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INFLUENCE OF BENZOYLATION ON THE MASS SPECTRA OF ACYLATED ALDOSYLAMINES*

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ABSTRACT

The mass spectra of three perbenzoylated aldopyranosylamines, five *O*-acetyl-*N*-benzoylaldopyranosylamines, and two *N*-acetyl-*O*-benzoylaldofuranosylamines were recorded. The spectra are similar to, but less complex than, those of the corresponding acetates, and the presence of the benzoyl group increases the stability of high-molecular-weight fragments.

INTRODUCTION

The mass spectra of several derivatives of carbohydrates are recorded in the literature, but benzoylated sugars have not been so extensively studied[2,3]. Recently, D'Accorso and Thiel[4] reported the mass spectra of per-*O*-benzoylated aldopyranoses and aldofuranoses.

Previously, we have studied the fragmentation pathways of aldopyranosyl-[5] and aldofuranosyl-amine[1] acetates and propanoates, and we now report the electron-impact mass spectra of perbenzoyl-, *O*-acetyl-*N*-benzoyl, and *N*-acetyl-*O*-benzoyl derivatives of aldopyranosyl- and aldofuranosyl-amines. The fragmentation pathways have been compared with those of acetylated aldosylamines, emphasizing the influence of the benzoyl group on the decomposition mechanisms.

RESULTS AND DISCUSSION

The mass-spectral data (*m/z* values and relative intensities of the more significant fragments) for *N*-benzoyltetra-*O*-benzoyl-β-D-glucopyranosylamine (**1**), *N*-benzoyltetra-*O*-benzoyl-α-D-galactopyranosylamine (**2**), *N*-benzoyltri-*O*-benzoyl-β-D-xylopyranosylamine (**3**), *N*-benzoyltetra-*O*-acetyl-β-D-glucopyranosylamine (**4**), *N*-benzoyltetra-*O*-acetyl-β-D-mannopyranosylamine (**5**), *N*-benzoyltri-*O*-acetyl-β-D-xylopyranosylamine (**6**), *N*-benzoyltri-*O*-acetyl-α-L-arabinopyranosyl-

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TABLE I

PRINCIPAL FRAGMENT-IONS[a] OBSERVED IN THE MASS SPECTRA OF THE *N*-BENZOYLALDOPYRANOSYLAMINE BENZOATES AND ACETATES **1–8**

m/z	**1**	**2**	*Series*	**3**	*Series*	**4**	**5**	*Series*	**6**	**7**	*Series*	**8**	*Series*
577		6	H										
456	12	17	H,K										
455	30	30	H										
335		6	A										
334	19	24	H,K										
333	42	54	H										
332						9	8	K					
331						21	16	A,H					
322				27	H,K,is[b]								
321	22	21	is[b]	100	H								
320	100	100	B										
319										10			
295				6	E′,G								
294				10	E,G								
282		6											
281		5	C										
274												15	K
273												65	A,H
272						9	9	K					
271						15	15	A,H					
260									22	30	K		
259						13	13	A	96	59	A,H		
258						78	83	B				6	B
243						5		E′					
232												6	G
231												30	A,H
230		5	H			5	10	K					
229		7	H			13	15	A,H					
228	5	14											
218									9	7	C′		
217						6	8		30	15	H		
216				5	B	38	50	B	5		B,H		
214												9	K
212	6	11											
205						5	7	D′,F				13	D′,F
203		6	A,E′										
202	6	9	E,H										
201	13	19	A,H						10				
200		6		8	K	6	6	E		11	K		
192						6	8	I	5	6	G′,I	19	I
185												13	E′
184												9	E
177		5	C										
176						5	5	C′				7	C′
174		6								6	G′		
173		10											
171									14	21	E′,G		
170									22	21	E		
169						8		A					
164						6	7					10	

TABLE I *(continued)*

m/z	**1**	**2**	*Series*	**3**	*Series*	**4**	**5**	*Series*	**6**	**7**	*Series*	**8**	*Series*
163						18	31	D′	9	7	D′	66	D′
158						6	6	H					
157						15	17	A,C	16	12	A,C	38	C
151						6	6		7	8		9	
150						53	62	I	88	91	I	100	I
144						6	6	D				9	D
143												8	A
142						5						20	E,H
141						36	37	A,E′					
140						10	10	E,H					
139						12	10	A					
129									14	15	A,G		
128									50	40	E		
127									9	5	B		
126						5	6	B,H					
123		10							11				
116						6	6	H					
115						25	24	A,C	20	16	A,C	24	C
112						17	17	B	5		B		
109						9	6	A					
107	5	6											
104		5				5			5				
102						17	18	D	10	8	D	24	D
100									5			17	H
99						20	20	A				13	
98						33	32	E,H					
97	7	9	A			17	15	A					
86									17	14	H		
85	7		B						24	15	B		
84												7	B,D
83	11											60	A,E′
82						8	8					10	E,H
81	25	29	A,E′			100	100	A,E′					
75		6											
74		7											
73						6	6	C					
71												18	
70						16	15	I	7	6	I	5	I
69		8	A	11	A,E′	7	16	A	100	100	A,E′	9	
68				13	E				26	23	E,H		
60						11	6	D					

[a]Only fragments having intensities >5% are considered; the fragments derived from the aromatic nucleus, and acylium and oxonium cations have been excluded; the following, most-intense peak equals 100. [b]is = isotopic contribution.

amine (**7**), and *N*-benzoyltri-*O*-acetyl-α-L-rhamnopyranosylamine (**8**) are given in Table I.

The mass-spectral data for *N*-acetyltetra-*O*-benzoyl-α-D-glucofuranosylamine (**9**) and *N*-acetyltri-*O*-benzoyl-α-D-xylofuranosylamine (**10**) are given in Table II.

As expected, the molecular ions failed to appear, and the (M + 1) ions were

TABLE II

PRINCIPAL FRAGMENT-IONS[a] OBSERVED IN THE MASS SPECTRA OF THE *N*-ACETYLALDOFURANOSYLAMINE BENZOATES **9** AND **10**

m/z	**9**	*Series*	**10**	*Series*	*m/z*	**9**	*Series*	**10**	*Series*
516	14	is[b]			204	13	B		
515	41	H			203	17	A,E′,H		
429	17	E			202	40	E,H		
428	14	E			201	29	A	5	A
410	5				190			23	E,G,H
394	18	K			188	9			
393	11	H			177	5	C		
381			18	H	175	6	F,H		
369	5				174	32	E		
368	21	B			167	14	H		
351	7	H			166	8			
335	15	A,is[b]			164	5			
334	68	H			161			5	
333	7				156			15	
324	20	E			155			12	H
323	25	A			154	5	G′		
320	9				150	8	I,K		
306	7	E			146	5	D		
295	7	G	18	E′,G	139	12	H		
294	6		48	E	138	6		53	K
289	10	H			126	5	H		
288	6				125	14	H		
282	8				124	83	B	33	B
281	20	C	10	C	123	11			
276			5		113	8	F,H	5	F,H
273	11	is[b]			112	31	N	18	N
272	66	K			108	10			
271	100	H			107	22		10	
269	24	L			104	18		8	
260			37	K	98	5	E,H		
259	11	is[b]	100	H	97	43	A		
258	66	G′			96	13	C′	40	C′,H
246	22	B	6	B,G′	95			8	F
234	6	N			85	6			
231	6	A			84	16		7	
230	29	H,K			83	6	D′		
229	15	H			82	10	B		
228	5				81	81	E′		
227	9				75	7			
219	13	A			74	8			
218	6	C′			71	7	H	5	H
217			10	F,H	70	5	I		
216	15	G′	10		69	5		25	E′
205	5	D′			68	6		51	E

[a]Only fragments having intensities >5% are considered; the fragments derived from the aromatic nucleus, and acylium and oxonium cations have been excluded; the following most intense peak equals 100.
[b]is = isotopic contribution.

detected for compounds **6, 7,** and **10** in only 1% intensity. In all of the spectra, the base peak corresponds to the cation $C_6H_5CO^+$, and the fact that it is also present in the spectra of compounds **4–8**, where the ratio of acetyl to benzoyl groups is 4:1 and 3:1, respectively, shows that, owing to its higher stability, participation of the benzoyl group in the formation of the acylium ion is favored.

Fragments *m/z* 122, 106, 78, 77, 76, and 51 are of high intensity, and originate from decomposition of the benzoyl group; these fragments, together with those of *m/z* 145, 103, 43, and 331 (oxonium cations), have been omitted from Tables I and II.

All of the compounds follow the fragmentation pathways of the corresponding peracetates, but the presence of the benzoyl groups promotes some series, and determines the general patterns of the spectra. In the decomposition of the aldosylamine peracetates[1,5], the fragments are produced mainly by elimination of neutral molecules, namely, acetic acid, ketene, or acetamide. Decomposition of benzoylated derivatives cannot take place by elimination of a ketene equivalent, and is only achieved through loss of benzoic acid molecules or benzamido radicals from the molecular ion or the primary fragments. This restriction in the fragmentation possibilities results in the production of less-complex spectra, and increases the stability of the high-molecular-weight fragments. Because the benzamido has a higher stability than the acetamido radical, series A (refs. 1 and 5) is increased for *N*-benzoylaldosylamines.

(a) *Aldopyranosylamine derivatives.* — The number of high-intensity peaks (≥10%) in a spectrum decreases as the degree of benzoylation of the molecule increases. Thus, 43 and 24 of those peaks are formed in the spectra of peracetylated gluco- and xylo-pyranosylamine, respectively[5], whereas 21 and 17 are produced by **4** and **6**, and only 8 and 5 for the perbenzoylated compounds **1** and **3**.

Another consequence of the benzoyl substitution is that series H (ref. 5) becomes predominant, and its importance parallels the degree of benzoylation, possibly by virtue of the stabilization of the radical-ions formed. Thus, the base peak for the peracetylhexopyranosylamines is found at *m/z* 81 (series A and E'); in the spectrum of *N*-benzoyltetra-*O*-acetyl-β-D-glucopyranosylamine (**4**), the base peak is also *m/z* 81, but peaks at *m/z* 331 and 271 become slightly higher than the corresponding peaks (*m/z* 269 and 209) in the spectrum of pentaacetylglucopyranosylamine[5]. For the perbenzoylated derivatives **1, 2,** and **3**, this trend is more significant. It is noteworthy that, for the latter compounds, fragment *m/z* 81, which involves the loss of benzoic anhydride, is of lower intensity.

A very important peak in the spectrum of the acetates of aldopyranosylamines[5] is formed by elimination of two molecules of acetic acid from B_1 (*m/z* 196). The intensity of the corresponding peak ($B_1 - 2\ PhCO_2H$) (*m/z* 320) is much higher for **1** and **2**, and this must be due to the fact that no subsequent elimination of ketene may take place.

Series J and K (ref. 5), which would be originated from the molecular ion by elimination of an acetate or benzoate radical from C-4, are favored when the latter is expelled, owing to its higher stability.

For compound **8**, the base peak is at *m/z* 150 (Series I)[5]; this peak is also important in the spectra of **4, 5, 6,** and **7**, and can be explained by taking into account the stability of the ion HCO-N^+H_2-COPh, produced by the loss of ketene from the primary fragment of series I (AcO-CH=N^+HCOPh). The corresponding fragment for the perbenzoylated derivatives **1, 2,** and **3** is not produced; nor is the cation (*m/z* 132), formed by the loss of a molecule of benzoic acid from it, detected.

(b) *Aldofuranosylamine derivatives.* — The fragmentation patterns are more complex than those of the aldopyranosylamine derivatives and, in this sense, are similar to that of the aldofuranosylamine acetates[1]. The most intense peaks in the spectra of hexofuranosylamine acetates are *m/z* 81 (series A and E′) and *m/z* 112 (series E, G′, and N).

In the spectrum of *N*-acetyltetra-*O*-benzoyl-α-D-glucofuranosylamine (**9**), fragment *m/z* 81 (series E′) still appears with high intensity, but the intensity of fragment *m/z* 112, which would originate from the low-intensity peak at *m/z* 234 (Series N)[1] by elimination of benzoic acid, is only 31% (see Table II).

Fragment *m/z* 209 (Series H)[1] of low intensity for the acetylated derivative, is shifted to *m/z* 271 for the *N*-acetyltetra-*O*-benzoyl derivative **9**, and becomes the base peak of the spectrum. The fragment *m/z* 271 is formed by elimination of three molecules of benzoic acid from the molecular ion (Series H); elimination of two molecules of benzoic acid and one of acetamide produces *m/z* 334, which is also very intense.

The formation of an acetylenic bond in the side chain of the secondary fragment *m/z* 196 (Series G′) of hexofuranosylamine acetates, shifted to *m/z* 258 for compound **9**, is precluded for the corresponding pentose derivatives.

Series K (refs. 1 and 5) produces only a few, but intense, peaks, and this may be explained by the stability of the benzoate radical expelled in the first step, and the subsequent loss of benzoic acid molecules to form a double bond conjugated with the positive charge.

In the spectrum of *N*-acetyltri-*O*-acetyl-α-D-xylofuranosylamine[1], the base peak is at *m/z* 128 (series E, G, and H); for the *N*-acetyltri-*O*-benzoyl derivative **10**, this peak is shifted to *m/z* 190, and its intensity is only 23%. The base peak is at *m/z* 259, and is formed by elimination of two molecules of benzoic acid from the molecular ion (Series H).

It is noteworthy that fragment E_1, reported for aldofuranosylamine acetates[1], is not actually a primary fragment. This may be inferred from the spectra of *N*-acetyl-hexo- and -pento-furanosylamine benzoates: fragments *m/z* 324 and *m/z* 190 must be respectively due to the elimination of benzoic anhydride from fragments *m/z* 550 and *m/z* 416; that is, the latter are derived from the molecular ion by elimination of *N*-formylacetamide in a first step.

EXPERIMENTAL

The compounds studied were prepared as reported[6,7]. Mass spectra were re-

corded 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 200 and 260°.

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