74.3/ 75.8	83.1	62.6		28
	B-(1→CH_3	103.2	77.5	75.7	83.1	64.2		27
D-*Fructopyranose (Frup)*								
A = α-Fru*p*								
	A	65.9	99.1	70.9	71.3	70.0	61.9	29
CH_3→3)-A		64.7	98.7	81.4	75.0	70.3	61.9	29
B = β-Fru*p*								
	B*	64.8	99.0	68.5	70.6	70.1	64.2	26,29
	B-(2→CH_3	61.8	101.4	69.3	70.5	70.0	64.7	30
CH_3→3)-B		64.9	99.0	78.4	70.8	70.3	64.3	29
α-Glc-(1→4)-B	Maltulose	65.0/ 64.6	99.4	68.1	79.2	70.3	64.6/ 65.0	7
α-Glc-(1→5)-B	Leucrose	65.1	99.2	69.2	71.2	80.2	63.4	7
D-*Fructofuranose (Fruf)*								
A = α-Fru*f*								
	A*	63.9	105.4	82.9	77.0	82.2	62.0	26,29

TABLE I *(continued)*

		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ref.*
A-(2→CH_3		58.7	109.1	81.0	78.2	84.0	62.1	30
CH_3→3)-A		63.1	104.9	92.2	78.1	82.0	64.3	29
α-Glc-(1→4)-A	Maltulose	64.6	106.4	83.4	81.3	82.3	62.5	7
α Glc (1 →6) A	Isomaltulose (Palatinose)*	63.9/ 58.4	105.8	82 8	77 2	81 1	67 9	7,31
B = β-Fru*f*								
B*		63.7	102.4	76.4	75.4	81.6	63.3	26,29
B-(2→CH_3		60.0	104.7	77.7	75.9	82.1	63.6	30
B-(2→1)-β-Fru*f*-R	1-Kestose, Nystose *	61.6	104.5	77.9	75.8	82.3	63.4	7
B-(2→1)-α-Glc-R	Sucrose, Raffinose *	63.4/ 62.2	104.5	77.3	74.9	82.2	63.4/ 62.2	26,32,33
CH_3→3)-B		63.8	102.4	85.5	75.1	81.7	64.7	29
α-Glc-(1→4)-B	Maltulose	63.7/ 63.9	103.1	76.5	82.4	81.2	63.9/ 63.7	7
α-Glc-(1→6)-B	Isomaltulose (Palatinose)*	63.8	102.8	76.5	75.7	80.0	68.9	7,31
α-Glc-(1→2)-B-(1→2)-β-Fru*f*-R	1-Kestose, Nystose *	62.1	104.9	77.9	75.1	82.4	63.5	7
R-β-Fru*f*-(1→2)-B-(1→2)-β-Fru*f*	Nystose	62.2	104.3	78.7	75.5	82.3	63.5	7
α-Glc-(1→3)-B-(2→1)-α-Glc	Melezitose	62.9	104.6	84.2	74.3	82.2	63.1	31
L-*Fucopyranose (Fuc*p)								
A = α-Fu*cp*								
A		93.1	69.1	70.3	72.9	67.8	16.6	26
≠ A-(1→CH_3		100.5	69.0	70.6	72.9	67.5	16.5	27
A-(1→4)-GlcNAc-R*		99.8	68.9†	70.1†	72.9†	67.8	16.3	13,14
A-(1→6)-GlcNAc-R		99.9	68.3†	70.0†	72.3†	67.1	15.8	13
A-(1→2)-Gal-R*		101.0	69.9	70.3	73.0	68.3	16.0	12
A-(1→3)-Gal-R		102.1	69.9/ 69.7†	70.7†	73.0†	68.4	16.6	34

B = β-Fuc*p*							
B	97.1	72.7	73.9	72.4	71.7	16.6	26
≠ B-(1→CH_3	104.8	71.5	74.1	72.4	71.9	16.5	27
B-(1→3)-Gal-R	103.8	72.5/ 72.3	74.1	72.5/ 72.3	70.7	16.6	34
(≠ These are the values for D-Fuc)							
D-*Galactopyranose (Gal*p)							
A = α-Gal*p*							
A	93.2	69.4	70.2	70.3	71.4	62.2	26
A-(1→CH_3	100.1	69.2	70.5	70.2	71.6	62.2	26
A-(1→4)-Gal-R*	101.3	69.5	70.0	69.9	71.9	61.5	35
A-(1→6)-Glc Melibiose	99.02(α) 98.98(β)	69.3	70.3	70.0	71.8	61.9	33
A-(1→4)-L-Rha-R*	100.5	69.3	69.9	69.9	70.7	61.6	36
α-L-Rha-(1→2)-A	92.6	77.8	69.1	70.3		61.9	37
α-L-Rha-(1→3)-A	93.1	68.5	77.9	70.0	71.2	61.8	37
β-Gal-(1→3)-A	93.0	68.3	80.2	69.9	70.9	62.0	1
β-L-Rha-(1→3)-A	92.8	67.7	76.9	67.4	71.0	61.8	37
α-L-Rha-(1→4)-A	91.8	70.2	68.0	76.2	69.4	60.9	37
β-Gal-(1→4)-A	93.2	69.7	70.6/ 70.5	79.2	70.5/ 70.6	61.6	1
R-α-L-Rha-(1→6)-A *e.g.* Robinobiose / Rhamninose* / Isorhamninose	93.1	69.1	69.8	70.2	69.9	68.2	37,38,39
β-L-Rha-(1→6)-A	93.6	69.5†	70.4†	70.4†	71.2†	69.3	40
CH_3→6)-A	93.5	69.7	70.0	70.7	69.5	73.0	41
β-Glc-(1→3)-A-(1→CH_3	100.0	69.6	80.4	67.9	71.1	61.9	42
α-Gal-(1→4)-A-(1→CH_3	100.4	69.3/ 69.5	71.9	79.8	70.1/ 70.0/ 69.9	61.5	35
CH_3→4)-A-(1→CH_3	101.4	70.5	72.0	81.1	72.4	62.0	43
R-α-L-Rha-(1→3)-A / α-Glc-(1→4)-A	93.6	69.9	78.3	76.5	72.8	61.8	44
CH_3→3)-A / CH_3→4)-A	93.4	69.0	80.5	76.7	72.0	62.2	44
α-L-Rha-(1→3)-A / α-Glc-(1→6)-A	93.6	70.4	78.4	69.8	70.8	67.7	45
CH_3→2)-A-(1→CH_3 / CH_3→6)-A-(1→CH_3	96.8	77.5	68.6	69.5	73.2	71.9	46

TABLE I *(continued)*

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ref.*
B = β-Gal*p*							
B	97.3	72.9	73.8	69.7	76.0	62.0	26
B-(1→CH_3	104.5	71.7	73.8	69.7	76.0	62.0	26
B-(1→3)-GalNAcol	104.4	71.7	73.1	69.1	75.6	61.6	12
B-(1→3)-GlcNAc-R*	104.1	71.4	73.2	69.2	75.9	61.4	13,47
B-(1→4)-GlcNAc-R*	104.0	72.2	73.8	69.8	76.3	62.2	15,47
B-(1→6)-GlcNAc-R	104.2	71.6	73.6	69.5	76.0	61.8	47
B-(1→2)-Gal-R*	104.5	73.2	73.7	69.4	76.3	61.7	48
B-(1→3)-Gal-R*	105.1	72.0	73.4	69.4	75.9	61.8	1,2
B-(1→4)-Gal	105.1	72.2	73.6	69.5	76.0	61.8	1
B-(1→6)-Gal-R	103.8	71.1	73.1	69.5/ 69.06	75.6	61.4	49
B-(1→4)-Glc-R* Lactose	103.7	71.9	73.5	69.5	76.2	62.0	1,26
B-(1→4)-Man Epilactose	104.2	72.2	73.7	69.8	76.5	62.3	50
B-(1→2)-L-Rha	105.9(α) 105.1(β)	72.2	73.7	69.7	76.2	62.2	9
B-(1→3)-L-Rha-R*	105.2	72.1	73.5	69.6	75.9	61.9	9,51
B-(1→4)-L-Rha	104.9	72.9	74.0	69.8	76.4	62.1	9
α-L-Rha-(1→2)-B	96.1	79.6	74.2	69.4	75.6	61.7	37
α-Glc-(1→3)-B	97.7	71.5	78.8	66.3	76.1	62.2	44
R-α-L-Rha-(1→3)-B*	97.4	72.3	81.6	69.6	76.1	61.9	37,45
β-Gal-(1→3)-B	97.0	71.8	83.3	69.4	75.6	61.8	1
R-β-L-Rha-(1→3)-B*	97.4	71.9	80.4	66.8	75.9	62.0	37,45
α-Glc-(1→4)-B	97.9	73.1	73.1	78.6	76.3	61.4	44
α-L-Rha-(1→4)-B	96.0	71.4	73.0	75.5	74.5	61.0	37
β-Gal-(1→4)-B	97.3	73.1	74.1/ 75.1	78.1	75.1/ 74.1	61.4	1
R-α-L-Rha-(1→6)-B *e.g.* Robinobiose / Rhamninose* / Isorhamninose	97.4	72.8	73.7	69.7	74.3	67.8	37–40
β-L-Rha-(1→6)-B	97.8	73.1	74.2	70.0	76.3	69.5	40
CH_3→6)-B	97.6	73.0	74.4/ 73.9	70.2	73.9/ 74.4	72.8	41

α-L-Fuc-(1→2)-B-(1→3)-Gal-NAcol-R*	102.9	80.0	72.6	69.2	75.6	61.6	12
α-L-Fuc-(1→2)-B-(1→3)-Glc-NAc-R*	101.1	77.1	72.4	69.0	75.9	61.7	12
β-Gal-(1→2)-B-(1→2)-Gal-R	103.3/ 103.4	81.0/ 81.1	73.4	69.5	75.9	61.6/ 61.7/ 61.9	48
β-Gal-(1→2)-B-(1→CH_3	103.2	79.3	73.6	69.6	75.9	61.7	48
α-L-Fuc-(1→3)-B-(1→4)-Glc	103.9	71.7	81.6	69.7/ 69.9	76.5	62.2	34
β-L-Fuc-(1→3)-B-(1→4)-Glc	101.7	71.7	80.9	67.3	76.3	62.1	34
β-Gal-(1→3)-B-(1→3)-Gal-R	104.9	71.1	82.9	69.4	75.9	61.9	2
R-β-Gal-(1→3)-B-(1→4)-Glc*	103.5	71.1	82.7	69.3	75.9	61.9	1,2
CH_3→3)-B-(1→CH_3	103.9	69.8	82.0	64.2	75.1	61.2	46
α-GlcNAc-(1→4)-B-(1→3)-GalNAcol-R*	105.0	70.4	72.7	77.6	76.1	61.1	12
α-GlcNAc-(1→4)-B-(1→4)-GlcNAc-R*	104.0	70.4	72.7	77.4	76.4	61.0	12
α-Gal-(1→4)-B-(1→4)-Glc-R	103.9/ 104.2	71.8/ 71.9	76.3/ 75.4/ 75.7	78.3	73.8/ 73.1	61.2/ 61.0/ 61.5	35
β-Gal-(1→6)-B-(1→6)-Gal-R	103.8	71.1	73.0	69.5/ 69.1	74.2	69.1	49
R-β-Gal-(1→6)-B-(1→CH_3*	104.3	71.2	73.1	69.3	74.2	69.1	49
R-α-L-Rha-(1→3) α-Glc-(1→4)>B	97.8	73.3	80.8	76.5	76.1	61.6	44
CH_3→3) CH_3→4)>B	97.7	72.4	84.0	76.5	75.9	61.9	44
α-L-Rha-(1→3) α-Glc-(1→6)>B	97.6	72.5	87.7	68.9	75.3	67.6	45
β-GlcNAc-(1→6) β-Gal-(1→3)>B-(1→4)-Glc	103.3	70.7	82.2	69.2	74.5/ 75.7	69.1	3
CH_3→2) CH_3→3) CH_3→4)>B-(1→CH_3 CH_3→6)	103.4	79.8	85.2	73.1	74.9	71.0	46
D-*Galactofuranose (Galf)*							
A = α-Gal*f*							
A-(1→CH_3*	103.5	77.8	75.9	82.7	74.1	63.8	23,27
B = β-Gal*f*							
B-(1→CH_3*	109.6	81.6	78.1	84.4	71.9	63.8	23,27

TABLE I *(continued)*

	C-1	C-2	C-3	C-4	C-5	C-6	Ref.
D-*Glucopyranose (Glcp)*							
A = α-Glc*p*							
A	92.9	72.5	73.8	70.6	72.3	61.6	26
A-(1→CH_3	100.0	72.2	74.1	70.6	72.5	61.6	26
A-(1→2) β-Fru*f*-R *e.g.* Sucrose, 1-Kestose, Nystose, Melezitose *	93.2	72.2	73.8	70.4	73.4	61.3	7,26,31,32
A-(1→3)-Fru*f*-R	101.1	72.4/	74.1/	70.6/	73.3/	61.6/	31
Melezitose		72.0	73.8	70.5	73.2	61.3	
A-(1→4)-Fru*p*	101.6	73.0	74.0	70.8	73.5	61.8	7
Maltulose	98.9(α)						
A-(1→4)-Fru*f*		72.4	73.9	70.6	73.5	61.6	7
Maltulose	99.4(β)						
A-(1→5)-Fru*p*	101.5	73.2	74.2	70.9	73.3	61.9	7
Leucrose	99.6(α)						
A-(1→6)-Fru*f**		72.5	74.1	70.7	73.0	61.7	7,31
Isomaltulose (Palatinose)	99.3(β)						
A-(1→3)-Gal	96.6	72.6†	74.1	70.7	73.0†	61.7	44
A-(1→4)-Gal-R*	101.4	73.2†	73.9	70.5	73.7†	61.5	44
A-(1→6)-Gal-R	99.5	72.5	74.3	70.8	73.1	61.8	45
A-(1→1)-α-Glc	94.0	72.0	73.5	70.6	73.0	61.5	26
α,α-Trehalose							
A-(1→1)-β-Glc	100.9	72.4	73.8	70.4	73.6	61.6	26
α,β-Trehalose	96.9(α)						
A-(1→2)-Glc-R*		72.8	74.1	71.0	72.9	61.8	52,53
e.g. Kojibiose	99.0(β)						
A-(1→3)-Glc	99.8	72.8	74.1	71.3	72.8	61.8	52
Nigerose							

A-(1→4)-Glc-R* *e.g.* Maltose	101.1	73.4†	74.6	71.0	74.3†	62.4	52
A-(1→6)-Glc-R *e.g.* Isomaltose, Panose *	99.4	73.1	74.7	71.2	73.2	62.3	52,54
A-(1→1)-α-Man	94.6	72.0†	74.3	70.7	73.6†	61.7	21
A-(1→1)-α-Xyl*p*	94.5	72.2†	73.7	70.9	73.3†	61.8	21
α-Glc-(1→2)-A Kojibiose	90.8	77.1	73.1	71.1	73.1	62.0	52
β-Glc-(1→2)-A Sophorose	93.1	82.1	73.2	71.1	72.5	62.4	52
CH_3→2)-A	90.7	81.9	73.5	71.3	72.8	62.4	52
α-Glc-(1→3)-A Nigerose	93.1	71.3	80.8	70.6	72.2	61.8	52
β-Glc-(1→3)-A Laminaribiose	93.4	72.2	84.2	69.6	72.4	62.4	52
CH_3→3)-A	93.4	72.6	84.1	70.6	72.8	62.3	52
R-α-Glc-(1→4)-A *e.g.* Maltose, Maltotriose, Panose *	93.3	73.2	74.6	78.5	71.6	62.4	52
R-β-Gal-(1→4)-A *e.g.* Lactose*	92.8	72.1	72.4	79.4	71.1	61.1	1,2,34
R-β-Glc-(1→4)-A *e.g.* Cellobiose, Cellotriose *	92.7	72.1	72.2	79.5	71.0	60.9	26,55
R-β-Man-(1→4)-A*	93.5	72.2	73.0	80.6	71.6	62.0/62.4	56
CH_3→4)-A	93.2	73.0	73.9	80.5	71.7	62.1	52
α-Gal-(1→6)-A Melibiose	93.0	72.3	73.8	70.4	70.9	66.8	33
R-α-Glc-(1→6)-A *e.g.* Isomaltose*	93.3	72.9	74.2	70.7	71.2	67.2	53,54
α-L-Rha-(1→6)-A Rutinose*	93.1	72.6	73.8	71.0	71.5	68.3	39,40
R-β-Glc-(1→6)-A Gentiobiose*, Gentiotriose	93.4	73.0	74.4	71.2	71.5	70.1	52
β-L-Rha-(1→6)-A	93.5	72.9	74.0	70.7	71.9	69.0	40
CH_3→6)-A	93.3	73.0	74.3	71.4	71.4	72.6	52
α-Glc-(1→2)-A-(1→6)-Glc	97.0	76.5	72.7	70.4	73.2	61.5	53
β-Glc-(1→2)-A-(1→CH_3	100.0	81.7	73.3	71.3	72.5	62.2	52
α-Glc-(1→4)-A-(1→4)-Glc Maltotriose	101.1	73.1	74.7	78.5	72.7	62.4	52
CH_3→4)-A-(1→CH_3	101.1	72.8	76.1	83.0	72.1	61.4	57
α-Gal-(1→6)-A-(1→2)-β-Fru*f* Raffinose	92.9	71.8	73.5	70.3	72.2	66.7	33
α-Glc-(1→6)-A-(1→4)-Glc Panose	101.1	74.3	74.6	71.2	71.2	67.4	52
α-L-Rha-(1→6)-A-(1→CH_3	100.1	72.8	73.9	70.4	71.1	68.8	39
CH_3→6)-A-(1→CH_3	100.8	72.6	74.5	71.6/71.2	71.2/71.6	72.6	57

TABLE I *(continued)*

		C-1	C-2	C-3	C-4	C-5	C-6	Ref.
B = β-Glc*p*								
	B	96.7	75.1	76.7	70.6	76.8	61.7	26
	B-(1→CH$_3$	104.0	74.1	76.8	70.6	76.8	61.8	26
	B-(1→3)-Gal-R	104.5	74.1	76.4/ 76.2	70.1	76.2/ 76.4	61.2	42
	B-(1→1)-α-Glc α,β-Trehalose *	103.6	74.1	76.4	70.4	77.0	62.0	26
		105.1(α)						
	B-(1→2)-Glc-R*		74.7	77.2	71.2	77.2	62.3	52
	e.g. Sophorose	103.9(β)						
	B-(1→3)-Glc Laminaribiose	103.9	74.8	77.1	71.2	77.1	62.4	52
	B-(1→4)-Glc-R Cellobiose * Cellotriose	103.3	74.1	76.5	70.4	76.8	61.6	26,55
	B-(1→6)-Glc-R *e.g.* Gentiobiose * Gentiotriose	103.8	74.4	77.1	71.1	77.1	62.5	52
		105.3(α)						
	B-(1→2)-L-Rha		74.5	77.0	70.5	76.7	61.7	9
		104.6(β)						
	B-(1→3)-L-Rha	105.0	74.7	76.9	70.8	76.9	61.9	9
	B-(1→4)-L-Rha	104.4	75.1	77.2/ 77.0	70.8	77.0/ 77.2	61.9	9
	B-(1→4)-Man	104.2	74.7	77.6	71.2	77.1	62.0/ 62.2	56
α-Glc-(1→2)-B	Kojibiose	97.5	79.9	75.8	71.1	77.1	62.0	52
β-Glc-(1→2)-B	Sophorose	95.8	82.8	77.2	71.1	77.2	62.4	52
CH$_3$→2)-B		97.1	85.2	76.8	71.3	77.3	62.4	52
α-Glc-(1→3)-B	Nigerose	97.0	74.1	83.2	70.6	76.6	61.8	52
β-Glc-(1→3)-B	Laminaribiose	97.2	74.8	86.7	69.6	77.1	62.4	52
CH$_3$→3)-B		97.2	75.1	86.7	70.4	77.3	62.3	52
R-α-Glc-(1→4)-B	Maltose Maltotriose * Panose	97.1	75.7	77.8	78.6	76.1	62.4	52

R-β-Gal-(1→4)-B *e.g.*	Lactose*	96.8	74.9	75.4	79.3	75.8	61.1	1,2,34
β-Glc-(1→4)-B	Cellobiose / Cellotriose *	96.6	74.9	75.2	79.5	75.6	61.0	26,55
R-β-Man-(1→4)-B*		97.4	75.5	76.2	80.6	75.8	62.0/62.4	56
CH_3→4)-B		97.1	75.8	76.7	80.5	76.1	62.1	52
α-Gal-(1→6)-B	Melibiose	96.9	74.9	76.7	70.3	75.2	66.7	33
R-α-Glc-(1→6)-B *e.g.*	Isomaltose*	97.2	75.3	77.2	70.7	75.5	67.2	53,54
α-L-Rha-(1→6)-B	Rutinose*	97.1	75.2	76.8	71.0	75.8	68.0	39,40
R-β-Glc-(1→6)-B	Gentiobose / Gentiotriose *	97.3	75.5	77.0	71.2	76.1	70.1	52
β-L-Rha-(1→6)-B		97.4	75.5	76.9	71.5	76.0	69.0	40
CH_3→6)-B		97.3	75.8	77.2	71.4	75.8	72.6	52
α-Glc-(1→2)-B-(1→CH_3		105.0	79.0	75.8	70.8	77.1	62.5	52
α-Glc-(1→4)-B-(1→CH_3		104.4	74.6	77.8	78.7	76.1	62.3	52
β-Gal-(1→4)-B-(1→CH_3		103.8	73.8	75.3	79.3	75.6	61.1	26
β-Glc-(1→4)-B-(1→4)-Glc		103.2	73.8	74.9/74.8	79.3	75.7	60.8	55
β-Glc-(1→4)-B-(1→CH_3		104.5	74.2	75.9†	80.3	76.4†	61.8	52
β-Man-(1→4)-B-(1→4)-Man		104.2	74.2	76.0†	80.6	77.0†	62.0/62.4	56
β-Glc-(1→6)-B-(1→6)-Glc	Gentiotriose	103.7	74.6	77.1	71.2	76.1	70.0/70.2	52
β-Glc-(1→6)-B-(1→CH_3		104.5	74.0	71.0/71.2	71.2	76.1	70.0	52
D-*Glucofuranose (Glcf)*								
A = α-Glc*f*								
A-(1→CH_3		104.0	77.7	76.6	78.8	70.7	64.2	23
B = β-Glc*f*								
B-(1→CH_3		110.0	80.6	75.8	82.3	70.7	64.7	23
D-*Idopyranose (Idop)*								
A = α-Idop								
A-(1→CH_3		101.5	70.9	71.8	70.3	70.8	60.2	25
D-*Lyxopyranose (Lyxp)*								
A = α-Lyx*p*								
A		94.9	71.0	71.4	68.4	63.9		22
A-(1→CH_3		102.0	70.4	71.6	67.7	63.3		22

TABLE I *(continued)*

		C-1	C-2	C-3	C-4	C-5	C-6	Ref.
D-*Lyxofuranose (Lyx*f)								
A = α-Lyx*f*								
	A-(1→CH_3	109.1	77.0	72.0	81.3	61.2		58
B = β-Lyx*f*								
	B-(1→CH_3	103.2	72.9	70.7	81.9	62.4		58
D-*Mannopyranose (Man*p)								
A = α-Man*p*								
	A	95.5	72.3	71.9	68.5	73.9	62.6	59
	A-(1→CH_3	102.2	71.4	72.1	68.3	73.9	62.5	59
	A-(1→1)-α-Glc	96.1	71.1	71.4	67.8	73.7	62.1	21
	A-(1→2)-Man-R*	105.0	73.1	72.8	69.8	76.0	63.7	60
	A-(1→3)-Man-R*	103.7	71.8/ 71.6	71.6/ 71.8	68.3/ 68.2	74.7	62.6/ 62.43/ 62.37	20
	A-(1→6)-Man-R	100.6	72.0/ 71.4	71.4/ 72.0	68.3/ 68.2	74.0	62.6/ 62.43/ 62.37	20
	A-(1→4)-L-Rha-R*	102.5	71.5	71.6	67.8	74.3	61.9	45
α-Man-(1→2)-A*		95.4	81.9	72.8	69.5	75.3	63.7	60
CH_3→2)-A		91.5	81.4	70.9	68.1	73.2	61.9	
α-Glc-(1→4)-A	Epimaltose	93.9	71.1	70.8	75.4	71.9	61.1	50
β-Gal-(1→4)-A	Epilactose	95.0	71.4	70.2	77.8	72.2	61.6	50
R-β-Glc-(1→4)-A*		95.3	71.8	70.7	78.5	72.5	62.0/ 62.4	56
R-β-Man-(1→4)-A*		95.3	71.8	70.4	77.9	72.4	62.0/ 62.4	56
α-Man-(1→2)-A-(1→2)-Man		103.3	81.2	72.7	69.7	75.9	63.6	60
α-Man-(1→3) \ α-Man-(1→6) / A-(1→6)-Man-R		101.1	70.8	80.8	67.1	72.2	66.6	17
B = β-Man*p*								
	B	95.2	72.8	74.8	68.3	77.6	62.6	59
	B-(1→CH_3	102.3	71.7	74.5	68.4	77.6	62.6	59
	B-(1→4)-Glc-R*	101.7	72.2	74.4	68.3	77.5	62.0/ 62.4	56

B-(1→4)-Man-R*		101.6	72.0	74.3	68.3	77.9	62.0/62.4	56
B-(1→4)-L-Rha-R*		101.8	71.9	74.3	68.1	77.4	62.3	44
CH_3→2)-B		94.8	82.3	74.3	67.9	77.1		61
α-Glc-(1→4)-B	Epimaltose	93.7	71.3	73.7	74.8/74.9	74.8/74.9	61.0	50
β-Gal-(1→4)-B	Epilactose	94.9	71.8	74.9	77.4	76.1	61.6	50
R-β-Glc-(1→4)-B*		95.3	72.0	73.5	78.5	76.3	62.0/62.4	56
R-β-Man-(1→4)-B*		95.3	72.0	73.1	78.1	76.3	62.0/62.4	56
β-Man-(1→4)-B-(1→4)-Glc		101.7	71.5	73.0	77.9	76.5	62.0/62.4	56
β-Man-(1→4)-B-(1→4)-Man		101.6	71.4	73.0	77.9	76.5	62.0/62.4	56
α-Man-(1→3) R-α-Man-(1→6)>B-(1→4)-GlcNAc-R		101.7	71.4	82.0	66.9	75.7	67.2	17
D-*Mannofuranose (Manf)*								
A = α-Man*f*								
A-(1→CH_3		109.7	77.9	72.5	80.5	70.6	64.5	23
B = β-Man*f*								
B-(1→CH_3		103.6	73.1	71.2/71.0	80.7	71.0/71.2	64.4	23
D-*Psicopyranose (Psip)*								
A = α-Psi*p*								
A		64.1	98.5	66.6	72.7	66.8	58.9	62
A-(2→CH_3		61.1	100.7	67.3	72.1	66.7	58.9	30
CH_3→5)-A		63.7	98.9	66.2	70.2	75.7	56.8	30
B = β-Psi*p*								
B		65.0	99.3	71.3	66.1	70.0	65.0	62
B-(2→CH_3		57.7	102.6	69.7	65.7	69.9	65.4	30
CH_3→5)-B		64.6	99.4	71.1	66.0	79.2	60.0	30
D-*Psicofuranose (Psif)*								
A = α-Psi*f*								
A		64.34	104.1	71.3	71.3	83.6	62.3	59
CH_3→6)-A		64.1	104.3	71.2	70.7	81.5	72.7	30

TABLE I *(continued)*

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ref.*
B = β-Psif							
B	63.5	106.5	75.7	71.9	83.6	63.7	62
CH_3→6)-B	63.3	106.7	75.3	72.1	81.5	74.7	30
L-*Rhamnopyranose (Rha*p)							
A = α-Rha*p*							
A	95.0	71.9	71.1	73.3	69.4	18.0	27
A-(1→CH_3*	102.1	71.2	71.5	73.3	69.5	17.9	27,40
	103.2(α)			72.8(α)		17.5(α)	
A-(1→2)-Gal		70.9	70.1		69.8		37
	101.8(β)			72.9(β)		17.3(β)	
A-(1→3)-Gal-R*	103.4	71.2	71.2	73.1	70.2	17.7	37,45
A-(1→4)-Gal	101.1	69.8	69.7	71.4	68.8	16.2	37
	101.3(α)						
A-(1→6)-Gal Robinobiose*		70.8	71.0	72.8	69.4	17.4	37,39
	101.1(β)						
	101.7(α)						
A-(1→6)-Glc-R } *		71.1	71.3	73.0	69.6	17.6	39,40
e.g. Rutinose }	101.6(β)						
	102.8(α)						
A-(1→2)-L-Rha-R*		70.8	70.8	72.8	69.8	17.6	38,63,64
	102.2(β)						
A-(1→3)-L-Rha-R*	103.0	71.2	71.0	72.9	69.8	17.4	39,63,64
A-(1→4)-L-Rha-R*	102.4	71.7	71.4	72.9	70.1	17.6	38,40,63
e.g. Isorhamninose							
R-α-L-Rha-(1→2)-A*	93.4	79.8	70.8	73.3	69.1	17.5	51,63,64
β-Gal-(1→2)-A	94.1	81.7	71.1	73.6	69.3	18.1	9
β-Glc-(1→2)-A	94.0	82.1	70.9	73.5	69.3	17.9	9
CH_3→2)-A	91.6	81.7	70.8	73.5	68.9		64
R-α-L-Rha-(1→3)-A*	94.6	71.4	78.5	72.4	69.2	17.5	39,63,64
β-GlcNAc-(1→3)-A	94.8	71.8	81.0	72.3	69.8	18.0	9
β-Gal-(1→3)-A	95.0	71.9	81.0	72.4	69.5	18.1	9
β-Glc-(1→3)-A	95.0	71.8	81.0	72.5/ 72.3	69.5	18.1	9

$CH_3 \rightarrow 3)$-A	94.8	67.8	80.5	72.0	69.1		64
α-Gal-(1→4)-A	94.3	71.8	69.6	82.1	68.1	17.9	36
α-Man-(1→4)-A	91.8	72.2	70.1	82.7	69.0	18.2	45
α-L-Rha-(1→4)-A	94.5	71.3	71.5	80.7	67.3	18.3	63
β-Gal-(1→4)-A	95.0	72.0	71.2	82.3	68.1	18.2	9
β-Glc-(1→4)-A	95.0	72.0	71.2	82.5	68.0	18.2	9
β-Man-(1→4)-A	95.1	72.2	71.2	80.8	68.2	18.3	44
	99.9(α)						
α-L-Rha-(1→2)-A-(1→6)-Gal		79.2	70.8	72.8	69.6	17.4	38
	99.8(β)						
α-L-Rha-(1→2)-A-(1→CH_3	100.5	79.0	70.9	73.1	69.2	17.7	63
$CH_3 \rightarrow 2)$-A-(1→CH_3	98.0	80.8	71.6	73.6	68.3	17.6	63
	102.5(α)						
R-α-L-Rha-(1→3)-A-(1→2)-L-Rha*		70.4	78.5	72.2	69.9	17.6	51,64
	101.9(β)						
α-L-Rha-(1→3)-A-(1→3)-L-Rha	102.5	70.8/ 71.0	79.0	72.2	69.7/ 69.9	17.5	64
α-L-Rha-(1→3)-A-(1→6)-Gal Rhamninose	101.2	70.6	79.0	72.2	69.6	17.4	39
L-α-Rha-(1→3)-A-(1→CH_3*	101.6	70.9	78.8	72.2	69.4	17.8	63,65
β-Gal-(1→3)-A-(1→3)-L-Rha-R	102.6	70.6	80.7	71.9	69.7	17.7	51
$CH_3 \rightarrow 3)$-A-(1→CH_3	101.0	67.2	81.6	71.5	68.2	17.7	63
α-Man-(1→4)-A-(1→3)-Gal	103.2	71.6	70.2	82.5	69.3	18.1	45
α-L-Rha-(1→4)-A-(1→6)-Gal Isorhamninose	101.0	71.4	71.3	80.4	67.9	18.1	38
α-L-Rha-(1→4)-A-(1→CH_3*	101.8	71.6	71.8	80.8	67.9	18.5	40,63
	102.7(α)						
β-Man-(1→4)-A-(1→3)-Gal-R		71.5	71.5	79.4	68.2	18.2	44
	102.9(β)						
β-L-Rha-(1→4)-A-(1→CH_3	102.0	71.9	70.5	83.9	68.1	17.8	40
$CH_3 \rightarrow 4)$-A-(1→CH_3	101.0	71.4	71.3	83.4	67.4	18.0	63
α-Gal-(1→4) $\searrow$ A β-Glc-(1→2) $\nearrow$	93.4	81.9	69.4	81.8	68.2	17.9	36
B = β-Rha*p*							
B	94.6	72.4	73.8	72.9	73.1	18.0	27
B-(1→CH_3	102.4	71.8	74.1	73.4	73.4	17.9	40
	97.7(α)	71.8(α)	73.4(α)				
B-(1→3)-Gal				72.8	73.0	17.5	37
	97.8(β)	71.7(β)	73.5(β)				
B-(1→6)-Gal	101.2	71.8	73.9	73.4	73.4	17.9	40

TABLE I *(continued)*

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ref.*
B-(1→6)-Glc	101.3	71.9	74.0	73.4	73.5	18.0	40
B-(1→4)-L-Rha-R	101.8	70.7	74.1	73.2	73.5	18.0	40
β-Gal-(1→2)-B	93.9	82.4	74.2	73.3	73.6	17.9	9
β-Glc-(1→2)-B	93.9	82.4	74.3	73.2/ 73.8	73.8/ 73.2	17.9	9
CH_3→2)-B	94.7	82.4	74.1	73.1	72.8		64
R-α-L-Rha-(1→3)-B*	94.1	71.7	81.3	72.4	72.9	17.5	39,64
β-GlcNAc-(1→3)-B	94.5	72.3	83.4	72.3	73.3	18.0	9
β-Gal-(1→3)-B	94.5	72.4	83.4	72.4	73.0	18.1	9
β-Glc-(1→3)-B	94.6	72.3/ 72.5	83.5	72.3/ 72.5	73.0	18.1	9
CH_3→3)-B	94.4	68.1	82.9	71.6	72.7		64
α-Gal-(1→4)-B	94.1	72.3†	72.4	81.6	72.0†	17.9	36
α-Man-(1→4)-B	94.6	72.7	72.8	82.3	72.2	18.2	45
β-Gal-(1→4)-B	94.6	72.5	74.0	81.9	71.8	18.2	9
β-Glc-(1→4)-B	94.6	72.5	74.0	82.0	71.6	18.2	9
β-Man-(1→4)-B	94.5	72.8†	74.0	80.4	71.8†	18.3	44
α-Man-(1→4)-B-(1→3)-Gal	98.1	72.4	72.6/ 72.4	82.5	72.4/ 72.6	18.1	45
α-Gal-(1→4) / β-Glc-(1→2) > B	93.3	82.5	72.4	81.4	72.4	17.9	36
D-*Ribopyranose (Rib*p)							
A = α-Rib*p*							
A	96.2	72.8	72.0	70.00/ 69.95	65.7		66
B = β-Rib*p*							
B	96.6	73.75/ 73.70	71.7	70.00/ 69.95	65.7		66
B-(1→CH_3	103.9	70.4	69.9	72.7	65.6		67
D-*Ribofuranose (Rib*f)							
A = α-Rib*f*							
A	99.0	73.70/ 73.75	72.8	85.8	64.1		66

	A-(1→CH_3	104.2	72.1	70.8	85.5	62.2	27
B = β-Ribf							
	B	103.7	78.0	73.2	85.2	65.2	66
	B-(1→CH_3*	108.5	74.8	71.4	83.5	63.4	27,67
L-*Sorbopyranose (Sorp)*							
A = α-Sorp							
	A	64.5	98.6	71.4	74.8	70.3	62.7	68
	A-(2→CH_3	61.2	100.9	72.0	74.5	70.1	63.0	30
B = β-Sorp							
	B	64.6	99.5	70.2	73.6	71.1	59.8	68
L-*Sorbofuranose (Sorf)*							
A = α-Sorf							
	A	64.2	102.5	77.0	76.3	78.6	61.6	68
	A-(2→CH_3	60.7	104.2	80.0	76.5	78.8	61.6	30
B = β-Sorf							
	B	63.6	106.3	82.3	74.2	81.1	62.1	68
	B-(2→CH_3	57.7	109.9	80.3	77.2	83.4	62.1	30
D-*Tagatopyranose (Tagp)*							
A = α-Tagp							
	A	64.8	99.0	70.7/ 71.8	71.8/ 70.7	67.2	63.1	30
	A-(2→CH_3	61.0	102.4	69.6/ 71.7	71.7/ 69.6	66.8	63.4	30
B = β-Tagp							
	B	64.4	99.1	64.6	70.7/ 70.1	70.1/ 70.7	61.0	30
	B-(2→CH_3	61.7	101.4	65.5	71.5/ 70.4	70.4/ 71.5	61.1	30
D-*Tagatofuranose (Tagf)*							
A = α-Tagf							
	A	63.3	105.7	77.6	71.9	80.0		68
	A-(2→CH_3	58.8	108.7	75.2	71.9	80.6	60.8	30
CH_3→6)-A		63.4	105.8	77.7	72.0	78.2		30

TABLE I *(continued)*

	C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ref.*
B = β-Tag*f*							
B	63.5	103.3	71.7/ 71.8	71.8/ 71.7	80.9	61.9	30
B-(2→CH_3	60.3	105.3	73.4	71.7	82.0	61.9	30
CH_3→6)-B	63.4	103.3	71.4/ 72.0	72.0/ 71.4	79.1	72.6	30
D-*Talopyranose (Tal*p)							
A = α-Tal*p*							
A	95.5	71.7	66.0	70.6	72.0	62.4	69
B = β-Tal*p*							
B	95.0	72.5/ 69.6	69.6/ 72.5	69.4	76.5	62.2	26
D-*Talofuranose (Tal*f)							
A = α-Tal*f*							
A	101.85	76.1	72.7	82.7	71.6	63.7	26
B = β-Tal*f*							
B	97.3	71.6	72.0	83.3		63.8	26
D-*Xylopyranose (Xyl*p)							
A = α-Xyl*p*							
A	93.1	72.5	73.9	70.4	61.9		26
A-(1→CH_3	100.6	72.3	74.3	70.4	62.0		27
A-(1→1)-α-Glc	94.6	72.2	73.9	70.7	62.8		21
A-(1→2)-Xyl-R*	97.8(α) 99.1(β)	72.7	74.2	70.7	62.7		70,71
A-(1→3)-Xyl-R*	100.1	72.8	74.3	71.0	62.7		70,71
A-(1→4)-Xyl-R*	101.5	73.0	74.3	70.7	62.9		70,71
α-Xyl-(1→2)-A	90.9	77.1	72.5	70.7	62.1		71
β-Xyl-(1→2)-A	93.1	81.9	73.0	70.4	61.7		71
CH_3→2)-A	90.7	81.8	73.3	70.5	61.9		71
α-Xyl-(1→3)-A	93.6	70.8	80.1	70.6	62.4		71
β-Xyl-(1→3)-A	93.3	72.1	82.9	68.9	62.1		71

$CH_3\rightarrow$3)-A	93.4	72.2	84.0	70.1	62.2	71
α-Xyl-(1→4)-A	93.2	72.4/ 72.9	72.9/ 72.4	79.3	61.3	71
R-β Xyl-(1→4)-A*	92.9	72.4/ 71.9	71.9/ 72.4	77.5	59.8	55,71
$CH_3\rightarrow$4)-A	93.4	72.8	73.0	80.0	59.8	71
B = β-Xyl*p*						
B	97.5	75.1	76.8	70.2	66.1	26
B-(1→CH_3	105.1	74.0	76.9	70.4	66.3	27
B-(1→2)-Xyl-R*	105.9(α) 104.5(β)	74.7	76.9	70.6	66.5	70,71
B-(1→3)-Xyl-R*	104.5	74.4	76.8	70.4	66.4	70,71
B-(1→4)-Xyl-R*	102.9	73.8	76.8	70.4	66.4	55,70,71
α-Xyl-(1→2)-B	98.2	79.4	75.6	70.7	66.2	71
β-Xyl-(1→2)-B	96.5	82.9	74.5	70.4	66.2	71
$CH_3\rightarrow$2)-B	97.7	84.9	76.5	70.7	66.3	71
α-Xyl-(1→3)-B	97.9	73.8	82.7	70.6	66.2	71
β-Xyl-(1→3)-B	97.6	74.9	85.3	68.9	65.5	71
$CH_3\rightarrow$3)-B	97.9	74.7	86.5	69.9	66.3	71
α-Xyl-(1→4)-B	97.7	75.1	76.1	79.3	65.5	71
R-β-Xyl-(1→4)-B*	97.4	74.9	74.9	77.4	63.9	55,71
$CH_3\rightarrow$4)-B	97.9	75.4	76.1	80.0	64.1	71
α-Xyl-(1→2)-B-(1→CH_3	105.4	78.5	75.5	70.7	66.1	70
β-Xyl-(1→2)-B-(1→4)-Xyl-R	101.8	82.0	76.5	70.3	66.2	70
β-Xyl-(1→2)-B-(1→CH_3	104.9	81.8	76.4	70.2	65.9	70
α-Xyl-(1→3)-B-(1→4)-Xyl-R	103.3	72.6	82.6	70.6	66.1	70
α-Xyl-(1→3)-B-(1→CH_3	105.3	72.7	82.9	70.6	66.2	70
β-Xyl-(1→3)-B-(1→4)-Xyl-R	103.0	73.8	84.9	69.0	66.2	70
β-Xyl-(1→3)-B-(1→CH_3	104.9	73.7	85.3	69.0	66.0	70
α-Xyl-(1→4)-B-(1→CH_3	105.2	74.1	76.0	79.4	65.4	70
β-Xyl-(1→4)-B-(1→4)-Xyl-R*	102.8	73.9	74.8	77.5	64.1	55,70
R-β-Xyl-(1→4)-B-(1→CH_3*	105.1	74.1	75.1	77.7	64.1	70
β-Xyl-(1→2) β-Xyl-(1→4)> B-(1→CH_3	105.3	81.9	75.0	77.9	63.9	70
β-Xyl-(1→3) β-Xyl-(1→4)> B-(1→4)-Xyl-R	102.4	73.6	80.6	74.3	63.7	70
β-Xyl-(1→3) β-Xyl-(1→4)> B-(1→CH_3	104.5	73.6	80.8	74.2	63.4	70

TABLE I *(continued)*

		C-1	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*Ref.*
D-*Xylofuranose (Xylf)*								
A = α-Xyl*f*	A-(1→CH_3	103.0	77.7	76.0	79.3	61.5		58
B = β-Xyl*f*	B-(1→CH_3	109.6	80.9	76.0	83.5	62.1		58

in Table I are in p.p.m. relative to that of Me_4Si. In twelve entries in Table I, reassignments of data have been made in order to achieve consistency with other data therein. For β-L-Rha-(1→6)-A, where A is α-D-Gal, the reassignment has been based on the empirical rules (see below).

EMPIRICAL RULES

(*1*) With the exceptions noted below, the chemical shift of a resonance from a particular carbon atom of a particular sugar residue in an oligosaccharide (solvent H_2O/D_2O) should be within ±0.3 p.p.m. of that of the resonance of the C atom of the monosaccharide (see Table II).

(*2*) The resonance of a carbon atom involved in a linkage or attached to a methyl group (*C*-O-$\overset{|}{\underset{|}{C}}$H, see Table III) is shifted downfield by 4–10 p.p.m.

(*2a*) The resonances of the α- and β-anomeric forms of a carbon atom involved in a linkage or attached to a methyl group are shifted downfield by the same amount. This rule was true for 8 out of 11 examples of 2-linkages, and in all the 46 examples of 3-, 4-, and 6-linkages.

(*2b*) Since the chemical shifts of the resonances for C-4 and C-6 of pyranoid α- and β-monosaccharides are similar (see Table II), substitution at position 4 and 6 of a reducing residue produces a pair of downfield-shifted resonances that are nearly coincident.

(*3*) The resonances of carbon atoms adjacent to the linked carbon atom are

TABLE II

^{13}C-N M R. CHEMICAL SHIFTS OF THE MORE COMMON MONOSACCHARIDES[a]

Carbon atom		*Fuc*	*Fruf*	*Gal*	*Glc*	*GlcNAc*	*Man*	*Rha*	*Xyl*
1	α	93.1	63.9	93.2	92.9	92.1	95.5	95.0	93.1
	β	97.1	63.7	97.3	96.7	96.2	95.2	94.6	97.5
2	α	69.1	105.4	69.4	72.5	55.3	72.3	71.9	72.5
	β	72.7	102.4	72.9	75.1	58.0	72.8	72.4	75.1
3	α	70.3	82.9	70.2	73.8	72.0	71.9	71.1	73.9
	β	73.9	76.4	73.8	76.7	75.2	74.8	73.8	76.8
4	α	72.9	77.0	70.3	70.6	71.4	68.5	73.3	70.4
	β	72.4	75.4	69.7	70.6	71.2	68.3	72.9	70.2
5	α	67.8	82.2	71.4	72.3	72.8	73.9	69.4	61.9
	β	71.7	81.6	76.0	76.8	77.2	77.6	73.1	66.1
6	α	16.6	62.0	62.2	61.6	61.9	62.6	18.0	—
	β	16.6	63.3	62.0	61.7	62.0	62.6	18.0	—
HN*C*=O	α	—	—	—	—	175.7	—	—	—
	β	—	—	—	—	175.9	—	—	—
O*C*H$_3$	α	—	—	—	—	23.3	—	—	—
	β	—	—	—	—	23.5	—	—	—

[a]In the pyranose form, except for fructose. A full listing of monosaccharides is given in Table I.

TABLE III

SHIFTS OF ^{13}C-N.M.R RESONANCES OF REDUCING SUGARS RESULTING FROM LINKAGE TO A CARBON ATOM BY A SUGAR RESIDUE OR A METHYL GROUP

C-atom linked	*Group linked to a C-atom*[a]		*Shifts (in p.p.m.) of C-resonances at the link and at adjacent positions (downfield positive, upfield negative)*		
			(link − 1) C[b]	*link C*	*(link + 1) C*[b]
C-2	α Sugar	Range of 8	−2.2 to +0.8	+4.3 to +9.6	−1.4 to +0.9
C-2	β Sugar	Range of 8	−1.0 to +0.2	+7.7 to +10.2	−2.3 to +0.5
C-2	Methyl	Range of 8	−4.0 to +0.4	+9.1 to +10.1	−1.0 to +0.3
C-3	α Sugar	Range of 10	−1.7 to −0.1	+5.0 to +9.6	−3.4 to +0.4
C-3	β Sugar	Range of 15	−1.8 to 0	+6.6 to +10.4	−2.9 to −0.3
C-3	Methyl	Range of 6	−4.3 to +0.1	+9.1 to +10.3	−4.6 to 0
C-4	α Sugar	Range of 16	−2.2 to +1.1	+6.5 to +9.4	−2.7 to +0.3
C-4	β Sugar	Range of 26	−1.9 to +0.4	+7.1 to +10.2	−2.2 to −0.7
C-4	Methyl	Range of 4	−0.9 to +0.1	+9.6 to +9.9	−2.1 to −0.6
C-6	α Sugar	Range of 8	−1.7 to −0.8	+5.0 to +6.7	
C-6	β Sugar	Range of 6	−0.8 to +0.3	+7.1 to +8.5	
C-6	Methyl	Range of 4	−2.1 to −0.9	+10.8 to +11.0	

[a]The sugar group is linked (α or β) through position 1 to the numbered carbon on the reducing residue.
[b]The large variations of these values are due to the different orientations (whether equatorial or axial) of the carbon atoms adjacent to the linked carbon atom[72].

usually shifted upfield by a small, but not necessarily similar, amount (see Table III).

(*3a*) The resonances of the α- and β-anomeric forms of carbon atoms adjacent to the carbon involved in a linkage are shifted (usually upfield) by the same amount. This is true in all 46 examples of 3-, 4-, and 6-linkages, but is only valid for about half of the 11 examples of 2-linked sugars.

(*4*) The C-1 resonances of aldoses are of particular importance since they are readily observed due to their downfield positions (see Table IV).

(*4a*) The type of linkage (α or β) may be distinguished by the chemical shift of the C-1 resonance of pyranoses, except for such sugars as rhamnose and mannose where the values for C-1α and C-1β are indistinguishable (Table II). Substitution of the sugar at position 2 may cause a small upfield shift of the C-1 resonance (rule *3*) that may tend to confuse its assignment as α or β (*e.g.*, ref. 5).

(*4b*) For a sugar linked to a reducing sugar residue, the resonance for C-1 is split into a doublet by the nearby α and β anomers, the extent (p.p.m.) of which depends on the linkage position: C-2, 0.5–1.5; C-3, 0.1–0.15; C-4, zero; and C-6, 0.04–0.3 (see Table I). If the reducing residue is a ketofuranose, an appreciable splitting (0.5 p.p.m.) may occur even for a linkage at position 4. The splitting of the C-1′ resonance for kojibiose [α-D-Glc-(1→2)-D-Glc] and sophorose [β-D-Glc-(1→2)-D-Glc] at 20.0 and 67.9 MHz is 1.4 and 1.2 p.p.m., respectively, irrespective of field strength. However, in spectra obtained at low field, the splitting is not always visible.

TABLE IV

^{13}C-N M R CHEMICAL SHIFTS, ARRANGED IN NUMERICAL ORDER, OF C-1 RESONANCES OF SUGARS LINKED AT THE C-1 ATOM[a]

Chemical shift (p.p.m.)	
110.0	β-**Glcf**-(1→CH_3
109.7	α-**Manf**-(1→CH_3
109.6	β-**Galf**-(1→CH_3, β-**Xylf**-(1→CH_3
109.3	α-**Araf**-(1→CH_3
109.0	β-**Allf**-(1→CH_3
108.5	β-**Ribf**-(1→CH_3
107.0	α-**Ara**-(1→CH_3
105.9	β-**Gal**-(1→2)-α-Rha, β-**Xyl**-(1→2)-α-Xyl
105.4	→2)-β-**Xyl**-(1→CH_3
105.3	β-**Glc**-(1→2)-α-Rha, →3)-β-**Xyl**-(1→CH_3, $^{\rightarrow 2)}_{\rightarrow 4)}$>β-**Xyl**-(1→$CH_3$
105.2	β-**Gal**-(1→3)-Rha, →4)-β-**Xyl**-(1→CH_3
105.1	β-**Gal**-(1→3)-Gal, β-**Gal**-(1→2)-β-Rha, β-**Glc**-(1→2)-α-Glc, β-**Xyl**-(1→CH_3, →4)-β-**Xyl**-(→CH_3
105.0	β-**Glc**-(1→3)-Rha, α-**Man**-(1→2)-Man, →4)-β-**Gal**-(1→3)-GalNAcol, →2)-β-**Glc**-(1→CH_3
104.9	β-**Gal**-(1→4)-Rha, →3)-β-**Gal**-(1→3)-Gal, 2)-β-**Xyl**-(1→CH_3, →3)-β-**Xyl**-(1→CH_3
104.8	β-**Fuc**-(1→CH_3
104.6	β-**Glc**-(1→2)-β-Rha
104.5	β-**Gal**-(1→CH_3, β-**Gal**-(1→2)-Gal, β-**Glc**-(1→3)-Gal, β-**Xyl**-(1→2)-β-Xyl, β-**Xyl**-(1→3)-Xyl, →4)-β-**Glc**-(1→CH_3, →6)-β-**Glc**-(1→CH_3, $^{\rightarrow 3)}_{\rightarrow 4)}$>β-**Xyl**-(1→$CH_3$
104.4	β-**Gal**-(1→3)-GalNAcol, β-**Glc**-(1→4)-Rha, →4)-β-**Glc**-(1→CH_3
104.3	β-**GlcNAc**-(1→3)-Gal
104.2	β-**Gal**-(1→6)-GlcNAc, β-**Gal**-(1→4)-Man, β-**Glc**-(1→4)-Man, α-**Ribf**-(1→CH_3, →4)-β-**Glc**-(1→4)-Man
104.1	β-**Gal**-(1→3)-GlcNAc
104.0	β-**Gal**-(1→4)-GlcNAc, β-**Glc**-(1→CH_3, α-**Glcf**-(1→CH_3, →4)-β-**Gal**-(1→4)-GlcNAc, →4)-β-**Gal**-(1→4)-Glc, →6)-β-**Gal**-(1→CH_3
103.9	β-**GlcNAc**-(1→3)-Rha, β-**Glc**-(1→2)-β-Glc, β-**Glc**-(1→3)-Glc, β-**Rib**-(1→CH_3, →3)-β-**Gal**-(1→4)-Glc, →3)-β-**Gal**-(1→CH_3
103.8	α-**Allf**-(1→CH_3, β-**Fuc**-(1→3)-Gal, β-**Gal**-(1→6)-Gal, β-**Glc**-(1→6)-Glc, →6)-β-**Gal**-(1→6)-Gal, →4)-β-**Glc**-(1→CH_3
103.7	β-**Gal**-(1→4)-Glc, α-**Man**-(1→3)-Man, →6)-β-**Glc**-(1→6)-Glc
103.6	β-**Glc**-(1→1)-α-Glc, β-**Manf**-(1→CH_3
103.5	α-**Galf**-(1→CH_3, →3)-β-**Gal**-(1→4)-Glc
103.4	α-**Rha**-(1→3)-Gal, →2)-β-**Gal**-(1→2)-Gal
103.3	β-**GalNAc**-(1→6)-GalNAc, β-**Glc**-(1→4)-Glc, →2)-α-**Man**-(1→2)-Man, →3)-β-**Xyl**-(1→4)-Xyl
103.2	β-**Araf**-(1→CH_3, β-**Lyxf**-(1→CH_3, α-**Rha**-(1→2)-α-Gal, →2)-β-**Gal**-(1→CH_3, →4)-β-**Glc**-(1→4)-Glc, →4)-α-**Rha**-(1→3)-Gal
103.0	β-**Ara**-(1→CH_3, α-**Rha**-(1→3)-Rha, α-**Xylf**-(1→CH_3, →3)-β-**Xyl**-(1→4)-Xyl
102.9	β-**Xyl**-(1→4)-Xyl, →2)-β-**Gal**-(1→3)-GalNAcol, →4)-α-**Rha**-(1→3)-β-Gal
102.8	β-**GlcNAc**-(1→6)-Gal, α-**Rha**-(1→2)-α-Rha, →4)-β-**GlcNAc**-(1→4)-GlcNAc, →4)-β-**Xyl**-(1→4)-Xyl
102.7	β-**GlcNAc**-(1→4)-GlcNAc, →4)-α-**Rha**-(1→3)-α-Gal

TABLE IV *(continued)*

Chemical shift (p.p.m.)	
102.6	→4)-β-**GlcNAc**-(1→4)-GlcNAc, →3)-α-**Rha**-(1→3)-Rha
102.5	β-**GlcNAc**-(1→CH_3, α-**Man**-(1→4)-Rha, →3)-α-**Rha**-(1→2)-α-Rha, →3)-α-**Rha**-(1→3)-Rha
102.4	α-**Rha**-(1→4)-Rha, β-**Rha**-(1→CH_3, $^{\rightarrow 3)}_{\rightarrow 4)}$>β-**Xyl**-(1→4)-Xyl
102.3	β-**Man**-(1→CH_3, →4)-β-**GlcNAc**-(1→CH_3, →6)-β-**GlcNAc**-(1→CH_3
102.2	α-**Man**-(1→CH_3, α-**Rha**-(1→2)-β-Rha, →3)-β-**GlcNAc**-(1→CH_3, $^{\rightarrow 3)}_{\rightarrow 4)}$>β-**GlcNAc**-(1→$CH_3$, $^{\rightarrow 3)}_{\rightarrow 6)}$>β-**GlcNAc**-(1→$CH_3$, $^{\rightarrow 4)}_{\rightarrow 6)}$>β-**GlcNAc**-(1→$CH_3$
102.1	α-**Fuc**-(1→3)-Gal, α-**Rha**-(1→CH_3
102.0	α-**Lyx**-(1→CH_3, →4)-β-**GlcNAc**-(1→6)-GalNAcol, →4)-α-**Rha**-(1→CH_3
101.9	→3)-α-**Rha**-(1→2)-β-Rha
101.8	β-**Man**-(1→4)-Rha, α-**Rha**-(1→2)-β-Gal, β-**Rha**-(1→4)-Rha, →4)-α-**Rha**-(1→CH_3, →2)-β-**Xyl**-(1→4)-Xyl
101.7	β-**Man**-(1→4)-Glc, α-**Rha**-(1→6)-α-Glc, →3)-β-**Gal**-(1→4)-Glc, →4)-β-**Man**-(1→4)-Glc, $^{\rightarrow 3)}_{\rightarrow 6)}$>β-**Man**-(1→4)-GlcNAc
101.6	α-**Glc**-(1→4)-Fru, β-**Man**-(1→4)-Man, α-**Rha**-(1→6)-β-Glc, →4)-β-**Man**-(1→4)-Man, →3)-α-**Rha**-(1→CH_3
101.5	α-**Glc**-(1→5)-Fru, α-**Ido**-(1→CH_3, α-**Xyl**-(1→4)-Xyl
101.4	α-**Glc**-(1→4)-Gal, →4)-α-**Gal**-(1→CH_3
101.3	α-**Gal**-(1→4)-Gal, α-**Rha**-(1→6)-α-Gal, β-**Rha**-(1→6)-Glc
101.2	β-**Rha**-(1→6)-Gal, →3)-α-**Rha**-(1→6)-Gal
101.1	α-**Alt**-(1→CH_3, α-**Glc**-(1→3)-Fruf, α-**Glc**-(1→4)-Glc, α-**Rha**-(1→4)-Gal, α-**Rha**-(1→6)-Gal, →2)-β-**Gal**-(1→3)-GlcNAc, →4)-α-**Glc**-(1→4)-Glc, →4)-α-**Glc**-(1→CH_3, →6)-α-**Glc**-(1→4)-Glc, $^{\rightarrow 3)}_{\rightarrow 6)}$>α-**Man**-(1→6)-Man
101.0	α-**Fuc**-(1→2)-Gal, →3)-α-**Rha**-(1→CH_3, →4)-α-**Rha**-(1→6)-Gal, →4)-α-**Rha**-(1→CH_3
100.9	α-**Glc**-(1→1)-β-Glc
100.8	→6)-α-**Glc**-(1→CH_3
100.6	α-**Man**-(1→6)-Man, α-**Xyl**-(1→CH_3
100.5	α-**Fuc**-(1→CH_3, α-**Gal**-(1→4)-Rha, →2)-α-**Rha**-(1→CH_3
100.4	α-**All**-(1→CH_3, →4)-α-**Gal**-(1→CH_3
100.1	α-**Gal**-(1→CH_3, α-**Xyl**-(1→3)-Xyl, →6)-α-**Glc**-(1→CH_3
100.0	α-**Glc**-(1→CH_3, →3)-α-**Gal**-(1→CH_3, →2)-α-**Glc**-(1→CH_3
99.9	α-**Fuc**-(1→6)-GlcNAc, →2)-α-**Rha**-(1→6)-α-Gal
99.8	α-**Fuc**-(1→4)-GlcNAc, α-**Glc**-(1→3)-Glc, →2)-α-**Rha**-(1→6)-β-Gal
99.6	α-**Glc**-(1→6)-α-Fruf
99.5	α-**Glc**-(1→6)-Gal
99.4	α-**Glc**-(1→4)-β-Fruf, α-**Glc**-(1→6)-Glc
99.3	α-**Glc**-(1→6)-β-Fruf
99.1	α-**Xyl**-(1→2)-β-Xyl
99.0	α-**Gal**-(1→6)-Glc, α-**Glc**-(1→2)-β-Glc
98.9	α-**GlcNAc**-(1→CH_3, α-**Glc**-(1→4)-α-Fruf
98.7	α-**GlcNAc**-(1→4)-Gal, →3)-α-**GlcNAc**-(1→CH_3
98.6	$^{\rightarrow 3)}_{\rightarrow 4)}$>α-**GlcNAc**-(1→$CH_3$, $^{\rightarrow 3)}_{\rightarrow 6)}$>α-**GlcNAc**-(1→$CH_3$
98.5	→6)-α-**GlcNAc**-(1→CH_3
98.4	→4)-α-**GlcNAc**-(1→CH_3, $^{\rightarrow 4)}_{\rightarrow 6)}$>α-**GlcNAc**-(1→$CH_3$

TABLE IV *(continued)*

Chemical shift (p.p.m.)	
98.1	→4)-β-**Rha**-(1→3)-Gal
98.0	→2)-α-**Rha**-(1→CH_3
97.8	β-**Rha**-(1→3)-β-Gal, α-**Xyl**-(1→2)-α-Xyl
97.7	β-**Rha**-(1→3)-α-Gal
97.0	→2)-α-**Glc**-(1→6)-Glc
96.9	α-**Glc**-(1→2)-α-Glc
96.7	α-**Glc**-(1→3)-Gal
94.7	α-**All**-(1→1)-α-Glc
94.6	α-**Glc**-(1→1)-α-Glc, α-**Xyl**-(1→1)-α-Glc
94.5	α-**Glc**-(1→1)-α-Man,
94.0	α-**Glc**-(1→1)-α-Glc

[a]The sugar residue is printed in bold-face type, and the type of linkage to the adjacent residue is also recorded. Residues also substituted at another position are indicated, *e.g.*, →6)-β-**Gal**-(1→4)-Glc; all sugars are pyranoid unless indicated with f.

DETERMINATION OF THE STRUCTURE OF TRISACCHARIDES OF KNOWN MONOSACCHARIDE COMPOSITION

For a reducing trisaccharide consisting of 3 hexoses, there will be 12 ^{13}C-resonances for the α and β forms of the reducing residue, and 12 resonances for the two other residues. The former resonances are readily identified because their intensities are smaller than those of the latter. Usually, the intensities of the resonances of the α and β anomers are different, and hence the α and β resonances may be distinguished. However, the intensities of resonances are not strictly proportional to the number of carbon atoms because of differences in n.O.e. values and relaxation times of different nuclei.

The analysis commences with the 12 resonances of the reducing residue, the chemical shifts of which are compared with those of the three component monosaccharides. After due allowance for the shifts of resonances at, and adjacent to, the linkage position (rules *2* and *3*), the residue with the best fit of the data must be the reducing-end residue. If there is no fit of the data, then the reducing residue may be branched and this can be treated[5] using the same general rules.

The twelve single-carbon resonances are then compared with those of the two remaining sugar residues (both α and β forms). The residue at the non-reducing end may often be identified next because it is linked only through position 1 and hence only the C-1 and C-2 resonances should be shifted (rules *2* and *3*). Finally, the data for the central, disubstituted residue are compared with those for the appropriate monosaccharide in order to determine the α or β configuration and also the position of the linkage.

The procedure is illustrated for a trisaccharide, consisting of L-fucose, D-galactose, and D-glucose, that was chosen from the literature[34]. The chemical-shift

TABLE V

STRUCTURAL ANALYSIS, FROM THE ^{13}C-N.M R. DATA, OF A TRISACCHARIDE CONTAINING L-FUCOSE, D-GALACTOSE, AND D-GLUCOSE[34]

Chemical shift	*Assignments*[a]		
	Reducing residue (D-Glucose)	*Non-reducing-end residue (α-L-Fucose)*	*Central residue (β-D-Galactose)*
103.9			1′
102.1		1″	
97.0 r[b]	1β		
93.0 r	1α		
81.6			3′
79.8 r	4α		
79.7 r	4β		
76.5			5′
76.0 r	5β		
75.6 r	3β		
75.1 r	2β		
73.0		4″	
72.7 r	3α		
72.4 r	2α		
71.7			2′
71.3 r	5α		
70.7		3″	
69.9			4′
69.7		2″	
68.4		5″	
62.2			6′
61.4 r	6β		
61.3 r	6α		
16.6		6″	

[a]C, C′, and C″ denote carbon atoms in the reducing, second, and third residues, respectively. [b]Reducing sugar.

data are given in Table V. When the twelve resonances associated with the reducing residue are compared with the chemical-shift data for L-fucose, D-galactose, and D-glucose in Table II, L-fucose can be eliminated because the C-6 resonances of the reducing residue occur at δ 61.4 and 61.3. The resonances at δ 79.8, 79.7 are clearly associated with the linkages (because they are considerably downfield of the C-2 to C-6 resonances of Gal and Glc in Table II). Because the resonances are nearly coincident, the linkage must be at position 4 or 6 (rule *2b*), and position 6 is excluded because the C-6 resonances occur at δ 61.4 and 61.3. Small, equal shifts of the 3α and 3β, and the 5α and 5β, resonances would therefore be expected (rule *3a*). This would be true for glucose (3α, 3β, 5α, and 5β resonances each move upfield by 1.1 p.p.m.) but not for galactose (the 3α, 3β, and 5α resonances are shifted downfield by 2.2, 1.8, and 1.3 p.p.m., respectively, but the 5β resonance is not shifted). Furthermore, the resonance assignments for C-2 and C-6 in galactose do

not fit (rule *1*). It is concluded that the reducing residue is D-glucose and that it is linked at position 4.

The twelve single-carbon resonances in Table V are now compared with the chemical-shift data for the α and β forms of L-fucose and D-galactose in Table II. The identity of the non-reducing-end residue is indicated by a comparison of the chemical shifts of the C-1 resonances δ 103.9 and 102.1 with those in Table IV (rule *4*). That for β-D-galactose linked to D-glucose is found at or near to δ 103.9, and there is one entry of β-L-fucose linked to D-galactose at δ 103.8. However, β-L-fucose is eliminated as the non-reducing-end residue because of the poor fit of the C-3,4,5 resonances to those at δ 73.0, 71.7, and 70.7 in the unknown. At δ 102.1 (Table IV) is C-1 of α-L-fucose linked to D-galactose, and there are no entries near δ 102.1 for α-D-galactose links. This eliminates α-D-galactose and leaves α-L-fucose and β-D-galactose as possibilities for the non-reducing-end unit. α-L-Fucose gives a better fit of the chemical-shift data (however, C-5 shows a difference of 0.6 p.p.m.) than does β-D-galactose (where C-3 and C-5 show differences of 0.8 and 0.5 p.p.m., respectively); hence, it is concluded that α-L-fucose is the non-reducing-end residue.

The central residue is β-D-galactose, and the six remaining single-carbon resonances at δ 103.9, 81.6, 76.5, 71.7, 69.9, and 62.2 are assigned to β-D-galactose (1→4)-linked to D-glucose (δ 103.9 fits C-1 exactly, see Table IV). The resonance at δ 81.6 is that for the linkage carbon which fits well with C-3. Linkage through position 4 is precluded because the downfield shift of 11.9 p.p.m. (from δ 69.7 to 81.6) associated with such a linkage exceeds the maximum of 9.4 p.p.m. given in Table III. Also, the C-4 resonance at δ 69.7 fits the resonance at δ 69.9. Linkage through position 2 is not possible because it would require the C-1 resonance to occur in a more upfield position (*e.g.*, δ 103.4, see Table IV) and would also require the C-3 resonance to be at δ 71.7, which is 2.1 p.p.m. upfield of its normal position. This is greater than the largest recorded value (1.4 p.p.m.) in Table III and is further evidence against linkage through position 2. The full structure of the trisaccharide is thus α-L-Fuc-(1→3)-β-D-Gal-(1→4)-D-Glc, which agrees with the published findings[34].

This type of analysis has been made for five other examples drawn from the literature[1,36,53,56,64] and for one trisaccharide β-D-Gal-(1→4)-β-D-Gal-(1→4)-D-Glc obtained from Dr. P. A. J. Gorin; in each case, it accorded with the structure determined by chemical methods. In applying the rules to non-reducing trisaccharides, account would need to be taken of differences in the ^{13}C-n.m.r. spectra of non-reducing and reducing trisaccharides.

Attempted application of ^{13}C-n.m.r. analysis to two tetrasaccharides[44,51] failed because of the additional possibilities introduced by the presence of an extra sugar residue. The analysis was much more complex and, even if the reducing and the non-reducing end residues can be identified, there is still the problem of the sequence of the internal residues. As with the trisaccharide, branching may also cause difficulties in the analysis. Overlapping of signals is also more likely for tetra-

saccharides, and resonances of lower intensity from the α and β forms of the reducing-end unit may be obscured by the more-intense single and double carbon resonances.

The analysis of the structure of tetrasaccharides and larger oligosaccharides cannot therefore be resolved *ab initio* by this type of analysis, but has been carried out by ourselves[2-5] and by others[9,51,52,55,56,64] by working with a series of oligosaccharides of similar structure and building-up from the trisaccharide. The data in Table I may be useful in this context. Elaboration of other n.m.r. procedures (n.O.e., T_1 measurements, deuterium isotope effects[26], and two-dimensional n.m.r.[33]), as well as combination with other techniques, should allow the extension of the range of application of ^{13}C-n.m.r. spectroscopy to the solution of the structures of larger oligosaccharides.

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