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MASS SPECTROMETRY OF THE POSITIONALLY ISOMERIC, MONOBENZYL ETHERS OF METHYL GLYCOPYRANOSIDES

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ABSTRACT

The electron-impact, mass-spectrometric behavior of all theoretically possible, positionally isomeric monobenzyl ethers of methyl pento-, hexo-, and 6-deoxyhexo-pyranosides is described, on the basis of 70- and 12-eV mass spectra, *O*-deuterium-labeling experiments, elemental composition, and metastable-transition measurements. The semiempirical MNDO quantum-chemical method was used for calculation of both the geometrical parameters (bond lengths, bond angles, and dihedral angles) and the distribution of net charges in the cyclic and acyclic forms of the abundant $[C_4H_7O_3]^+$ and $[C_5H_9O_4]^+$ ions. The results obtained show that the cyclic structures of both ions are the more stable. Differences in the fragmentation of the compounds studied have been applied for establishing criteria that permit simple and unambiguous localization of the benzyl group in monobenzyl ethers of methyl glycopyranosides.

INTRODUCTION

Benzyl groups are very often used for protection of hydroxyl groups in carbohydrate chemistry. Facile routes for the preparation of partially benzylated derivatives of saccharides include partial benzylation[1] of compounds having several OH groups, and nucleophilic opening of the anhydro ring of sugar epoxides by the benzylalkoxide anion[2]. Following these procedures, it is necessary to determine the positions of benzyl groups in the isolated, partially benzylated saccharides. In connection with preparation of new benzylated derivatives of saccharides, we first applied methods, similar to methylation analysis, for determination of the position of benzyl groups. A sample was methylated, debenzylated, and the position of the benzyl group in the parent saccharide determined from the mass spectrum of the partially methylated derivative[3–5]. However, this approach is time consuming and therefore, in our studies of the mass-spectrometric fragmentation of partially benzylated methyl glycosides of various saccharides (Table I), we set out to develop a method that would enable routine, direct estimation of this group in the sugar derivatives.

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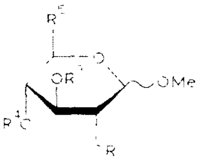
TABLE I

COMPOUNDS INVESTIGATED



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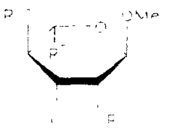
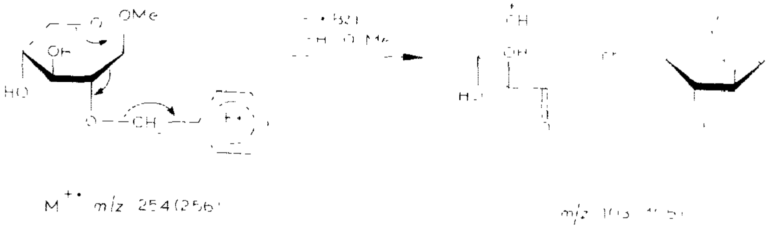


9 – 11

Compound no.	*Anomeric configuration*	R^2	R^3	R^4	R^5
1	β-D	Bzl	H	H	H
2	β-D	H	Bzl	H	H
3	α-D	H	Bzl	H	H
4	β-D	H	H	Bzl	H
5	α-D	Bzl	H	H	CH_2OH
6	α-D	H	Bzl	H	CH_2OH
7	α-D	H	H	Bzl	CH_2OH
8	α,β-D	H	H	H	CH_2OBzl
9	α-L	Bzl	H	H	CH_3
10	α-L	H	Bzl	H	CH_3
11	α-L	H	H	Bzl	CH_3

RESULTS AND DISCUSSION

Methyl O-benzyl pentopyranosides (**1**–**4**). — Mass spectra (12 eV) of the title compounds are given in Table II. All of them afforded a molecular-ion peak at *m/z* 254. The position of the benzyl group at O-2 of compound **1** is characterized by very intense ions at *m/z* 163 of the fragmentation series F (ref. 6), and by ions at *m/z* 103 (105) that are presumably formed in the manner shown in Scheme 1. The MNDO quantum-chemical calculations[7] demonstrated that, of the two possible structures for the ions (Scheme 1), the cyclic one is the more stable.



Scheme 1

The theoretical structures of both isomers of $[C_4H_7O_3]^+$ (*m/z* 103) are schematically depicted, together with the atom numbering and heats of formation

TABLE II

MASS SPECTRA (12 eV) OF METHYL *O*-BENZYLPENTOPYRANOSIDES

m/z	$\%\Sigma_{45} \times 100$				m/z	$\%\Sigma_{45} \times 100$			
	1	**2**	**3**	**4**		**1**	**2**	**3**	**4**
254	15	99	149	333	122	105	104	78	
253	9				121	184	135	90	102
236	25			5	120				61
223	41	113		44	117	168			197
222		167	761	130	116	197	497	2594	91
205	35			27	115		206	166	47
204		24	53		114	302	2061	1156	133
193	47		42	122	106		120	62	80
186		35	19		105		49	19	141
179				50	104		67	50	25
176	175	241	101	264	103	1147	135	90	189
175			45		100		135	93	
163	3538	1030	479	3560	99	149	49	42	38
162			73		98	213	42	180	83
158	92	85	45	22	87	286	263	200	778
151		675	366	30	86		497	648	
150	204	138	81	108	85	210	177	121	185
149				63	84	235			
148			62	30	82		67	36	194
147			36	33	75	66			55
146	79	284	124	69	74	102	426	282	122
145	153	71	50	108	73	669	497	338	667
144			64		70	89	266	197	222
136			14		69	172	462	366	86
135		21	22	58	68		117	78	
134		31	19	111	61	92	63	42	94
133	350	88	70	333	60	95			333
132	60	39	39	30	58		78	50	
131	137	103	146	50	57	105	49	62	108
130	70	56	42	194	54				72
129	111	42	22	27	45	255	53	25	72

(ΔH_f), in Scheme 2. The geometrical parameters are listed in Table III. A large energy-difference (45.3 kcal.mol^{-1}) between the acyclic and cyclic structures is calculated. Table IV gives the net charges of individual atoms in both structures. A higher possibility for positive-charge delocalization is evident, from the large difference in charges, at C-2, C-5 and O-1 (Table IV).

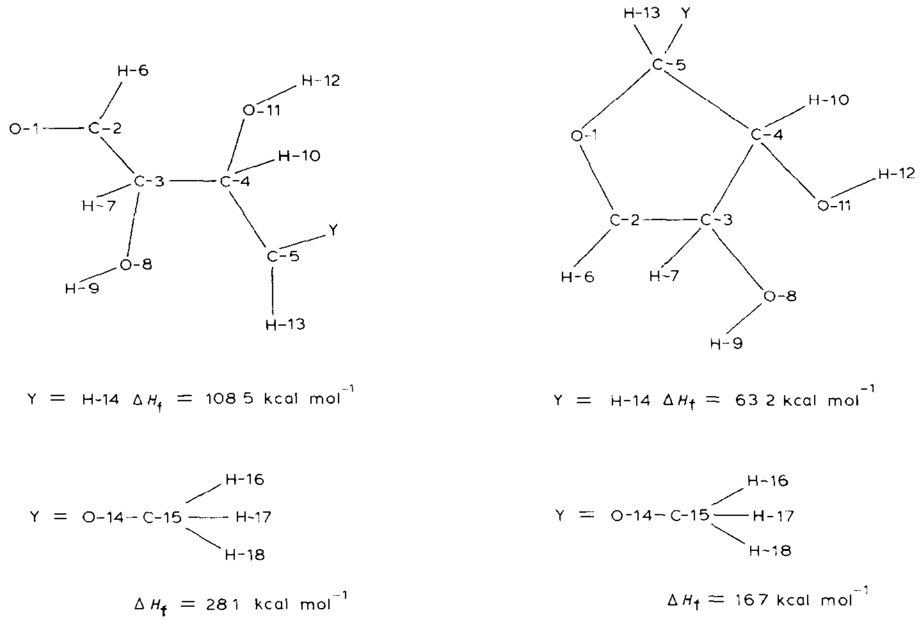
Ions having *m/z* 114 (114) formed by elimination of MeOH and PhCH$_2$OH from the molecular ions give the most intense peak in the mass spectrum of compound **2** (Scheme 3). In compound **2**, presence of the benzyl group at O-3 is also evident from an intense peak at *m/z* 151 (151) for ions of the fragmentation series J. Ions of the fragmentation series B are also intense. Measurements of metastable-ion transitions and *O*-deuteration experiments have revealed that the ions

TABLE III

BOND LENGTHS (pm), BOND ANGLES AND DIHEDRAL ANGLES (deg) OF THE ISOMERS $[C_4H_7O_3]^+$ AND $[C_5H_9O_4]^+$ IN THEORETICAL STRUCTURES CALCULATED BY THE MNDO METHOD

Parameter	*$[C_4H_7O_3]^+$*		*$[C_5H_9O_4]^+$*	
	Cyclic	*Acyclic*	*Cyclic*	*Acyclic*
O-1–C-2	128.3	121.3	127.8	121.5
C-2–C-3	155.3	156.6	155.0	156.2
C-3–C-4	160.5	159.8	160.0	158.6
O-1–C-5	145.2		149.4	
C-5–O-14			136.4	127.5
O-6–C-14			142.0	144.5
C-2–H-6	110.1	110.4	110.2	110.5
C-3–H-3	112.2	112.8	112.2	112.9
C-6–O-8	137.9	139.1	138.2	139.4
O-8–H-9	95.0	95.0	95.0	94.9
C-4–H-10	112.7	113.9	112.7	113.0
C-4–O-11	137.7	138.6	137.3	137.9
O-11–H-12	94.9	95.0	95.0	95.0
C-5–H-13	111.5	109.6		
C-5–H-14	111.6	109.4	112.5	110.7
C-7–H-16			111.4	111.3
C-7–H-17			111.5	111.4
C-7–H-18			111.4	111.3
C-4–C-5	158.3	150.4	160.5	155.9
O-1–C-2–C-3	113.1	120.5	113.4	121.0
C-2–C-3–C-4	101.44	113.5	102.0	113.3
C-2–O-1–C-5	114.8		114.8	
O-14–C-5–C-4			112.9	120.1
C-15–O-14–C-5			123.1	128.2
C-5–C-4–C-3		111.4		109.4

Parameter	*$[C_4H_7O_3]^+$*		*$[C_5H_9O_4]^+$*	
	Cyclic	*Acyclic*	*Cyclic*	*Acyclic*
H-6–C-2–O-1	119.8	123.4	120.1	123.9
H-7–C-3–C-2	108.0	106.1	108.3	105.8
O-8–C-3–C-2	108.6	114.3	107.5	113.9
H-9–O-8–C-3	113.4	114.5	113.1	114.0
H-10–C-4–C-3	109.5	105.8	109.6	107.4
O-11–C-4–C-3	114.5	117.2	115.1	117.0
H-12–O-11–C-4	114.8	115.8	115.4	115.6
H-13–C-5–C4	112.8	122.6	112.5	117.2
H-14–C-5–C-4	115.1	120.8		
H-16–C-7–O-6			111.2	109.8
H-17–C-7–O-6			11.5	109.9
H-18–C-7–O-6			105.9	105.6
C-4–C-3–C-2–O-1	8.4	178.4	8.8	183.7
C-5–C-4–C-3–C-2		184.4		184.5
C-5–O-1–C-2–C-3	0.7		1.9	
O-14–C-5–C-4–C-3			263.8	243.8
C-15–O-14–C-5–C-4			209.8	181.3
H-6–C-2–C-1–O-5	180.21	2.4	180.9	2.5
H-7–C-3–C-2–O-1	250.3	62.2	250.7	67.4
O-8–C-3–C-2–O-1	127.3	229.6	128.5	305.8
H-9–O-8–C-3–C-2	139.7	51.4	151.9	51.7
H-10–C-4–C-3–C-2	102.2	296.9	98.5	296.1
O-11–C-4–C-3–C-2	220.3	56.0	217.2	56.0
H-12–O-11–C-4–C-3	65.0	27.2	60.6	35.9
H-13–C-5–C-4–C-3	131.1	58.3	112.5	66.0
H-14–C-5–C-4–C-3	256.6	236.0		
H-16–C-15–O-14–C-5			62.1	60.8
H-17–C-15–O-14–C-5			299.7	298.7
H-18–C-15–O-14–C-5			180.9	179.7

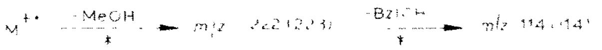


Scheme 2

TABLE IV

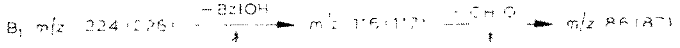
DISTRIBUTION OF NET CHARGES IN (10^3 e) ON THE ATOMS OF CYCLIC AND ACYCLIC ISOMERS OF IONS $[C_4H_7O_3]^+$ AND $[C_3H_9O_4]^+$ AS CALCULATED BY THE MNDO METHOD

Atom	$[C_4H_7O_3]^+$		$[C_5H_9O_4]^+$	
	Cyclic	*Acyclic*	*Cyclic*	*Acyclic*
O-1	−86.9	−197.8	−138.3	−215.1
C-2	377.3	225.7	399.1	228.0
C-3	56.6	80.8	53.9	54.4
C-4	80.4	50.2	96.4	138.3
C-5	74.3	515.5	246.6	383.9
O-14			−338.1	−131.9
C-15			202.0	183.7
H-6	187.2	71.8	180.8	67.1
H-7	84.6	43.4	84.7	35.1
O-8	−283.5	−348.8	−290.5	−345.9
H-9	242.0	248.6	240.8	237.8
H-10	114.0	127.4	103.5	92.1
H-11	−258.4	−290.2	−260.4	−283.4
H-12	204.1	238.3	216.2	230.8
H-13	113.8	128.4	110.5	118.9
H-16			21.5	57.6
H-17			15.0	92.0
H-18			57.0	56.5
H-14	94.5	110.7		



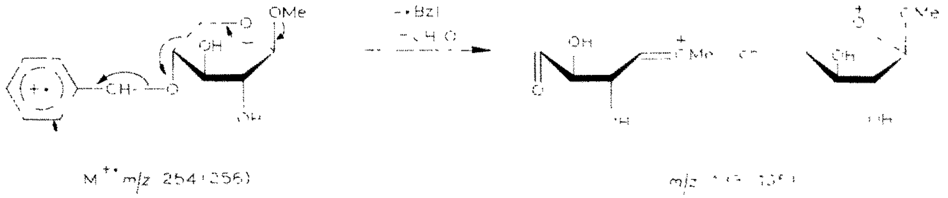
Scheme 3

$[C_5H_8O_3]^+$ at *m/z* 116 (117) are formed from $[M - CH_2O]^{+\cdot}$ (B_1) ions (a peak for the latter is absent from the spectrum) by the elimination of benzyl alcohol, and are further cleaved by loss of formaldehyde to give the ions having *m/z* 86 (87) and elemental composition $C_4H_6O_2$ (Scheme 4). In contrast to the mass spectra of compounds **1**, **3**, and **4**, the spectrum of **2** reveals two ions, A_1 at *m/z* 223 and $[M - MeOH]^+$ at *m/z* 222, having approximately the same intensities With the α anomer (**3**), the elimination of methanol is far more pronounced. Differences in relative proportions were also observed with other ions. Comparison of the intensities of ions at *m/z* 114 and 116 showed that, in the β anomer, the processes of subsequent elimination of MeOH and BzlOH, or BzlOH and MeOH, were favored over processes leading to ions at *m/z* 116 (a peak at *m/z* 114 is the most abundant). In contrast, in the α anomer, the process depicted in Scheme 4 (*m/z* 116 is the base peak) is favored. Differences in the spectra are caused by the different steric arrangement of the methoxyl group and thus in the ability to eliminate MeOH. The intensity ratios of the ions at *m/z* 114 and 116 remained almost the same, for both anomers, independent of the applied ionization energy and the construction of the instrument (Table V).



Scheme 4

As expected, the ions of series F at *m/z* 163 ($C_{10}H_{11}O_2$) are the most intense in the mass spectrum of the 4-benzyl ether **4**. Ions $[C_5H_9O_4]^+$ at *m/z* 133 (135) (Scheme 5), analogous to the ions at *m/z* 103 in the fragmentation of the 2-*O*-Bzl derivative, are formed by a mechanism similar to that for **1** (Scheme 1).



Scheme 5

As in the preceding case, the MNDO calculations for tentative structures of the $[C_5H_9O_4]^+$ ions revealed the cyclic structure to be the more stable (Scheme 2, Tables III and IV). The presence of a methoxyl group enhances the possibility of charge delocalization in both structure, and simultaneously decreases the energy difference to 11.4 kcal.mol^{-1}

TABLE V

RATIO OF PEAK INTENSITIES *m/z* 114/116 IN THE SPECTRA OF ANOMERIC METHYL 3-*O*-BENZYL-D-XYLOPYRANOSIDES

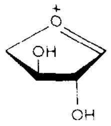
Compound no	m/z *114/116*		
	JMS-D100 (70 eV)	*JMS-D100 (12 eV)*	*Varian MAT-111 (70 eV)*
2	4 00	4.15	3.60
3	0.48	0.44	0 50

The strong differences in abundances of characteristic ions at *m/z* 114 and 103 (Table II) enable a simple and unambiguous localization of the benzyl group in methyl *O*-benzylpentopyranosides (Table VI).

Methyl O-*benzylhexopyranosides* (**5**–**8**). — The increased number of hydroxyl groups in the molecules **5**–**8** leads to mass spectra that are more complex (Table VII). The ion types characteristic of methyl *O*-benzylpentopyranosides (**1**–**4**) have their analogs in methyl *O*-benzylhexopyranosides. The mass spectra (Table V) show molecular ions at *m/z* 284 (287). The formation of isomeric ions of the series F (*m/z* 163, 87, 73) and H (*m/z* 150, 74, 60) prevails in this instance. Noteworthy is the elimination of methanol from the molecular ion of the 6-*O*-benzyl derivative; it proceeds very readily and the ions at *m/z* 252 (255) form the base peak of the spectrum. Experiments on *O*-deuterium labeling revealed that a proton of the methylene group takes part in the elimination of methanol from the molecular ion. Methyl 6-*O*-benzylglucopyranoside adopts mainly the ${}^4C_1$(D) conformation at room temperature, but on heating in the mass spectrometer, ready changes of conformation take place, through ${}^4H_3$, ${}^1S_3$ or ${}^4H_5$, ${}^1S_5$ to ${}^{1,4}B$ (ref. 8) (Scheme 6). Dreiding models show that, in the ${}^{1,4}B$ conformation a proton of the methylene

TABLE VI

CRITERIA FOR BENZYL-GROUP ASSIGNMENT IN METHYL *O*-BENZYL PENTOPYRANOSIDES

m/z	*Symbol*	$\%\Sigma_{45} \times$ *100*		
		2-O-Bzl	*3-O-Bzl*	*4-O-Bzl*
114	$[M - MeOH - BzlOH]^{+}$	· · ·[a]	xxx	· · ·
103		xx	· · ·	· ·

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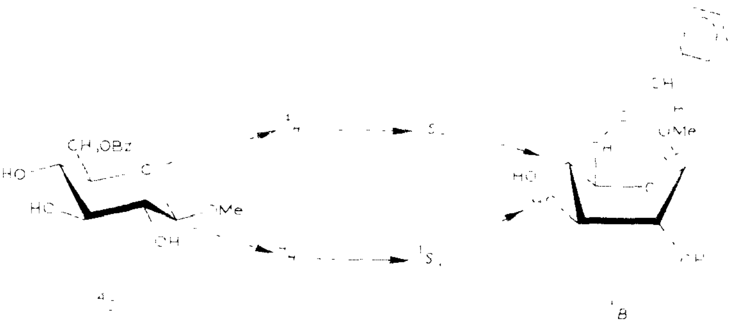
[a] Peak intensities (Table VI, VIII, and X): ·, 0 5%; · ·, 0.5–1%, · ·, 1–5%; x, 5–10%, xx, 10–20%, and xxx, 20%.



Scheme 6

group approaches the β-glycosidic methoxyl group close enough to permit its transfer to oxygen. From the mass spectra given in Table VII, we have selected those ions whose presence and abundances indicate the position of benzyl groups in the molecule (Table VIII).

Methyl O-benzyl-6-deoxyhexopyranosides (**9–11**). — The 12-eV mass spectra are given in Table IX. All compounds showed molecular ions at *m/z* 268. In comparison with methyl O-benzylpentopyranosides, ions of the H type (*m/z* 150) are more abundant. Ions at *m/z* 117 (119) are formed with compound **9** as for the ions at *m/z* 103 (105) from compound **1** (Scheme 1), but their relative proportion is lower. Subsequent eliminations of MeOH and BzlOH from molecular ions of the 3-*O*-benzyl derivative **10** proceed with equal ease as with compounds **2** and **3**. The result of this process is a concentration of the ions at *m/z* 128 (128), which constitute the base peak of the spectrum. The occurrence of ions having *m/z* 148 (148) in the spectrum of the 4-OBzl derivative **11** (K series) is surprisingly high in comparison with corresponding pentopyranosides (**4**, *m/z* 134) and hexopyranosides (**7**, *m/z* 164). From the mass spectra given in Table IX, characteristic ions have been selected that permit unambiguous determination of the position of the benzyl group in these compounds from the relative proportion of the ions at *m/z* 148 and 128 and from the ratio of the ions at *m/z* 150 and 148 (Table X).

EXPERIMENTAL

Materials. — Compound **1–11** were prepared according to published procedures[1,2,9–13]. The anomeric configurations of the samples were verified by ^{13}C-n.m.r. spectroscopy. The ^{13}C-n.m.r. spectrum of methyl 6-*O*-benzylglucopyranoside (**8**) confirmed the formation of a 1:1 anomeric mixture. ^{13}C-N.m.r. spectra were recorded in $CDCl_3$ with a Jeol FX-60 FT n.m.r. instrument; Me_4Si was the internal standard.

Mass spectra. — Mass spectra (70 and 12 eV) were recorded with a JMS-D 100 (Jeol) mass spectrometer operating with an emission current of 300 μA. The temperature at the site of sample evaporation of the direct-inlet system was 150–

TABLE VII

MASS SPECTRA (12 eV) OF METHYL *O*-BENZYLHEXOPYRANOSIDES

m/z	$\%\Sigma_{45} \times 100$				m/z	$\%\Sigma_{45} \times 100$			
	5	**6**	**7**	**8**		**5**	**6**	**7**	**8**
248	48	94	250	153	122	27			
253	13				121	360	337	139	49
252		37	134	1431	120	24	327		52
235	27	11	13		118	22		100	41
234	61	25	16	32	117	99	84	134	64
223	12				116	34	179	105	219
221	30	11	14		115	342	116	105	76
217			9	8	112			129	
216		116		7	111		116		
209				8	110		158		
206	37				105	48	179	139	248
205				17	104	78			86
204				11	103	48	168	72	73
203	51	105	27	13	100	68	406	673	51
198		13			99	20	263		51
193	30	22	55	96	98	34	232		35
191		39		27	97	342	179	250	48
188	49			13	87	132	295	720	1373
181				37	86	22	833		54
180			81	54	85	68	147	110	87
179	25		240	262	84				24
176	20	158		17	83				17
175	37	327		28	82		189	384	138
174				20	81			115	24
173				37	79				20
166			48		75		200	327	116
164	377		134	29	74	144	390	711	357
163	3378	274	644	189	73	960	844	841	555
162		94		438	72			134	
161	126			56	71	192	205	125	430
160	30			30	70	24		77	38
159				14	69	85	221	183	67
151	75	232		80	68			77	17
150	806	274	192	54	61	186	242	370	87
149		158		160	60	58		250	540
148			187	59	59				13
147	54		115	35	58				35
146	164	464	235	68	57	157	258	139	189
145	147	137	173	89	45	46	168	471	62
144		379		16					
143	89			13					
135	30		56	34					
134	34		50	94					
133	411	121	173	467					
132	46			61					
131				262					
129	30		91	32					
128	116	147	129	29					
127			38						
123				43					

TABLE VIII

CRITERIA FOR BENZYL GROUP ASSIGNMENT IN METHYL *O*-BENZYLHEXOPYRANOSIDES

m/z	*Symbol*	$\%\Sigma_{45} \times 100$			
		2-O-Bzl	*3-O-Bzl*	*4-O-Bzl*	*6-O-Bzl*
252	$[M - MeOH]^{+}$	0			vs
150	$[BzlOCH{=}CHOBzl]^{+}$ H	s			
87	$HOCH{-}CH{-}CH{=}\overset{+}{O}Me$ F			s	vs
86	$\left[M - BzlOH \quad \begin{matrix} CH_2OH \\ \vert \\ CH{-}O \end{matrix}\right]^{+}$		s	0	

180°, depending on the volatility of the samples, that of the ionizing chamber being 200°. The 70-eV spectra of compounds **2** and **3** were also recorded with a Varian MAT 111 instrument. The conditions of measurement were identical with those for the first instrument. Mass spectra in Tables II, VII, and IX do not include ions having *m/z* 91 and 65 in the summation. The relative intensities of ions having *m/z* 91 were ~1000%, as compared with the base peaks given in the Tables. Measurement of metastable transitions was made with a metastable-ion detector MS-MT-01. Elemental compositions of selected ions were estimated at 10,000 resolution by using a JMS-D 100 instrument. *O*-Deuterations were performed by dissolution of the samples in $CH_3OD + D_2O$ (10:1) and subsequent evaporation in the mass spectrometer. The degrees of deuteration achieved were ~80%. The *m/z* values in parentheses in the text and schemes refer to the spectra of *O*-deuterated compounds.

Both the structures and stabilities of $[C_4H_7O_3]^+$ and $[C_5H_9O_4]^+$ ions were calculated by using a semiempirical MNDO[7] quantum-chemical method. In the calculation, all bond lengths, bond angles, and dihedral angles were optimized

TABLE X

CRITERIA FOR BENZYL GROUP ASSIGNMENT IN METHYL *O*-BENZYL-6-DEOXYHEXOPYRANOSIDES

m/z	*Symbol*	$\%\Sigma_{45} \times 100$		
		2-O-Bzl	*3-O-Bzl*	*4-O-Bzl*
148	$[BzlOCH{=}CHCH_3]^{+}$ K			vs
128	$[M - MeOH - BzlOH]^{+}$		vs	0
150/148	H/K	5	115	0.7

TABLE IX

MASS SPECTRA (12 eV) OF METHYL *O*-BENZYL-6-DEOXYHEXOPYRANOSIDES

m/z	$\%\Sigma_{45}$ × *100*		
	9	**10**	**11**
268	71	45	340
237	26	42	71
236	20	49	126
223		9	
218		18	
206	270		18
200		17	
196		20	
195		9	
193	41	28	58
192		28	
191		18	
190		31	
181			40
180	15		
178	23		
177	23	17	55
176		28	
175	25	28	
164	169		120
163	571	233	402
162		20	
161	31	140	37
160		49	
151		685	
150	1420	1153	695
149	66	14	176
148	262	10	1020
147	20	12	
146	123	20	
145	29	42	
144	55	42	123
143	19		
136		26	
135	277	132	108
134	38	109	105
133	332	101	340
132	49	62	24
131	32	40	34
130	40	264	43
129	32		34
128	20	1309	
121	416	451	191
120		21	83
119	115		340
118		37	
117	339		136
116		857	
115	154	29	
113		32	
112	52	24	
105	447	28	98
103	33		46
101		109	30
100	262	545	34
99	239	57	52
88		514	
87	687	381	1206
86		116	
85	38	62	
84	67	140	170
83	44	202	40
82		59	
79	30	21	
77	27		
75	118	46	371
74	272	233	896
73	725	506	695
72		62	
71	335	140	340
70	34		
69	20	24	
68	17	14	77
61	247	37	151
60	138	18	188
59	139	32	64
58	208	171	
57	478	54	340
56		73	
45	193	26	463

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