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THE MASS SPECTRA OF ACETYLATED AND PROPANOYLATED ALDOPYRANOSYLAMINES*

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ABSTRACT

The mass spectra of six acetylated glycopyranosylamine compounds were recorded. As expected of such highly substituted molecules, the spectra are complex. The molecular ion failed to appear, but the (M + 1) ion was found, even if only in traces. Several fragmentation series have been detected: some are similar to those of glycopyranose acetates, but the presence of an acetamido group on C-1 increases the number of fragmentation pathways, branching off from those found in the decomposition of acylated glycopyranoses that carry a 1-acetoxyl group. Furthermore, other series are characteristic of this type of structure. All of the results are supported by the shifting of peaks in the spectra of three acylated derivatives having *O*- or *N*-propanoyl groups, or both.

INTRODUCTION

The mass spectra of several derivatives of cyclic and acyclic carbohydrates are recorded in the literature. Derivatives of acyclic sugars revealed simple, fragmentation patterns, but more-complex degradative pathways were found for the cyclic compounds. Thus, among others, the mass spectra and the fragmentation pathways of per-*O*-acetylaldoses[1–4], per-*O*-acetylated 2-acetamido-2-deoxyglucopyranoses[3,5,6], and the corresponding *N*-acylglucopyranosylamines[7,8], per-*O*-acetylated *N*-arylglycosylamine derivatives of oligosaccharides[9], acetylated glycosylamines containing the indole nucleus[10], methylated *N*-acetylglycosylamines[11], and methylated and acetylated 2-amino-2-deoxyglucopyranoses[6,11] have been investigated.

We now report the electron-impact mass spectra of *N*-acetyl- and *N*-propanoyl-hexo-, -6-deoxyhexo-, and -pento-pyranosylamine acetates or propanoates.

*Mass Spectra of Acylated Glycosylamines, Part I.
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TABLE I

PRINCIPAL FRAGMENT-IONS[a] OBSERVED IN THE MASS SPECTRA OF THE ACYLATED HEXOPYRANOSYLAMINES

m/z	1	2	3	*Series*[b]	4	*Series*[b]	5	*Series*[b]	m/z	1	2	3	*Series*[b]	4	*Series*[b]	5	*Series*[b]
404					2	M + 1			171	4	4	2	G	3	G	9	A,D′
390	tr.			M + 1					170					3	C′		
387							1	A	169	17	9	4	A	13	A		
343					1	H			168	22	20	12	H	41	B,H	34	B
331	tr.			A	2	A			167	15	15	11	H				
330		5		H,J	1	B,H	2	H	159	4	5		A	2	A		
329		3		H			1	H	158	18	9	6	H	8	H	6	I
316	1	3	1	B					157	61	30	31	A,C	32	A,C,D′,F	3	F
312							4	H,K	156	6	6	4	C′	3	J	5	J
311							7	H	155	9	6	5	B			21	A,E′
302					3	E′			154	30	32	35	B			7	E,H
301					2	F,H			153							8	A,H
288	3	9	2	H	6	H			145	36	84	24	Ac-[c]	20	Ac-[c]		
287	2	5	1	F,H					144	17	23	17	D	20	D,I		
285							4	E′	143	26	33	34	D′,F			2	G
284					8	K			142	9	30	8	J	7	G,J	3	G
283					18	H			141	40	88	33	A,E′	41	A,E′		
272							1	G	140	35	15	12	F,H	13	B,F,H	3	B
271	1	2	tr.	A					139	16	18	10	A,H	12	A,F		
270	5	12	4	H,K					131							9	Ac-[c]
269	7	9	7	H					130	17	29	27	B,I	4	B	5	B
259	2	1	tr.	A	1	A,F			129	7	8	6	G	5	G	25	C
256		1		B			4	H	128	6	6	4	G	10	C′,G	7	C′
255							2	H	127	14	10	6	A,B	7	A,B	5	A
245	1	1	1	F	1	F			126	24	20	19	B,H	12	H	22	H
244	2	6	2	J	2	G			125	8	10	6	F,H	4	F,H		

243	7	14	5	E′	9	E′			116	16	12	11		14		11	D
242	13	3	2	E	6	E			115	92	53	50	A,C	63	A,C,D′	18	A,D′
241					4	F,H			114	17	20	18	C′	3	C′		
238							5	H,K	112	34	45	45	B	30	B	6	B
237							6	H	109	21	15	10	A	12	A	11	A
230		tr.		G					103	56	38	41	Ac·[c]	27	Ac·[c]		
229	3	2	1	A	1	A	1	A	102	38	53	59	D	61	D,I	6	I
228	7	8	3	H	4	B,H	2	E	101	38	68	90	D′	4	D′		
227	5	11	4	F,H	1	F	2	A	100	12	21	24	J	14	J	10	J
224					5	H,K	35	B	99	37	51	39	A	28	A	8	A
223					14	H			98	87	59	60	E,H	43	E,H	31	D,E,H
214	2	5	1	B					97	37	25	27	A,H	20	A,D′,H	19	A,D′,H
213							2	F	88	37	96	58	I	10	I	3	
211	4	2	1	A	9	A			87	3	3	3	G				
210	10	11	5	H,K	71	B,H			86	11	9	11	G	6	G	3	G
209	12	11	10	H					85	23	17	18	B	8	B	4	B
201	5	6	3	A	5	A			84	16	22	34	B,D	10	B,D,I	9	B,I
200	22	7	5	E	7	B,E	3	H	83	13	3	11	D′				
199	10	3		A	6	A,F,H	4	G,H	82	11	12	14	J	9	J	8	J
196	51	51	46	B					81	100	100	100	A,E′	100	A,E′	100	A,E′
187	4	2		A			12	Ac·[c]	74							16	
186	4	4	2	B,H	4	H			73	26	12	21	C	9	C	2	C
185	7	10	7	F,H	2	F	15	C	72	12	18	27	C′	15	C′	10	C′
184							2	C′	70	28	26	50	I	22	I		
183							9	A	69	35	25	47	A	22	A	10	A
182	6	2			6		14	H	60	36	36	41	D	9	D	3	D
181					10	H	13	H	59	13	25	32	D′	14	D′	9	D′
173							4	A	57					[d]		base	
172	4	12	6	B			8	D,H	43	base	base	base		base[d]			

[a]For *m/z* values lower than 200, only fragments having intensities higher than 2% are considered; the second-most intense peak equals 100. [b]See text for explanation. [c]Ac· = acyloxonium ions. [d]Ratio 43/57 = 1:18.

TABLE II

PRINCIPAL FRAGMENT-IONS[a] OBSERVED IN THE MASS SPECTRA OF THE ACYLATED PENTOPYRANOSYLAMINES **6–8** AND THE 6-DEOXYHEXOPYRANOSYLAMINE **9**

m/z	6	7	Series[b]	8	Series[b]	9	Series[b]	m/z	6	7	Series[b]	8	Series[b]	9	Series[b]
360				1	M + 1			141				21	B		
332						1	M + 1	140						8	
318	tr	3	M + 1					139	2	2	A				
287						1	F	138	8	6	K	15	K		
285				1	H			131				22	Ac-[c]		
258		1	H					130	11	10	G',I	8	G'	31	I
245				2		1	F	129	14	14	A,G	43	C	2	A,G
244				3	H	2	J	128	48	51	E,G	2	C',G	2	G
243				1				127	8	9	B,H	3	G',H	4	B,G'
238	1							126	4	3	B	5	B	11	B,G'
237	1							125				4	F	4	E',F
229				2	H	1	H	116				9	D	2	
228				2	B	1		115	25	24	A,C	4	A,D'	29	C
227				2	A	3	F	114	8	10	C'	28	C'	15	C'
216	2	3	H					113	8	11	B,G'	34	B	21	B
215	2	1	B,H	3				112	8	6	B,G'	10	B,G'	3	B
214	2	1	B					111	3			2		3	A
213				3	F			110						7	H
212				15	K	5	H,K	103	22	18	Ac-[c]			14	Ac-[c]
211				72	H	24	H	102	13	17	D	6	I	41	D,G'

200				3	B	3		101	11	13	D′	11	D′	100	A,D′
199		2	A	13	E′,F,G			100	7	10	J	8	J	26	J
198	11	11	H,K	34	E			99	6			3		9	
197	26	52	B,H	2				98				3	D	2	
196						2	B	97	6	7	A	16	A		
187				6	Ac·[c]			96	9	14	H	25	H	7	
186				9	G′	3	B,G′	88	41	44	G′,I	14	G′	34	I
185				24	C	16	E′,F	87	7	6	A,G	4	A,G	3	G
184				3	G	9	E	86	20	22	G	12	G		
172	7	15	G′	3	D			85	25	31	B	32	B	3	B,G′
171	16	15	E′,G	6	A			84	5	8	B,D	10	B,I	16	B,D,G′
170	23	31	E,G	10	C′,H	2	G,H	83	2	2	D′	6	D′	46	A,D′,E′
169				5		12	H	82	2		J	2	J	8	E,H,J
158						4		73	7	7	C	4	C	7	C
157	16	19	A,C	4	D′	48	C	72	6	9	C′	7	C′	10	C′
156	8	9	C′,H	14		4	C′	71	4	4	G′	17	G′	23	
155	23	27	B,H	62	H			70	7	8	G′,I	8	G′,I	3	I
154	2		B	3	B	2	B	69	100	100	A,E′	100	A,E′		
153				3	A			68	24	33	E,H	33	E,H		
152						3	K	60	14	18	D	14	D	14	D
145	4	5	Ac·[c]			6	Ac·[c]	59	9	15	D′	10	D′	22	D′
144	2	2	D	7	B,G′,I	15	D,G′	57				base[d]			
143	2	3	D′	14	A,G	40	A,D′,F								
142				82	E,G	16	E,J	43	base	base			[d]	base	

[a]For *m/z* values lower than 200, only fragments having intensities higher than 2% are considered; the second-most intense peak equals 100. [b]See text for explanation. [c]Ac· = acyloxonium ions. [d]Ratio 43/57 = 1:18.

Several fragmentation series are similar to those of the corresponding glycopyranose acetates, but the influence of the nitrogen atom on C-1 produces branching of some members of the series, and gives rise to new fragmentation-patterns characteristic of this structure.

RESULTS AND DISCUSSION

The mass-spectral data (*m/z* values and relative intensities of the more-significant fragments) for *N*-acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-glucosylamine (**1**), *N*-acetyl-2,3,4,6-tetra-*O*-acetyl-α-D-galactosylamine (**2**), *N*-acetyl-2,3,4,6-tetra-*O*-acetyl-β-D-mannosylamine (**3**), 2,3,4,6-tetra-*O*-acetyl-*N*-propanoyl-β-D-glucosylamine (**4**), and *N*-propanoyl-2,3,4,6-tetra-*O*-propanoyl-β-D-glucosylamine (**5**) are given in Table I.

The mass-spectral data for *N*-acetyl-2,3,4-tri-*O*-acetyl-α-L-arabinosylamine (**6**), *N*-acetyl-2,3,4-tri-*O*-acetyl-β-D-xylosylamine (**7**), *N*-acetyl-2,3,4-tri-*O*-propanoyl-β-D-xylosylamine (**8**), and *N*-acetyl-2,3,4-tri-*O*-acetyl-β-L-rhamnosylamine (**9**) are given in Table II.

As expected of such highly substituted molecules, the spectra are very complex, and the molecular ion failed to appear in the collector, but the (M + 1) ion was detected for compounds **1**, **4**, and **6–9**. This behavior, common for amides, is caused by protonation of the nitrogen atom. Like other sugar acetates, epimers exhibit similar spectra, and the more-intense peak is found at *m/z* 43 (CH_3CO^+). Similarly, for the *O*-propanoylated derivatives, the most intense peak in the spectra corresponds to the propanoylium ion ($CH_3CH_2CO^+$, *m/z* 57). The spectrum of tetra-*O*-acetyl-*N*-propanoyl-β-D-glucopyranosylamine (**4**) showed that the intensity ratio of the acetylium–propionylium ions was 2:1, whereas for *N*-acetyltri-*O*-propanoyl-β-D-xylopyranosylamine (**8**), the propanoylium–acetylium ratio was 18:1; these results suggest that the propanoyl group participates preferentially in the formation of the acylium ion, independent of its function as amide or ester, possibly due to its higher stability.

The only peaks observable in the higher-mass range of the spectra of acetates of hexo-, 2-acetamido-2-deoxyhexo-, 6-deoxyhexo-, and pento-pyranoses are due to the loss of substituents, and a few high-intensity peaks are found all over the spectra[2,3,12]. The presence of an acylamido group on C-1 provides pathways for the formation of longer-lived ions, and then substantial proportions of high-intensity peaks appear in the spectra of acetates or propanoates of glycopyranosylamines.

It is noteworthy that the fragment (M − COR), formed by loss of the acyl group on C-1, is present in the spectra of acetates of glycopyranoses and of the 2-acetamido-2-deoxy derivatives[2–5], but not in those of acetates and propanoates of glycopyranosylamines; this can be rationalized by taking into account the partial double-bond character of the C–N linkage in amides.

The presence of an acetamido group on C-1 also increases the number of fragmentation pathways, branching off from those found in the decomposition of

acylated glycopyranoses that carry a 1-acetoxyl group. Furthermore, new pathways characteristic of the *N*-acylglycosylamine structure appear.

The mass spectra of the peracetylated and perpropanoylated derivatives of glucopyranosylamine are similar, with the peaks displaced by 14 mass units per acyl group in the spectrum of **5** with respect to the spectrum of **1**, showing that the additional methylene group does not alter the fragmentation pathways. Further discussion will concern only the acetylated derivatives, on the basis that the propanoylated ones have similar spectral patterns, and that the justification for the peaks in the first spectra is supported by the corresponding shift in the latter. The advantage of the use of propanoylated instead of deuterioacetylated derivatives to support the assignments of the peaks is that the first produce larger shifts, and that possible scrambling of the deuterium atoms is avoided.

It is known that the abundance of the various fragment-ions resulting from electron impact upon sugar derivatives may exhibit considerable variation according to the operational conditions of the mass spectrometer. A spectrum of penta-*O*-acetyl-β-D-glucopyranose recorded under the same conditions as those of the glycopyranosylamine derivatives showed a pattern similar to those previously reported[2,12]. Consequently, the spectra of the acylated glycosylamines may be compared with other published spectra.

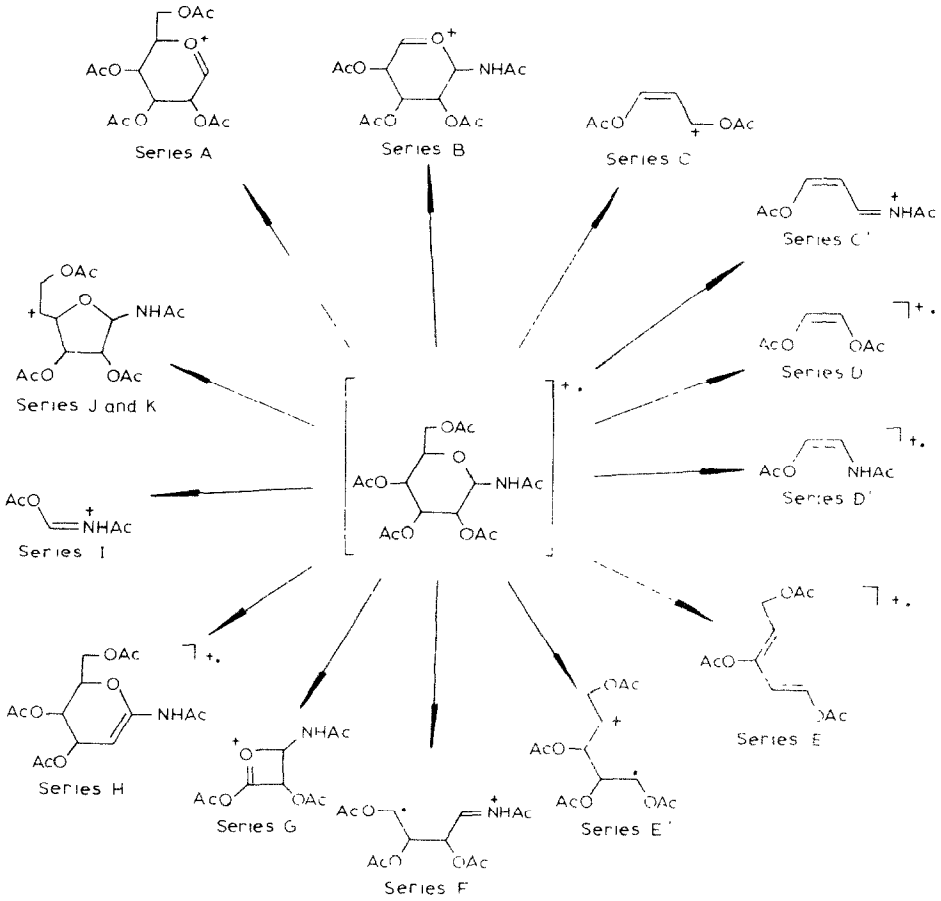
Several fragmentation-pathways were recognized; the individual peaks wereproduced by elimination of neutral molecules, mainly acetic acid, ketene, carbon monoxide, or acetamide. Occasionally, such other molecules as hydrocyanic acid or water were expelled, and, in a few cases, AcNHCHO or $AcOCH_2CHO$ were lost.

Some fragmentations are also found in the decomposition of glycopyranose and 2-acetamido-2-deoxyglycopyranose acetates[2,3,5,12], but other series are characteristic of the glycopyranosylamine acetates. Scheme 1 summarizes the primary fragments that give origin to the different series.

(1) Acylated hexopyranosylamines. — The spectral data for compounds **1–5** are given in Table I.

Series A should begin with the fragment A_1, formed from the molecular ion by loss of an acetamido radical. Fragment A_1, *m/z* 331, is only observed in traces in one spectrum (**1**), but the series contained all of the other ions proposed by Magnin and Stephen[10] for the spectra of indole-substituted glycopyranosylamines. Two reasons could explain the trace of A_1, namely, (*a*) loss of the substituent at C-1 producing A_1 diminishes[2], in the sequence phenoxy, methoxy, acetoxy, and hydroxy, according to the stabilization of the radical produced, and it could be expected that the elimination of the acetamido radical would be lower than that of the acetoxy radical, and this is in agreement with the lesser contribution of this series to the net ion-current; (*b*) the base peaks are much more intense than the peak *m/z* 115 (the most important peak in the spectra of glycopyranose acetates[2]), and therefore the relative importance of A_1 is diminished.

The high intensity of some peaks of the A series, namely, *m/z* 157, 141, 115,

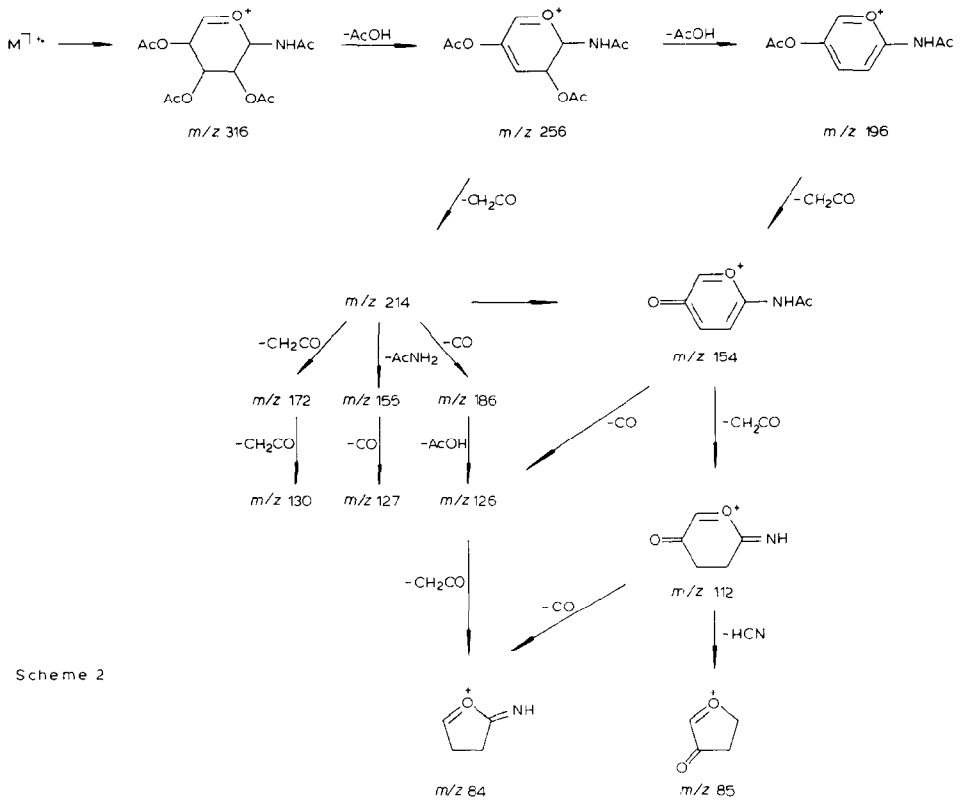


Scheme 1

and 81 (despite the secondary importance of the series) is explained by considering that the same ions are produced by other fragmentation-pathways.

The loss of the alternative α-substituent (CH_2OAc) leads to series B, as it does in the fragmentation of hexopyranose acetates[2,12]. Decomposition of B_1 proceeded analogously to that outlined for A_1 (see Scheme 2), with the difference that the pathway could be branched off by the alternative loss of acetamide or acetic acid. In the first case, further decompositions would be identical to that of the glycopyranose acetates[2], but the relevant ions of this series, *m/z* 215 and 197, were not observed, and *m/z* 155, at low intensity, was detected, showing that B_1 fragmentation was mainly through elimination of acetic acid. The most intense ions of the series (*m/z* 196, 154, 112, and 84) confirm the fragmentations postulated. The fragments *m/z* 257, 215, and 155 (not explained in the spectra of *N*-arylglycosylamine acetates[9]) may arise from this series.

Another series produced in the fragmentation of glycopyranose acetates[2,4,12]

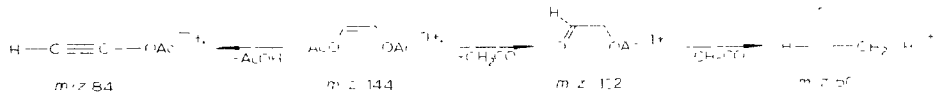


Scheme 2

originates from an allylic fragment (*m/z* 157) formed by carbon atoms 2, 3, and 4 of the pyranose ring; it is also found in the decomposition of hexopyranosylamine acetates (series C), but the presence of the 1-acetamido group leads to a parallel decomposition series (C′) from a similar allylic cation (*m/z* 156) comprising carbon atoms 1, 2, and 3 in which the 1-acetoxyl group has been formally replaced by a 1-acetamido group. Further loss of ketene gives rise to ions *m/z* 114 and 72. Fragment *m/z* 156 and its secondary fragments are also produced with very high yield in the fragmentationof the 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose[5] from carbon atoms 2, 3, and 4. The intensity of peaks *m/z* 73 and 72, corresponding to the terminal fragments of these two pathways, suggests that the cations of series C′ have lower energy, possibly by virtue of the lower electronegativity of the N atom.

Low-molecular-weight fragments of high intensity are very abundant in the spectra of peracetylated hexopyranosylamines. A very intense peak at *m/z* 88 appears in the spectra of permethylated glycopyranoses[3,11,13] for which an unsaturated structure of two ring-carbon atoms, namely C-2 and C-3, produced from the

molecular ion by a conjugated electronic shift, was postulated[11]. By analogy, we postulate series D starting from the radical-ion *m/z* 144 produced from the molecular ion through the aforementioned mechanism. The series comprises four peaks, and, in the spectra of glycopyranose acetates, there have been observed fragments having the same *m/z* values, but with low intensities[2,12].

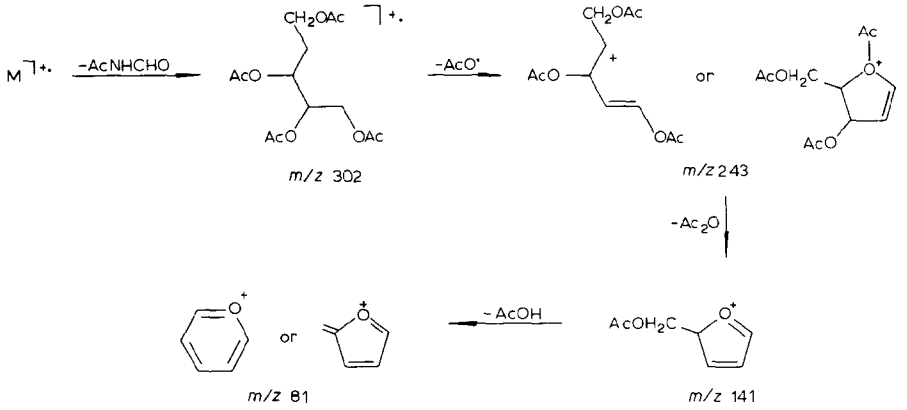


A sister series, D′, starting from the radical ion *m/z* 143, structurally similar to the aforementioned *m/z* 144, but with an acetamido instead of an acetoxyl group, justifies fragments *m/z* 143, 101, 83, and 59. These fragments appear, and are very important, in the fragmentation pathways of acetylated sialic acids[14]; they are also found, but with low intensity, in the high-resolution mass spectrum of 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose[5]. These two series are more important in the spectra of acetates of glycopyranosylamines than in those of acetates of glycopyranoses[2], but are less important than in those of permethylated glycopyranoses[11].

The loss of a molecule of acetic acid from the molecular ion (series E) originates a dihydropyran fragment of high energy, *m/z* 329, which decomposes by a retro-Diels–Alder reaction, expelling *N*-formylacetamide (AcNHCHO) and giving the species E_2, *m/z* 242. These fragmentations also occur with the acetates of glycopyranoses[2,12], and the ions detected in the spectra of glycopyranosylamine acetates, as well as the shift produced by propanoylation, confirm the mechanism suggested in the first case[12]. The detection of the *m/z* 329 ion shows that the formation of the radical ion *m/z* 242 is not a concerted, one-step process, but a stepwise one, as suggested by Biemann *et al.*[2].

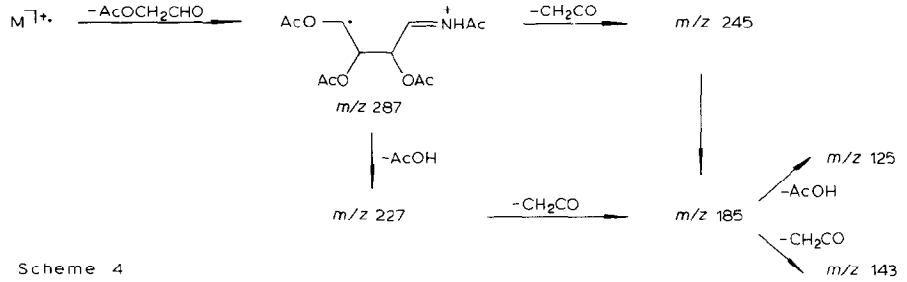
A noteworthy peak in the high-mass range of the spectra of hexopyranosylamine acetates at *m/z* 243 is shifted 42 mass units by propanoylation, showing that it contained three acetyl groups. This ion is formed from the molecular ion, which eliminates the C-1 imide of formic and acetic acid (*N*-formylacetamide), producing an intermediate (*m/z* 302) which loses an acetoxy radical, producing the *m/z* 243 fragment stabilized through the cyclic oxonium isomer[9]. Further shedding of acetic acid produces two fragments (*m/z* 141 and 81), which are the most important ions in the spectrum of hexopyranosylamine acetates. This is the E′ series (see Scheme 3). Fragment *m/z* 243 is found in the spectrum of penta-*O*-acetyl-α-D-mannopyranose[3], and it has a high intensity. This series also appears, at relatively high intensity, for the indole-substituted glycosylamines[10], and its equivalent appears for *N*-acetyl-2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosylamine[11] and for methyl 2,3,4-tri-*O*-methyl-β-L-arabinopyranoside (Kochetkov's series C)[13].

Elimination of the acetate of glycolaldehyde from the molecular ion produces



Scheme 3

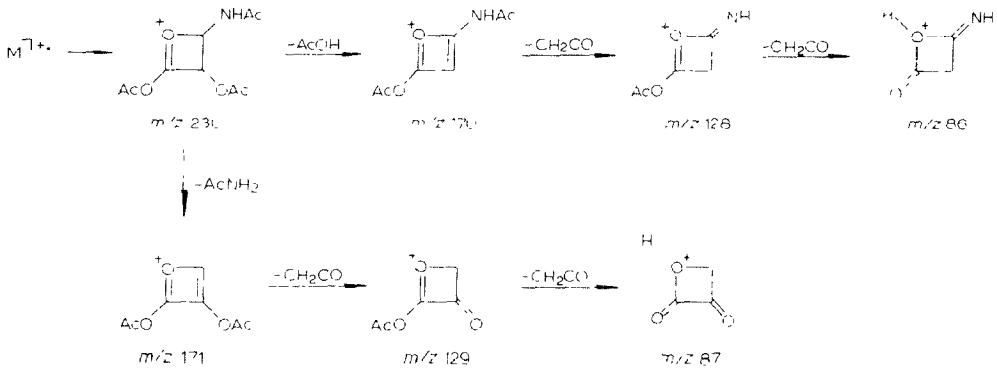
a radical cation, *m/z* 287, which, by subsequent elimination of acetic acid and ketene, gives rise to series F (see Scheme 4). A formally similar radical-ion was obtained in the decomposition of *N*-acetyl-2,3,4,6-tetra-*O*-methyl-β-D-glucopyranosylamine[11], and in the decomposition of methyl 2,3,4-tri-*O*-methyl-β-L-arabinopyranoside[13] by elimination of C-5 and oxygen as formaldehyde, but it is noteworthy that this elimination from the molecular ion is not produced for the pentopyranosylamine acetates (see later). This series is of little importance, and some of the peaks could be explained by ions produced in other series.



Scheme 4

Some peaks of medium intensity in the low-mass range of the spectra of hexopyranosylamine acetates can be justified through four-atom ring-fragments containing an oxygen atom. The series (G) would begin with a high-energy fragment, *m/z* 230, which presents the normal losses (see Scheme 5). The last pair of fragments, *m/z* 86 and 87, are stabilized by resonance.

The molecular ion is not detected, as already mentioned. However, consecutive eliminations of acetamide, acetic acid, ketene, and carbon monoxide from the molecular ion give rise to radical-ions forming series H (see Scheme 6), a series which is very important, and which was also encountered, but not justified, in the spectra of the glycopyranose acetates[2,12] and *N*-arylglycosylamine acetates[9].



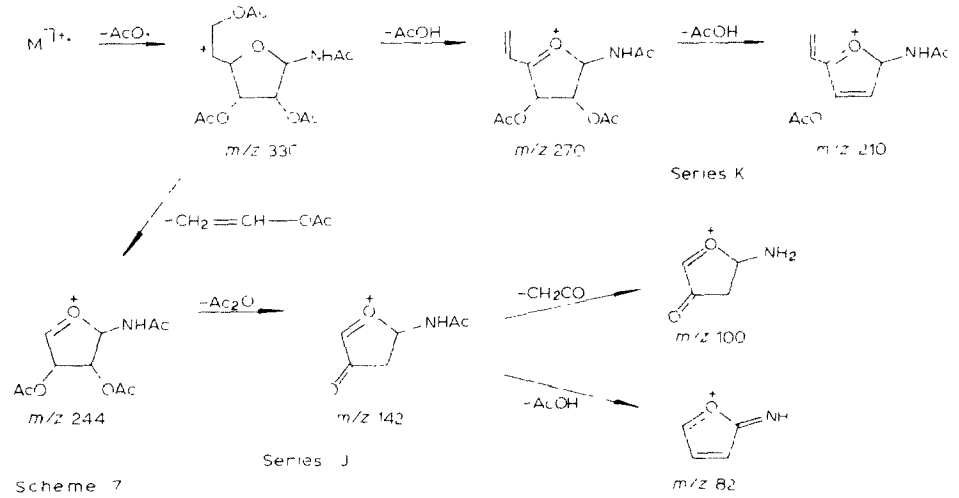
Scheme 5

Cleavage of the molecular ion according to Kochetkov's J-fragmentation pattern leads to ions having a charge on the nitrogen atom[9,13]. Series I is very important, despite the low basicity of the amidic nitrogen atom[9].

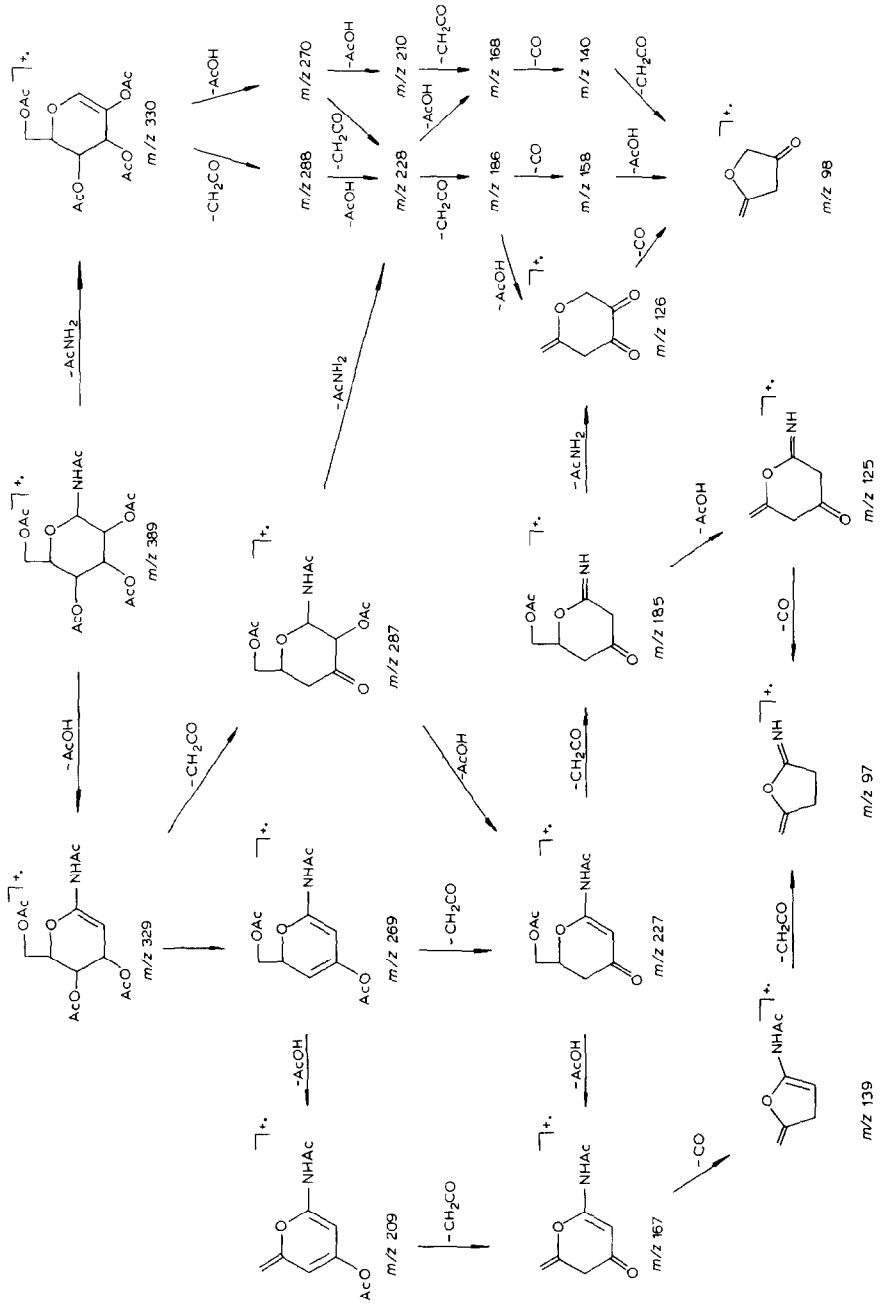
$$\underset{m/z\ 88}{H\text{-}C(=O)\text{-}NH_2\text{-}C(=O)\text{-}CH_3} \xleftarrow{-CH_2CO} \underset{m/z\ 130}{AcO\text{-}CH{=}NH\text{-}Ac} \xrightarrow{-AcOH} \underset{m/z\ 70}{HC{\equiv}N\text{-}C(=O)\text{-}CH_3}$$

Elimination of acetate with ring contraction yields the J series (see Scheme 7), similar to that proposed by Rosenthal[15] for the fragmentation of two unsaturated sugars, and by others[12,13] for 2-deoxyglycopyranose tetraacetates.

From the spectra of compounds **1**, **2**, and **3**, it was deduced that fragments *m/z* 270 and 210 contain the nitrogen atom, as they shift to *m/z* 284 and 224 in the



Scheme 7


m/z 330
m/z 389
m/z 329
m/z 288
m/z 270
m/z 228
m/z 210
m/z 186
m/z 168
m/z 158
m/z 140
m/z 126
m/z 98
m/z 287
m/z 269
m/z 185
m/z 125
m/z 227
m/z 209
m/z 167
m/z 139
m/z 97
-AcNH2
-AcOH
-CH2CO
-CO

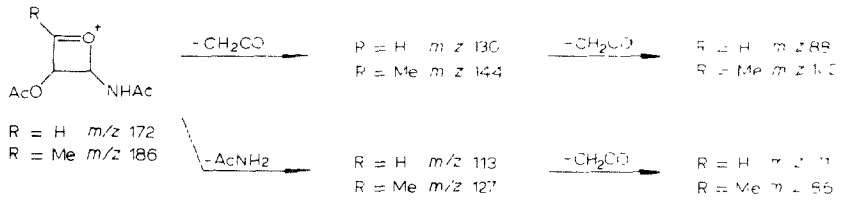
Scheme 6

N-propanoylated analog (**4**). Similar behavior was observed for the pentopyranosylamine derivatives; hence, fragment *m/z* 270 is formed by fission of an acetoxyl radical and acetic acid from the molecular ion, instead of elimination of acetic acid and acetamide (Series H). Fragment *m/z* 270 then expels acetic acid, to give fragment *m/z* 210. This series (K) may be originated in different ways; one of the possibilities is the ring contraction mentioned for series J, in which fragment *m/z* 330 would lose acetic acid instead of vinyl acetate (see Scheme 7).

(2) Acylated pento- and 6-deoxyhexo-pyranosylamines. — The spectral data for compounds **6–9** are given in Table II.

The decomposition pathways of pento- and 6-deoxyhexo-pyranosylamine acetates are similar to those of hexopyranosylamine acetates, with differences resulting from replacement of CH_2OAc by a hydrogen atom or a methyl group. For this reason, series B, which, for these compounds, implies the elimination of high-energy hydrogen or methyl radicals, respectively, has little importance.

Series F and G are of low intensity, or are not produced at all, and this may be related to the stability of the radical, expelled from the molecular ion. The production of the new series, G′, formally similar to G, but arising by the loss of a different two-carbon fragment, suggests that, in some of the decomposition reactions, there is a directing effect of the substituent on C-5.



Some of the decompositions, such as series C, C′, D, D′, I, and K, are not influenced by the C-5 substituent; thus, the peaks observed are in the same range of intensities as for the hexopyranosylamine acetates.

Series A again shows the lack of fragment A_1, and a few important peaks appear that could be produced by other fragmentation pathways.

Series J is not produced from pentopyranosylamine acetates, as it should proceed through the formation of the disfavored carbene. In the case of the acetate of rhamnopyranosylamine, the loss of ethylene gives rise to this series.

Series E′ and H have the same importance as for acetates of hexopyranosylamines; the lack of fragment *m/z* 81 (series E′) in the spectra of both title compounds is consistent with the fragmentation pathway proposed for the hexopyranosylamine acetates.

Series B and E are produced from the molecular ion by competitive losses of

the C-5 substituent, or acetic acid and a retro-Diels–Alder reaction, respectively. In the case of pentopyranosylamine acetates, the lack of a C-5 substituent directs the reaction pathway to the latter sequence, producing series E as the most important one in the decomposition of acylated pentopyranosylamines.

EXPERIMENTAL

The compounds studied were obtained as reported[16]. Mass spectra were recorded with a Varian MAT CH7 mass spectrometer at an ionizing energy of 70 eV, a filament current of 1 μA, and an inlet temperature, suitably selected in each case, that lay between 110 and 230°. A spectrum of penta-*O*-acetyl-β-D-glucopyranose recorded under these conditions showed a pattern similar to those previously reported[2,12]. Compound **8**, *N*-acetyl-2,3,4-tri-*O*-propanoyl-β-D-xylopyranosylamine, had m.p. 117–118°.

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