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MASS-SPECTRAL IDENTIFICATION OF VARIOUS DERIVATIVES OF 7-DEOXY-D-*glycero*-D-*galacto*- AND 7-DEOXY-L-*glycero*-D-*galacto*-HEPTOPYRANOSE

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ABSTRACT

The analysis of a range of methyl ethers derived from methyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**1**) and methyl 7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside (**2**) is examined in relation to their retention times in open-tubular gas–liquid chromatography, and to their electron-impact mass spectra and fragmentation patterns. In addition, the electron-impact and chemical-ionization mass spectra of the peracetylated and permethylated glycosides and alditol acetates of the novel 7-deoxyheptoses **1** and **2** are described. A fragmentation pattern for methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside was proposed, and verified by *O*-(trideuterioacetyl)ation.

INTRODUCTION

Mass spectrometry has become one of the most powerful techniques for the structural investigations of complex carbohydrates[1,2]. Interest in the synthesis of novel sugars has created the need for systematic, mass-spectral studies of these sugars. The availability of chemical-ionization mass spectrometry may provide complementary data in conjunction with electron-impact techniques[3,4]. Therefore molecular-weight information can be obtained which adds confirmatory evidence for proposed structures of carbohydrates and contributes to the growing data-bases of mass-spectral, structural analysis of these compounds[5,6].

In a continuation of our studies on the mass spectrometry of carbohydrates[7–12], we now report the electron-impact mass spectra, and retention times in open-tubular columns, of a range of twelve methyl ethers derived from methyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**1**) and seven methyl ethers derived from methyl 7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside (**2**). We also report the electron-impact and chemical-ionization mass spectra and proposed

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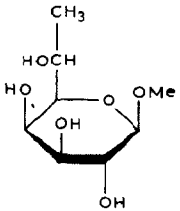
fragmentation patterns of the peracetylated and permethylated glycosides and alditol acetates of the novel 7-deoxyheptoses **1** and **2**. Glycosides **1** and **2** were synthesized as inhibitors for the precipitin reactions between artificial antigens possessing a β-D-galactopyranosyl haptenic structure and their specific antibodies[13,14].



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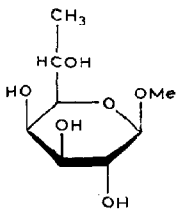

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RESULTS AND DISCUSSION

For the structural elucidation of complex polysaccharides, methylation analysis is an important method[15], which reveals structural information on the position of attachment of the interglycosidic linkages and on the carbohydrate composition[16,17]. Adequate information is available for the acetylated alditols of various methylated sugars, but somewhat fewer studies are available on the partially methylated alditol acetates from aminoheptoses and heptoses[5,18].

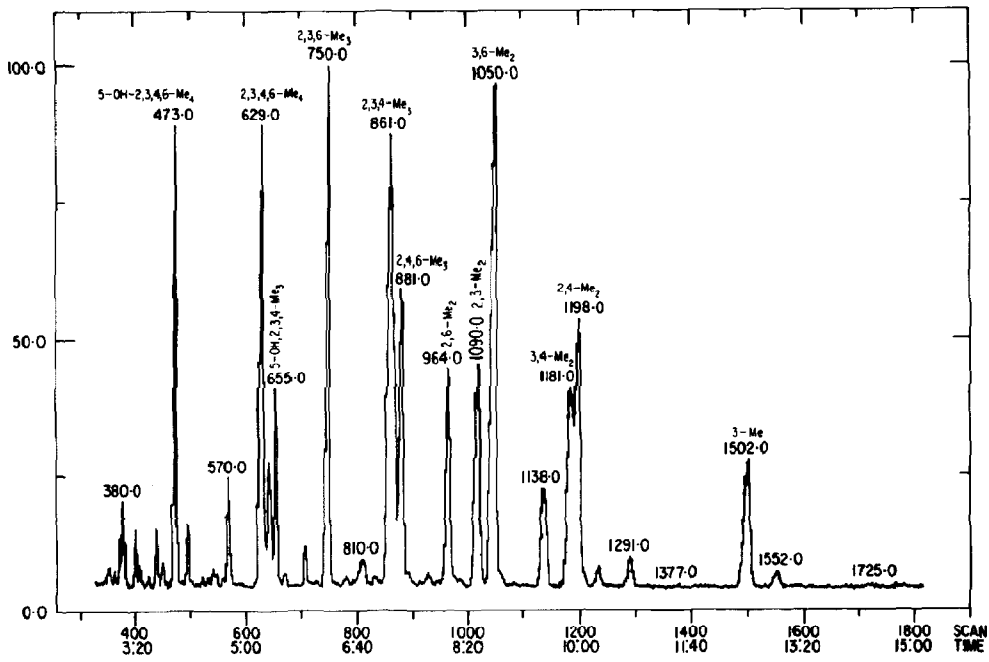


Fig. 1. The gas–liquid chromatogram of the partially methylated alditol acetates obtained from methyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**1**).

TABLE I

RELATIVE RETENTION-TIMES OF THE PARTIALLY METHYLATED ALDITOL ACETATES OF THE 7-DEOXY-HEPTOSES **1** AND **2**

Methylated alditol acetates (position of methyl groups in parent heptose)[a]	*Retention times*[b]	
	DD-*Hep*	LD-*Hep*
5-OH-2,3,4,6-	0.86	
2,3,4,6-	1.15	1.14
5-OH-2,3,4	1.20	
2,3,6-	1.37	1.46
2,3,4-	1.57	1.58
2,4,6-	1.61	1.54
2,6-	1.76	
2,3-	1.86	
3,6-	1.92	1.96
3,4-	2.17	2.18
2,4-	2.19	2.32
3-	2.75	

[a]2,3,4,6-stands for 1,5-di-*O*-acetyl-7-deoxy-2,3,4,6-tetra-*O*-methyl-D-*glycero*- or -L-*glycero*-D-*galacto*-heptitol. [b]Retention times relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol as unity.

The electron-impact mass spectra of partially methylated alditol acetates have been extensively studied, and the mode of fragmentation of these derivatives has been elucidated by deuterium-labelling techniques[19,20]. The electron-impact mass spectra of these derivatives are not sensitive to stereochemical differences, and do not usually contain the molecular radical-ion $M^{+\cdot}$.

The gas–liquid chromatogram of the partially methylated alditol acetates **3–14** obtained from methyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**1**) is shown in Fig. 1. The retention times (relative to that of 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol) of the partially methylated alditol acetates derived from the 7-deoxyheptoses **1** and **2**, are given in Table I.

As may be seen from Table I, it is necessary to obtain the mass spectrum and retention time of these partially methylated alditol acetates in order to identify them. It is obvious that the relative retention times cannot be depended on as a diagnostic tool.

The electron-impact mass spectra of each of the methyl ethers **3–14** obtained from methyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**1**) are presented in Table II. By examination of the mass spectra of this series of partially methylated alditol derivatives, it was possible to determine the location of the acetyl groups. The structures of these derivatives were deduced from the mass-spectral fragmentation-patterns in which the primary fragments were formed by α-cleavage resulting from fission between the carbon atoms in the alditol chain, and the order of precedence for cleavage was MeOCH–CHOMe > MeOCH–CHOAc > AcOCH–CHOAc[19,20] (see Fig. 2). The fragments bearing the methoxyl groups retain the

TABLE II

ELECTRON-IMPACT MASS SPECTRA OF THE PARTIALLY METHYLATED ALDITOL ACETATE DERIVATIVES **3–14** OBTAINED FROM METHYL 7-DEOXY-D-*glycero*-D-*galacto*-HEPTOPYRANOSIDE (**1**)

Compound	m/z *(Intensity)*
1-*O*-Acetyl-7-deoxy-2,3,4,6-tetra-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**3**)	235(2.0), 219(0.7), 203(2.1), 189(0.7), 175(7.3), 161(8.7), 145(4.0), 130(8.0), 117(36.7), 101(80.0), 89(26.7), 87(26.7), 71(10.7), 59(100) and 43(74.4)
1,5-Di-*O*-acetyl-7-deoxy-2,3,4,6-tetra-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**4**)	219(10.6), 203(1.0), 189(1.3), 175(12.7), 161(8.1), 159(13.3), 143(4.0), 131(7.3), 129(9.3), 117(30.1), 101(35.7), 87(16.1), 75(7.3), 59(100) and 43(77.3)
1,6-Di-*O*-acetyl-7-deoxy-2,3,4-tri-*O*-methyl-*glycero*-D-*galacto*-heptitol (**5**)	205(0.7), 175(1.2), 173(2.0), 161(16.2), 157(0.7), 143(1.3), 131(8.0), 117(43.4), 101(86.7), 87(13.3), 69(7.1), 59(8.7) and 43(100)
1,4,5-Tri-*O*-acetyl-7-deoxy-2,3,6-tri-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**6**)	247(13.3), 218(1.0), 187(1.4), 161(3.4), 145(4.7), 129(18.0), 127(17.4), 117(53.3), 113(38.0), 101(18.7), 87(22.7), 75(5.7), 59(50.7) and 43(100)
1,5,6-Tri-*O*-acetyl-7-deoxy-2,3,4-tri-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**7**)	247(6.7), 219(0.7), 203(6.7), 187(2.0), 173(4.7), 161(9.4), 143(20.7), 129(4.7), 117(43.3), 113(25.4), 101(46.0), 87(10.0), 71(4.0), 59(9.3) and 43(100)
1,3,5-Tri-*O*-acetyl-7-deoxy-2,4,6-tri-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**8**)	291(1.0), 233(4.7), 217(1.4), 189(1.3), 175(14.7), 159(4.0), 131(5.3), 129(4.7), 117(73.3), 101(18.0), 85(7.3), 74(6.7), 59(100) and 43(87.3)
1,3,4,5-Tetra-*O*-acetyl-7-deoxy-2,6-di-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**9**)	319(2.0), 201(1.2), 157(3.3), 117(100), 87(4.67), 69(4.0), 59(88.7) and 43(95.7)
1,4,5,6-Tetra-*O*-acetyl-7-deoxy-2,3-di-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**10**)	275(7.1), 219(0.7), 201(2.7), 173(12.0), 161(3.4), 156(3.3), 141(3.3), 129(6.7), 117(53.3), 101(15.3), 99(24.0), 87(12.7) and 43(100)
1,2,4,5-Tetra-*O*-acetyl-7-deoxy-3,6-di-*O*-methyl-D-*glycero*-D-galacto-heptitol (**11**)	247(8.0), 231(0.7), 214(2.7), 189(14.1), 172(2.0), 145(10.7), 129(73.3), 127(11.3), 113(26.1), 101(4.6), 87(48.0), 59(92.7) and 43(100)
1,2,5,6-Tetra-*O*-acetyl-7-deoxy-3,4-di-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**12**)	247(2.0), 233(3.3), 219(1.3), 203(14.7), 189(15.4), 173(4.0), 159(3.3), 143(38.0), 129(40.1), 117(11.3), 113(14.0), 101(17.3), 99(18.0), 87(18.0), 69(8.1) and 43(100)
1,3,5,6-Tetra-*O*-acetyl-7-deoxy-2,4-di-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**13**)	319(1.1), 259(0.7), 233(4.7), 219(0.7), 203(12.0), 185(1.3), 163(4.0), 159(6.7), 143(31.3), 127(5.3), 117(60.7), 101(20.7) and 43(100)
1,2,3,4,5-Penta-*O*-acetyl-7-deoxy-3-*O*-methyl-D-*glycero*-D-*galacto*-heptitol (**14**)	275(9.0), 219(2.0), 201(2.7), 189(22.1), 173(12.1), 141(4.7), 139(3.1), 129(58.1), 113(13.0), 99(23.5), 87(27.4) and 43(100)

positive charge, and the secondary fragment-ions resulted from elimination of acetic acid, ketene, methanol, or formaldehyde[20]. The fragmentation patterns were confirmed by deuterium-labelling techniques.

The electron-impact mass spectra of the seven partially methylated alditol acetates derived from methyl 7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside (**2**) are similar to those of their respective diastereoisomers.

The mass spectra of peracetylated and permethylated glycosides have been extensively studied, and the series **A–K** representing the fundamental modes of fragmentation are well documented[19,20].

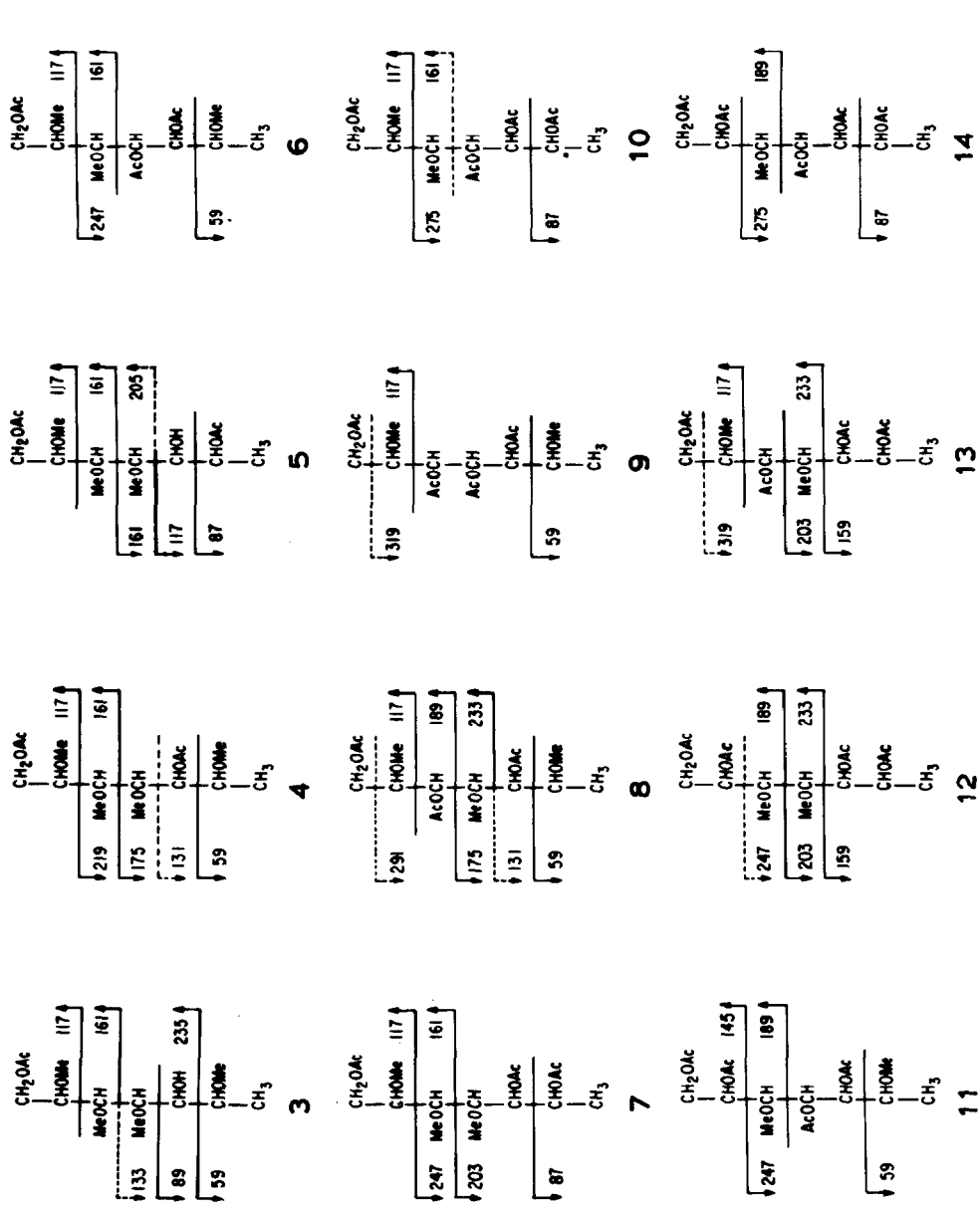


Fig. 2. Mass-spectral fragmentation patterns of the partially methylated alditol acetates 3–14.

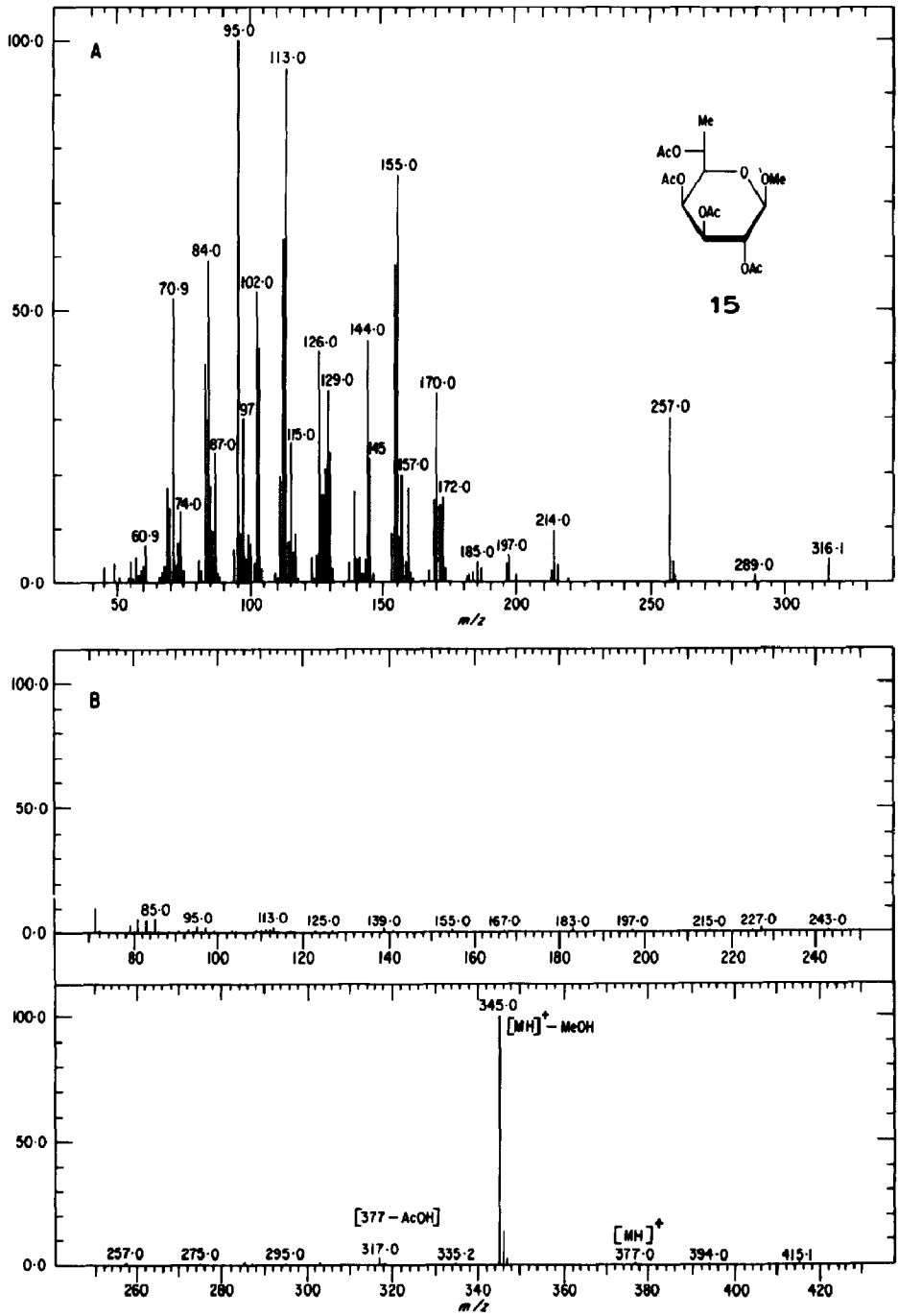


Fig. 3. Mass spectra of methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**15**). [(a) Electron-impact; (b) chemical-ionization.]

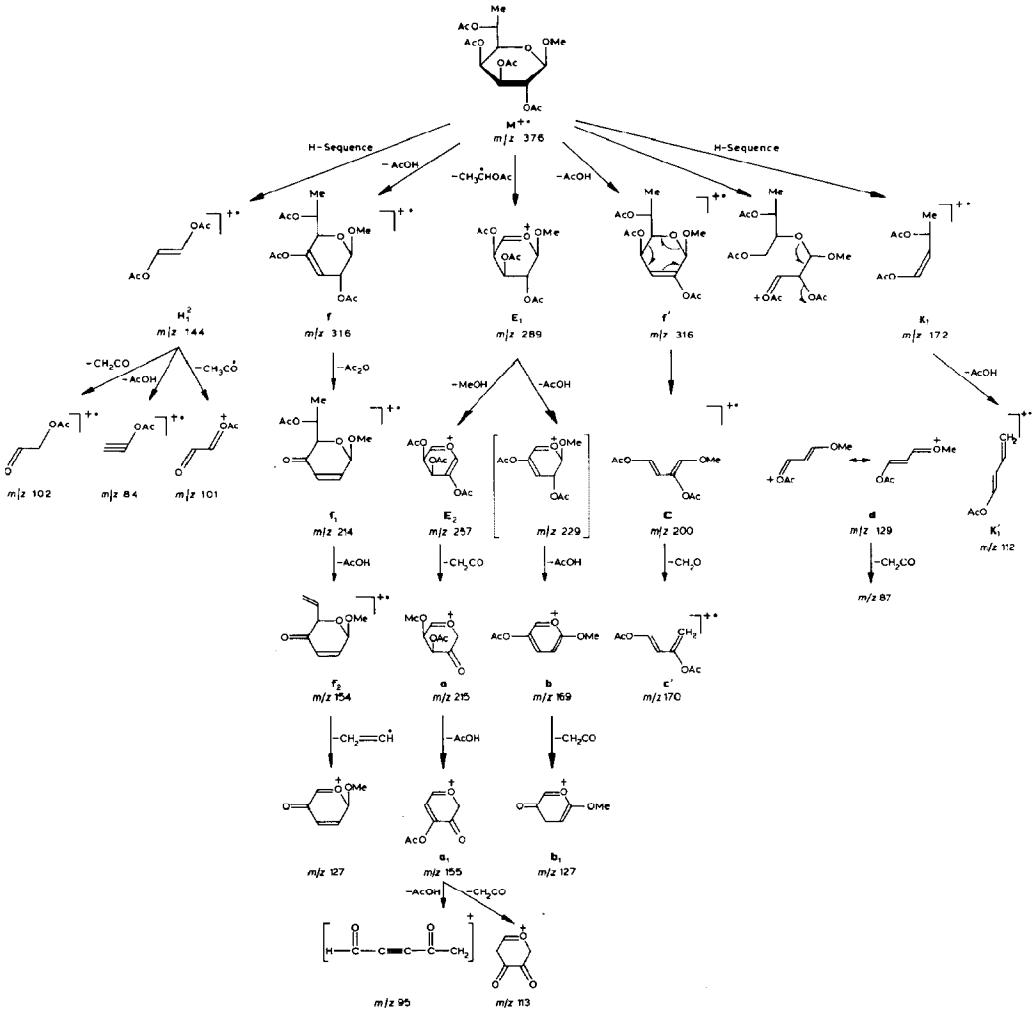


Fig. 4. Proposed fragmentation pattern of methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-D-*glycero*-*β*-D-*galacto*-heptopyranoside (**15**).

The electron-impact mass spectrum of methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-D-*glycero*-*β*-D-*galacto*-heptopyranoside (**15**) is shown in Fig. 3a.

A summary of the proposed modes of formation, and suggested structures, of the specific ions formed during the breakdown of the molecular radical-ion are given in Fig. 4.

It seems that one of the important initial cleavages is dominated by elimination of the side chain[19] from the molecular radical-ion $M^{+\cdot}$ to afford the primary fragment-ion $\mathbf{E}_1$ at *m/z* 289. Elimination of a molecule of methanol produces the secondary fragment-ion $\mathbf{E}_2$ at *m/z* 257. Elimination of a molecule of ketene from the ion $\mathbf{E}_2$ produces the fragment-ion at *m/z* 215, assigned structure **a**; this loses a

molecule of acetic acid to yield the intense ion at *m/z* 155, assigned structure $\mathbf{a}_1$. As it has been shown by deuterium-labelling experiments that two acetoxyl groups may be eliminated simultaneously[21,22], it is plausible to expect that the fragment-ion $\mathbf{E}_2$ at *m/z* 257 may eliminate one molecule of acetic anhydride to form the prominent ion at *m/z* 155. Elimination of a molecule of either acetic acid or ketene from the ion $\mathbf{a}_1$ at *m/z* 155 respectively affords the intense ions at *m/z* 95 (base peak) and *m/z* 113.

Elimination of the 3-acetoxyl group by two distinct routes, which involve loss of a molecule of acetic acid from the molecular radical-ion, from either C-3 and C-4 or C-2 and C-3, affords the primary fragment-ion at *m/z* 316, to which we tentatively assigned the two structures **f** and **f'**. The ion **f** loses a molecule of acetic anhydride to yield the secondary fragment-ion at *m/z* 214, assigned structure $\mathbf{f}_1$. The primary fragment-ion **f'** breaks down by electronic shifts to yield the low-abundant ion at *m/z* 200, to which we assigned structure **c**; this ion eliminates a molecule of formaldehyde to produce the ion at *m/z* 170, assigned structure **c'**.

The alternative, heterolytic cleavage of the C-3–C-4 bond of the sugar molecule logically leads to the primary fragment-ion at *m/z* 129, assigned structure **d**. The ion **d** is stabilized by resonance, and appears to be composed mainly of C-1, C-2, and C-3. The last ion loses a molecule of ketene to afford the ion at *m/z* 87.

Finally, the primary fragment-ion $\mathbf{H}_1^2$ at *m/z* 144, produced by fragmentation of the sugar molecule by the **H** sequence[20], fragments further by elimination of a molecule of either acetic acid or ketene, to afford the ions at *m/z* 84 and 102. Similarly, the primary fragment-ion $\mathbf{K}_1$ at *m/z* 172 is produced by the H-sequence, and fragments further by elimination of a molecule of acetic acid, to afford the ion $\mathbf{K}_1'$ at *m/z* 112.

The breakdown processes leading to the production of the proposed fragment-ions (see Fig. 3) were investigated by (trideuterioacetyl)ation. The electron-impact mass spectrum of the corresponding methyl 7-deoxy-2,3,4,6-tetra-*O*-(trideuterioacetyl)-D-*glycero*-β-D-*galacto*-heptopyranoside (**16**) gave, *inter alia*, peaks at the following *m/z* values: 325(3.9), 298(2.5), 266(36.5), 221(3.9), 220(12.1), 218(3.0), 217(12.4), 191(4.1), 178(13.9), 176(38.7), 172(13.7), 158(76.9), 154(31.9), 150(36.3), 132(23.1), 128(8.2), 127(8.0), 113(25.8), 115(58.1), 105(14.3), 14(4.0), 95(100), 90(23.1), 88(21.2), 87(32.1), 85(76.6), 84(20.5), 75(30.9), and 72(61.5). It is evident that the ions obtained in the mass spectrum of the per(trideuterioacetyl)ated methyl glycoside **16** are in agreement with the fragmentation pattern proposed in Fig. 4 for methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**15**). Thus, the primary fragment-ions **f** and **f'** at *m/z* 316, and $\mathbf{E}_1$ and $\mathbf{E}_2$ at *m/z* 289 and 257 respectively, have shifted to 9 a.m.u. higher than the corresponding ions in the electron-impact of mass spectrum methyl glycoside **15**. Similarly, the fragment-ions **a**, $\mathbf{K}_1$, **c**, and $\mathbf{H}_1^2$ at *m/z* 215, 172, 170, and 144, respectively, have shifted to 6 a.m.u. higher. Finally, the ions **b**, **d**, and $\mathbf{K}_1'$ at *m/z* 169, 129, and 112 have shifted to 3 a.m.u. higher.

The isobutane chemical-ionization mass spectrum of the peracetylated methyl glycoside **15** is shown in Fig. 3b. The salient feature of this c.i.-mass spectrum is the

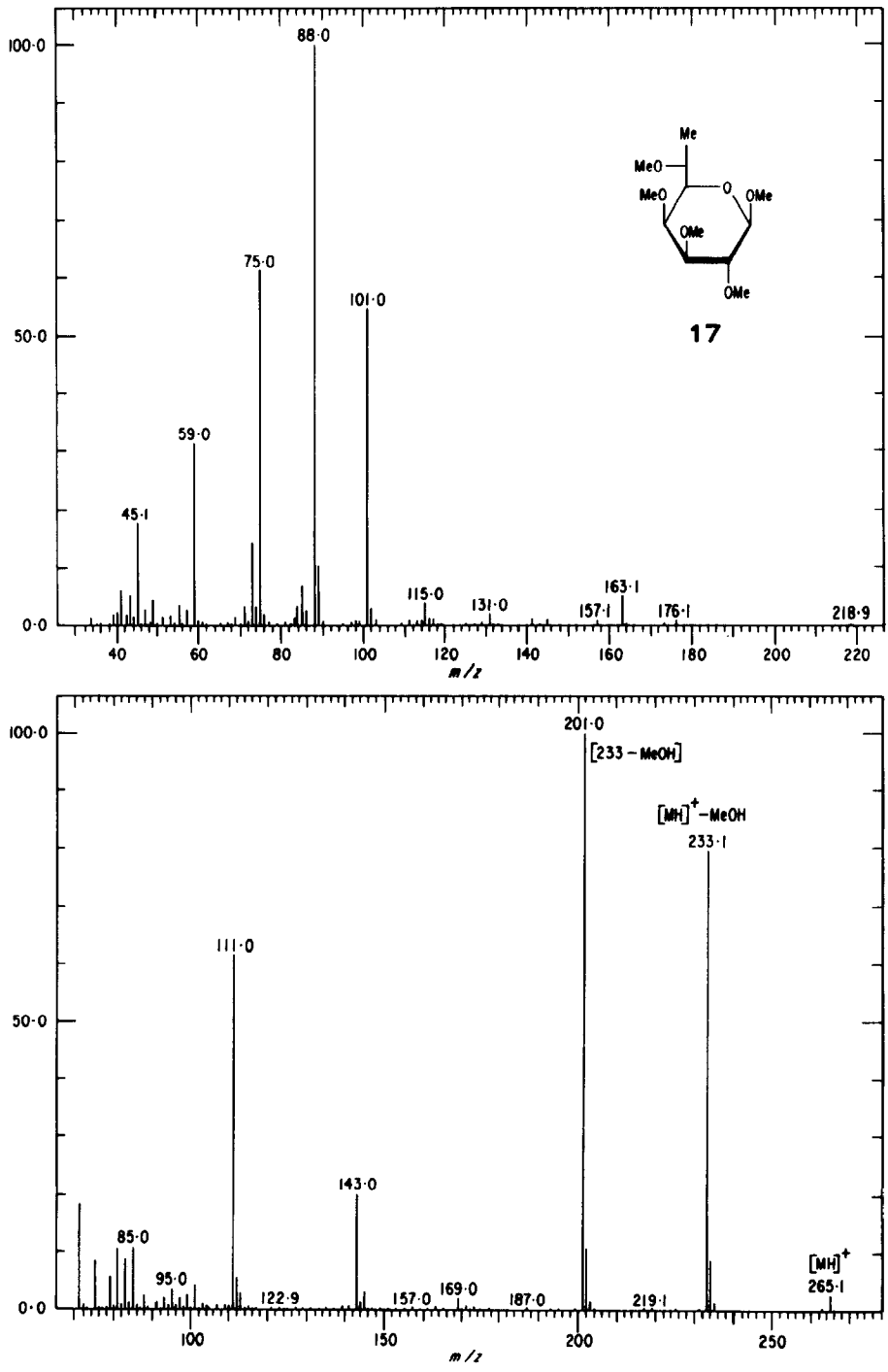


Fig. 5. Mass spectra of methyl 7-deoxy-2,3,4,6-tetra-*O*-methyl-D-*glycero*-β-D-*galacto*-heptopyranoside (**17**). [(a) Electron-impact; (b) chemical-ionization.]

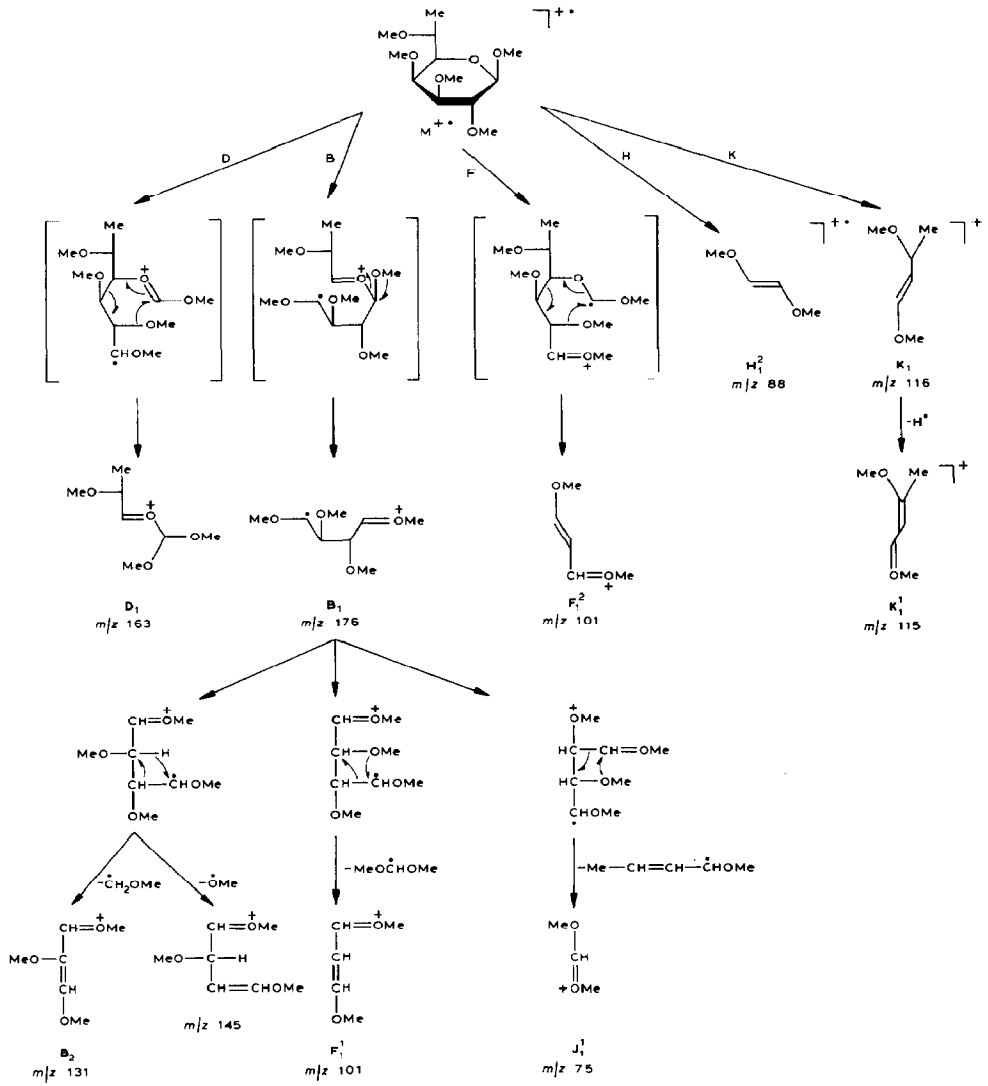


Fig. 6. Proposed fragmentation pattern of methyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**17**).

presence of minute proportions of the protonated molecular-ion $[M + H]^+$ at *m/z* 377. The primary fragment-ion at *m/z* 345 (base peak) is generated by the loss of a molecule of methanol from the protonated molecular-ion.

The electron-impact mass spectrum of methyl 7-deoxy-2,3,4,6-tetra-*O*-methyl-D-*glycero*-β-D-*galacto*-heptopyranoside (**17**) is shown in Fig. 5a.

A summary of the proposed modes of formation, and suggested structures of the specific ions formed during the breakdown of the molecular radical-ion, are given in Fig. 6. The electron-impact mass spectrum of the permethylated glycoside **17** showed typical ions derived from the specific degradation pathways **B, D, H,** and **K** suggested by Kochetkov and Chizhov[19].

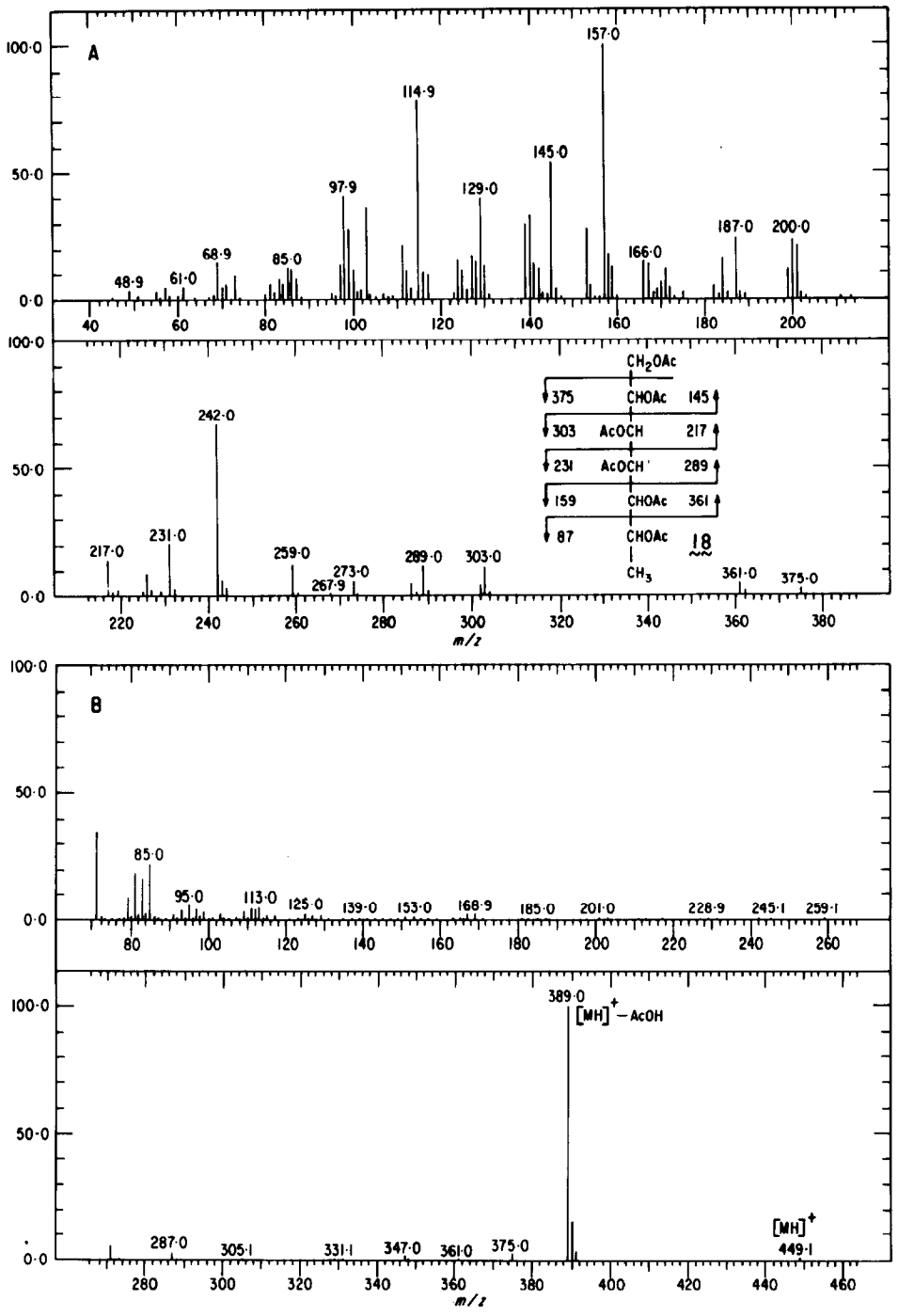


Fig. 7. Mass spectra of 1,2,3,4,5,6-hexa-*O*-acetyl-7-deoxy-D-*glycero*-D-*galacto*-heptitol (**18**). [(a) Electron-impact; (b) chemical-ionization.]

The isobutane chemical-ionization mass spectrum of the permethylated glycoside **17** is shown in Fig. 5b. The protonated molecular-ion $[M + H]^+$ at *m/z* 265 is observed. The primary fragment-ion at *m/z* 233 is generated by the loss of a molecule of methanol from the protonated molecular-ion. The prominent, secondary fragment-ion at *m/z* 201 (base peak) is produced by the loss of a molecule of methanol from the ion at *m/z* 233.

The simple and well established behavior of the alditol acetates[19,20] upon electron-impact makes these derivatives suitable for the identification of the 7-deoxyheptoses **1** and **2**.

The electron-impact mass spectrum of 1,2,3,4,5,6-hexa-*O*-acetyl-7-deoxy-D-*glycero*-D-*galacto*-heptitol **18**, shown in Fig. 7a, was found to obey the same fragmentation pattern as other sugars[19,20].

The isobutane chemical-ionization mass spectrum of alditol acetate **18** (see Fig. 7b) showed traces of the protonated molecular-ion $[M + H]^+$ at *m/z* 449, and the primary fragment-ion at *m/z* 389 is generated by the loss of a molecule of acetic acid from the $[M + H]^+$ ion.

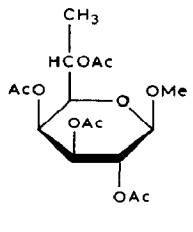
The electron-impact and isobutane chemical-ionization mass spectra of methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside (**19**), methyl 7-deoxy-2,3,4,6-tetra-*O*-methyl-L-*glycero*-β-D-*galacto*-heptopyranoside (**20**), and 1,2,3,4,5,6-hexa-*O*-acetyl-7-deoxy-L-*glycero*-D-*galacto*-heptitol (**21**) are similar to those of their respective diastereoisomers **15**, **17**, and **18**.

Finally, the gas–liquid chromatography retention-times, relative to that of hexa-*O*-acetyl-D-glucitol, for all the reported peracetylated and permethylated glycosides and alditol acetate derivatives of methyl 7-deoxy-D-*glycero*-β-D-*galacto* heptopyranoside (**1**) and methyl 7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside (**2**), are given in Table III.

EXPERIMENTAL

Reagents. — All of the reagents and solvents were of analytical grade, and were glass-distilled before use and stored over molecular sieves 4A.

Synthesis of the partially methylated alditol acetates **3**–**14**. — Methyl 7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**1**) and methyl 7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside (**2**) were novel, synthetic products prepared by the



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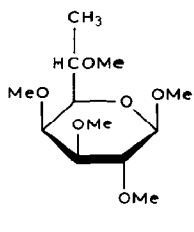

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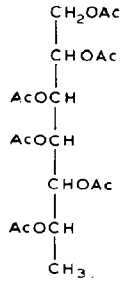

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TABLE III

RETENTION TIMES OF THE VARIOUS DERIVATIVES OF METHYL 7-DEOXY-D-*glycero*-β-D-*galacto*-HEPTOPYRANOSIDE (**1**) AND METHYL 7-DEOXY-L-*glycero*-β-D-*galacto*-HEPTOPYRANOSIDE (**2**)

D-glycero-D-galacto *Compound*	*RT*	*RT*[*Glc(OAc)*$_6$]	L-glycero-D-galacto *compound*	*RT*	*RT*[*Glc(OAc)*$_6$]
Peracetylated methyl glycoside (**15**)	6.45	0.58	Peracetylated methyl glycoside (**19**)	7.58	0.68
Permethylated glycoside (**17**)	2.42	0.22	Permethylated glycoside (**20**)	2.48	0.22
Alditol acetate (**18**)	10.07	0.91	Alditol acetate (**21**)	10.45	0.95

method of Lemieux *et al.*[14]. The series of synthetic, partially methylated alditol acetates were obtained by complete (1 mmol of sugar, 4 mmol of methylsulfinyl anion) and incomplete (1 mmol of sugar, 1 mmol of methylsulfinyl anion) Hakomori methylation[23] of the methyl glycosides **1** and **2**, followed by hydrolysis with M trifluoroacetic acid for 1 h at 100°, reduction of the sugars with sodium borohydride, and acetylation of the alditols with 1:1 acetic anhydride–pyridine for 1 h at 100°. In order to confirm the mass-spectral fragmentation-patterns of these novel series of partially methylated alditol acetates, reduction of the monosaccharides to the alditols was performed with sodium borodeuteride, followed by acetylation.

Synthesis of the methyl glycosides. — Methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-D-*glycero*-β-D-*galacto*-heptopyranoside (**15**), methyl 2,3,4,6-tetra-*O*-acetyl-7-deoxy-L-*glycero*-β-D-*galacto*-heptopyranoside (**19**), and methyl 7-deoxy-2,3,4,6-tetra-*O*-(trideuterioacetyl)-D-*glycero*-β-D-*galacto*-heptopyranoside (**16**) were obtained by acetylation of their respective precursors **1** and **2** with either 1:1 acetic anhydride–pyridine or trideuterioacetic anhydride–pyridine for 1 h at 100°, and the respective solutions were evaporated to dryness. Methyl 7-deoxy-2,3,4,6-tetra-*O*-methyl-D-*glycero*-β-D-*galacto*-heptopyranoside (**17**) and methyl 7-deoxy-2,3,4,6-tetra-*O*-methyl-L-*glycero*-β-D-*galacto*-heptopyranoside (**20**) were obtained by methylation of the corresponding methyl glycosides **1** and **2**, by the Hakomori method[23], and purified by passage through a column of Sephadex LH-20.

Synthesis of the alditol acetates. — The methyl glycosides **1** and **2** were hydrolyzed with M trifluoroacetic acid for 1 h at 100°, followed by evaporation to dryness. The resulting free sugars were reduced with sodium in methanol–acetic acid, and acetylation of the alditols with 1:1 acetic anhydride–pyridine for 1 h at 100° afforded respectively 1,2,3,4,5,6-hexa-*O*-acetyl-7-deoxy-D-*glycero*-D-*galacto*-heptitol (**18**) and 1,2,3,4,5,6-hexa-*O*-acetyl-7-deoxy-L-*glycero*-D-*galacto*-heptitol (**21**).

Gas–liquid chromatography. — Gas–liquid chromatography was performed on a DB-210 Megabore column (130 m × 0.53 mm i.d., 1.0 μm film thickness) (J & W Scientific) and on a WCOT CP-Sil 5CB fused-silica capillary column (Chromapack; 25 m × 0.23 mm i.d., 0.15 μm film thickness) at 180°. Both columns were mounted in a Perkin–Elmer Model 8310 gas chromatography equipped with a flame-ionization detector.

Gas–liquid chromatography–mass spectrometry. — Combined gas–liquid chromatography–mass spectrometry was performed in a Finnigan MAT 4510 GC/MS apparatus complete with Superincos Data system and EI/CI/PPNICI modes. The gas chromatography was a Finnigan 9611 unit, which was equipped with a 26-m WCOT CP-Sil 5CB fused-silica capillary column (0.23 mm i.d., film thickness 0.15 μm) installed directly at the ion source. The velocity of linear flow was set to 28.8 cm/s at the analysis temperature of 180°. The split was set at 30:1, and the sweep to 7 mL/min. The temperature for the analysis was 180°. E.i. mass spectra were recorded at 70 eV (emission current 0.25 mA; multiplier, 1450 V)

with a scan range of 45–475 a.m.u. at 0.45 s/scan. Samples **15, 16**, and **18** were generated at 50 eV with a scan range of 33–475 a.m.u. to enhance their fragmentation patterns. The e.i. mass spectra were recorded at an ion-source temperature of 120–190°. C.i. mass spectra were recorded using AGA ultra-high-purity isobutane at a source pressure of 80 Pa. The c.i. mass spectra were recorded at 70 eV with a scan range of 70–475 a.m.u. at 0.45 s/scan, at an ion-source temperature of 150°.

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