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THE MASS SPECTRA OF ACETYLATED AND PROPANOYLATED ALDOFURANOSYLAMINES*

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ABSTRACT

The mass spectra of six *N*-acetylaldofuranosylamine acetates and propanoates were recorded. The spectra are more complicated than those of the corresponding pyranoid compounds. As in that case, the spectra are rich in long-lived fragments, in agreement with the stabilizing influence of the nitrogen atom on the positive charge. Several fragmentation series are similar to those of the aldopyranosylamine derivatives, and others agree better with those of the aldofuranose acetates, thus allowing identification of the furanoid ring.

INTRODUCTION

The electron-impact, mass spectra of some derivatives of furanoid sugars have been reported in the literature. Thus, among others, the fragmentation pathways of per-*O*-acetylated aldofuranoses[2,3], methylated aldofuranosides[4–7] and aldofuranoses[8], partially methylated xylofuranosides[9], methylated and acetylated aldofuranoses[10], acetates of alkyl and aryl hexofuranosides[11], and *O*-isopropylidene derivatives[12,13] and trimethylsilyl derivatives[14] of furanoses have been investigated.

Previously[1], we studied the mass spectra of *N*-acetyl- and *N*-propanoyl-hexo-, -6-deoxyhexo-, and -pento-pyranosylamine acetates and propanoates, and found that several of their fragmentation series are similar to those of the corresponding aldopyranose acetates, but that the influence of the nitrogen atom on C-1 produces branching of some of the series, and gives rise to new fragmentation-patterns characteristic of this structure.

We now report the mass spectra of *N*-acetyl-hexo- and -pento-furanosylamine acetates and propanoates. The spectra are more complicated than those previously studied[1], and provide a firm basis for distinguishing the furanoses. Several fragmentation-series are similar to those of the corresponding al-

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dopyranosylamine acetates and others agree better with those of the aldofuranose acetates.

RESULTS AND DISCUSSION

The mass-spectral data (*m/z* values and relative intensities of the more significant fragments) for *N*-acetyl-2,3,5,6-tetra-*O*-acetyl-α-D-glucosylamine (**1**); *N*-acetyl-2,3,5,6-tetra-*O*-acetyl-α-D-mannosylamine (**2**); *N*-acetyl-2,3,5,6-tetra-*O*-acetyl-β-D-mannosylamine (**3**); *N*-acetyl-2,3,5,6-tetra-*O*-propanoyl-α-D-glucosylamine (**4**); *N*-acetyl-2,3,5-tri-*O*-acetyl-α-D-xylosylamine (**5**); and *N*-acetyl-2,3,5-tri-*O*-propanoyl-α-D-xylosylamine (**6**) are given in Table I. The nomenclature embraced for the series is the same as that used for the acylated aldopyranosylamines[1]. Scheme 1 summarizes the primary fragments that give rise to the different pathways

The spectra of the derivatives of the aldofuranosylamines, as well of as those of the aldopyranosylamines, are more complicated, and richer in long-lived fragments, than those of the peracetylated aldoses[3]. This is in agreement with the stabilizing influence of the nitrogen atom on the positive charge[15,16]; the same effect was found in the spectrum of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-α-D-gluco-

TABLE I

PRINCIPAL FRAGMENT-IONS[a] OBSERVED IN THE MASS-SPECTRA OF THE ACYLATED ALDOFURANOSYLAMINES **1–6**

m/z	**1**	**2**	**3**	*Series*	**4**	*Series*	**5**	*Series*	**6**	*Series*
446					2	M + 1				
390	1	4	5	M + 1						
372					5	K				
371					1	H				
360									1	M + 1
331		2	2	A						
330		1	2	H,K						
329	1	2	2	H						
318							3	M + 1		
316			1	G′	2	G′				
315					1	H				
302					4	G′				
299					3	G′				
298					13	K				
297					4	H				
295					4					
288		2	4	H						
287		1	2	H						
286					2				1	
285					8	E′			3	H
284					7	E,G′				
281					6					
274	2	3	3	G′						
272		tr.	tr.		17	B			4	B,G′
271	2	2	2	A	1	H				
270	10	13	17	H,K	1					
269	2		7	H						
259		1	1	A			2	A		
257					3	A	4	H		
256					2	H				
255					2	H				
246		1	1		3					
245	2	2	3	K						
244	10	22	21	B			6	B,G′		
243	7	12	14	E′,H	4	G′				
242	5	10	10	E	5	G′				
241					12	H				
239					3	A,F				
238					18	H				
233	4	7								
232	2	2	2							
230			tr.	G			tr.	G		
229	2	2	2	A	4	A,H				
228	4	6	7	H	19	E,G′				
227	8	13	16	H	13	A				
226			tr.						4	H
225					6	G′				
224					48	K				
223					17	H				
221					10					

TABLE I *(continued)*

m/z	1	2	3	*Series*	4	*Series*	5	*Series*	6	*Series*
215	3	2	3	F,G′	1	A,H	2	H	4	A,H
214	2		3	G′	2					
213					2	B			3	B,G′
212		1	tr		4	H			24	H,K
211	4	4	4	A	4				16	H
210	30	33	34	H,K	22	E,G′				
209	9	13	19	H						
203	3	1	1				2			
202		4	4		1		2	G′		
201	3	4	6	A,H	3	F,H				
200	13	21	23	E	4	H	1		2	
199	4	5	6	A	18	G,H	7	A	13	G,E′
198					18	B	46	H,K	39	B,E,G′
197		2	5	G′						
196	17	17	45	G′						
188					4					
187			2	A	53	F,H,Ac [b]	3	A,H	8	H,Ac [b]
186	3	5	6	H	13	N			6	N
185	9	11	15	B,H	44	C,H	3	B,G′	23	C
184	10	8	8	B,H	4	G	5	B,H,G′	4	G
183	2			H	13	A				
182			2	F	52	H				
181					5	H				
173					20	L	2	H	2	
172	6	9	11	N	14	D,E,H	7	N	2	D
171	5	9	9	G	14	A	17	G,E′	5	A
170	4	6	5	G	8	C′	58	E,G	11	C′,H
169	10	9	9	A	8	F,G′			6	H
168	42	47	48	H	29	G′			4	
167	8	20	24	H	29	H				
164					5					
162	3									
160		2	2		2					
159		2	3						4	
158	8	12	16	E,H	7		4		2	
157	26	48	57	A,C	7	B,D′	34	A,C	4	B,D′,G′
156	6	5	7	C′	21	B,H	19	C′,H	17	B,H,G′
155	5	4	7	F,G′	32	A,E′,H	39	H	34	H
154	13	12	33	G′	54	E,G′,H	11		9	
153					10	A			7	A
150	7	8	8	H	7					
149					4				4	
147					9					
146	2	4	4				2			
145	30	52	56	K,L,Ac [b]			16	Ac [b]		
144	7	9	15	D	11	I,N	2	D	9	I,N
143	12	13	27	B,D′	14	G	8	B,D′,G′	16	A,G
142	56	61	58	B,H	79	B,G	52	B,H,G′	100	B,E,G,H
141	28	44	54	A,E′,H	6	A,H			18	A,H
140	26	36	38	E,H	7		2		3	
139	8	12	16	A,H	4		12	A	6	
138	3	3	3		5		47	K	44	K
137		2	2	G′					3	

TABLE I *(continued)*

m/z	1	2	3	*Series*	4	*Series*	5	*Series*	6	*Series*
131	4				35	Ac.[b]	3		15	Ac.[b]
130	17	25	33	I,N	15	N	21	I,N	10	N
129	7	13	13	G	40	B,C	17	A,G	30	B,C
128	21	35	31	G	3	C′,G,H	100	E,G,H	4	C′,G,H
127	11	17	17	A	14	H	12	A,H	4	H
126	29	30	33	H	96	E,H	4		6	
125	13	13	14	H	18		3		6	
124	42	35	33	B	65	B	29	B	36	B,E
119	5									
117	5	4	5		6		3		3	
116		9	12		10	D	4		5	D
115	39	52	65	B,C	6	D′	34	B,C	5	D′
114	28	28	30	B,C′,H	27	B,C′	31	B,C′,H	29	B,C′,E
113	29	23	23	F,G′,H	36	F,G′,H	34	F,H	40	F,H
112	93	100	97	E,G′,N	38	G′,N	23	N	21	N
111	2	3	3		3				4	
110	2	2	2		2		3	E	3	
109	10	8	10	A	10	A	2		3	
108	10	7	8	H	8					
104	2	3	4				4			
103	50	65	65	K,L,Ac.[b]			31	Ac.[b]		
102	18	19	33	D	10	I	10	D	6	I
101	18	19	54	D′	12	D′	13	D′	8	D′
100	87	79	75	H	50	H	97	E,H	46	H
99	24	30	39	A,H	13	A,H,L	25	H	5	H
98	87	97	95	E,H	86	D,E,H	3		5	D
97	44	56	55	A,C	43	A	16	A	22	A
96	10	7	8	C′	10		50	H	47	H
95	4	2	2	F,G′	4	F,G′	5	F	10	F
94									53	
89	3	3	3				3			
88	53	64	70	I,N	20	I,N	59	I,N	16	I,N
87	5	5	5	G	3	G	4	G	3	G
86	34	42	37	G	15	G	51	E,G	22	E,G
85	45	33	32	A,L	17	A	48	A	26	A
84	33	31	34	D	22	I	20	D	14	I
83	8	5	7	B,D′	6	B,D′	6	B,D′	7	B,D′
82	14	13	15	B	12	B	12	B	6	B
81	100	98	100	A,E′	100	A,E′	2		4	
80	8	7	9		8		2			
79					4		25			
75					5				5	
74	3	2	2		4		2		4	
73	23	25	25	C	20	C	14	C	6	C
72	38	37	36	C′,H	18	C′,H	34	C′,H	17	C′,H
71	30	20	19	F,H	31	F,H	22	F,H	29	F,H
70	68	74	73	I	10	I	13	I	8	I
69	88	83	77	A	62	A	84	A,E′	54	A,E′
68	5	5	4				51	E	36	E
60	48	46	49	D	23	D	42	D	17	D
59	21	19	25	D′	10	D′	13	D′	7	D′
57					base[c]				base[d]	
43	base	base	base				base			

[a]For *m/z* values lower than 200, only fragments with intensities higher than 2% are considered; the second-most intense peak equals 100. [b]Ac. = acyloxonium ions. [c]Ratio 43/57 = 1:25. [d]Ratio 43/57 = 1:11.

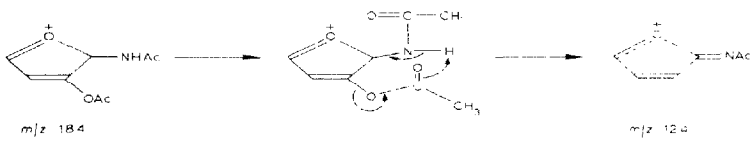
pyranose[17]. As in the case of other furanose-pyranose pairs of derivatives, the spectra of the peracetylated aldofuranosylamines are similar to, but more complicated than, those of the corresponding peracetylated aldopyranosylamines[1], and allow the identification of the furanoid ring.

Series C', D, D', E', G, I, and K are similar to those previously mentioned for the aldopyranosylamine derivatives[1] and will not be discussed further. Series B and H are also similar, but the peaks have an increased intensity, because the fission of the side chain, or the elimination reactions from the five-membered ring, lead to a planar ion[18], thermodynamically favored over the analogous ion having a six-membered ring. The importance of series B is also determined by stabilization of the two-carbon radical eliminated, as evidenced by the differences in intensities found in the spectra of hexo- and pento-furanosylamine acetates. The elimination of neutral molecules (Series H) gives rise to some peaks of high intensity, this being a characteristic feature of the spectra. This series has also been detected for acetyl[3] and other derivatives of sugars[8].

The decomposition of the molecular ion with formation of the glycosyl cation (Series A) also produces a planar ion, but its stability is lowered by the loss of the acetamido group.

It must be pointed out for peracetylated hexofuranosylamines that, besides the elimination of acetic acid or ketene from the furan ring, two molecules of acetic acid may be lost from the side chain, giving rise to an acetylenic bond.

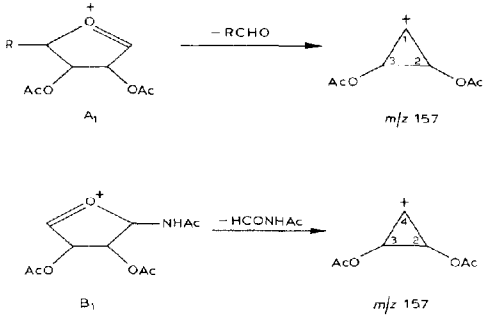
It is worth noting that fragment *m/z* 124, not shifted in the propanoylated compounds **4** and **6**, is derived from series B; the reaction may be represented as a process involving a seven-membered ring, as depicted in Scheme 2, with formation of a highly stabilized, planar ring.



Scheme 2

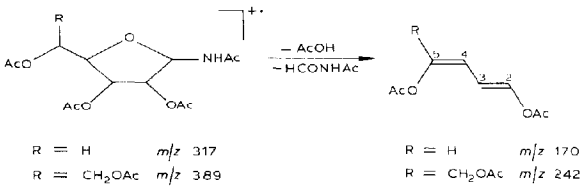
Series C cannot be produced from the allylic fragment *m/z* 157, which comprises carbon atoms 2, 3, and 4, as predicted by Biemann *et al.*[3]. However, a cyclopropyl ion structure[4] formed from A_1 or B_1, or both, may be ascribed to this fragment (see Scheme 3); further decomposition takes place through elimination of acetic acid and ketene.

The loss of a molecule of acetic acid from the molecular ion produces a dehydro fragment which, in the pyranoid derivatives, is stabilized through two competitive pathways, namely, further elimination of neutral molecules, giving rise to series H, or shedding of *N*-formylacetamide and rearrangement by a retro-Diels-



Scheme 3

Alder reaction to produce series E. The latter reaction is not possible for a five-membered ring, and, in this case, the dehydrofuranose fragment leads to series H, or expels *N*-formylacetamide to furnish a linear, highly conjugated fragment E_1, of high intensity, mainly for acylated pentofuranosylamines (see Scheme 4). The mass shift of the peak *m/z* 170 in the spectrum of **5** to *m/z* 198 in the spectrum of **6** confirms the structure of E_1. This fragmentation pathway had already been predicted for alkyl and aryl hexofuranoside acetates[11], but was not detected for hexofuranose peracetates[3].

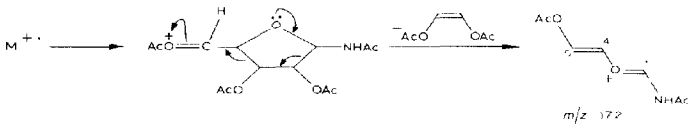


Scheme 4

Series F, as depicted for aldopyranosylamine acetates[1], cannot be produced from the corresponding furanoid derivatives but a formally similar, three-atom radical-ion may be postulated (see Scheme 1). As in the former instance, this series is of little importance, in agreement with the low stability of F_1.

Another series (L) found for the hexofuranosylamine derivatives, which was also found in the spectra of hexofuranose acetates[3], is formed by fission of the side chain with retention of the positive charge at C-5. The corresponding fragments *m/z* 145 and 103 can be differentiated from the acetoxonium ions by the shift in the spectrum of the propanoylated derivative **4**.

Series N begins with the loss of $\cdot CH_2OAc$ or H$\cdot$, followed by rearrangement of the ring to produce a nitrogen-containing, highly conjugated, linear cation, *m/z* 172, formally similar to that postulated for the decomposition of methyl tetra-*O*-methyl-D-glucofuranoside[7] (see Scheme 5). The fragment *m/z* 172 appears with higher intensity in the spectrum of hexofuranosylamine derivatives; this is in agreement with the greater stability of the radical expelled.



Scheme 5

EXPERIMENTAL

The compounds were obtained as reported elsewhere[19]. Mass spectra were recorded with a Varian MAT CH7 mass spectrometer at an ionizing energy of 70 eV, and a filament current of 1 μA; the inlet temperature was selected in each case, being varied between 100 and 230°. Compound **4** had m.p. 74–75°.

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