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MASS SPECTRA OF SOME BENZOYLATED, ACYCLIC-MONOSACCHARIDE DERIVATIVES

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ABSTRACT

Mass spectra of some benzoylated aldononitriles and 5-[poly(benzoyloxy)alkyl] tetrazoles are described, and their fragmentation patterns proposed.

INTRODUCTION

The mass spectra of acyclic monosaccharide derivatives have been reported for an important number of acetylated compounds having different structures[1–4].

Spectra of acetylated aldononitriles and acetylated deoxyaldononitriles recorded by Szafranek *et al.*[5] by electron-impact m.s., and of peracetylated aldononitriles and of per-*O*-acetylated *O*-methylaldononitriles by chemical ionization by Li *et al.*[6] have been discussed.

Dmitriev *et al.*[7] reported g.l.c. separation, and identification by m.s., of acetates of partially methylated aldononitriles, and Seymour *et al.* used g.l.c. separation, and m.s. with chemical ionization[8] and electron impact[9], for the identification of acetylated aldononitriles, deoxyaldononitriles, and other derivatives.

We now report the electron-impact, mass spectra of benzoylated aldononitriles and of the corresponding 5-(poly-*O*-benzoylalditol-1-yl)tetrazoles. As these compounds have several benzoyl groups, the leading aspect of the spectrum is given by the aromatic nucleus. The base peak in most of the compounds corresponds to the ion $[C_6H_5CO]^+$, and, in the rest of them, it is due to fragmentation thereof. Successive losses of benzoic acid or benzoic anhydride are observed. On the other hand, it is possible to correlate the fragmentation of each group of related compounds.

The mass spectrum of 2,3-di-*O*-benzoyl-DL-glyceronononitrile(**1**) shows the molecular ion with important relative abundance (*m/z* 295, 68.80%); also, the $(M^{\ddagger} + 1)$ and $(M^{\ddagger} + 2)$ peaks are observed, in agreement with natural, isotopic abundance of carbon and oxygen. The fragmentation pattern is presented in

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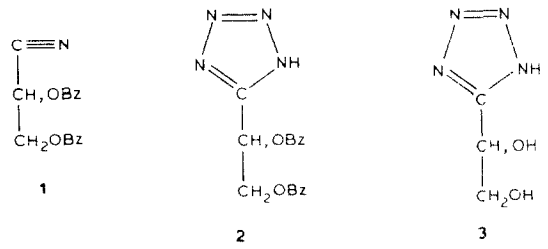
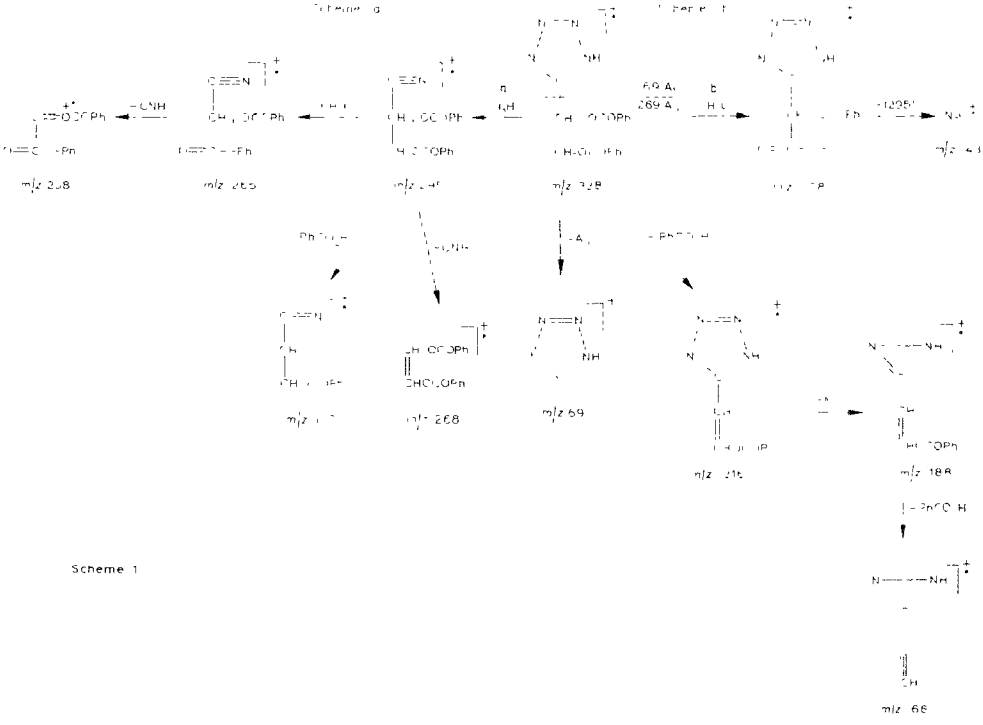


1 2 3

Scheme 1a. One of the primary fragments is formed by the loss of formaldehyde, with concomitant migration of the acyl group. This fragmentation was also observed for compounds **2** and **3**, but it is not detectable for the compounds of higher molecular weight. A similar splitting of the last chain-carbon atom was also described for acetylated aldononitriles[8]. The fragmentation of hydrogen cyanide gives rise to an important peak, but the base peak, as for the other benzoates, is due to the ion $[C_6H_5CO]^+$. The important peaks observed are listed in Table I.

The mass spectrum of 5-[1(*R,S*),2-dibenzoyloxyethyl]tetrazole (**2**), synthesized from nitrile **1**, showed the primary loss of hydrazoic acid, and good agreement with the fragmentation pattern proposed for compound **1** (see Scheme 1a). It also shows the particular fragmentation due to splitting of benzoate fragments, followed by elimination of nitrogenated fragments, as shown in Scheme 1b. In this



Scheme 1

TABLE I

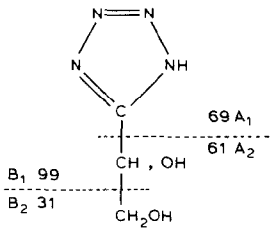
MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF 2,3-DI-*O*-BENZOYL-DL-GLYCERONONITRILE[a] (**1**) AND 5-[1(*R*,*S*),2-DIBENZOYLOXYETHYL]TETRAZOLE[a] (**2**)

	1		**2**	
m/z	*Int. (%)*[b]	*Assignments*[c]	*Int. (%)*[b]	*Assignments*[c]
338	—	—	1.06	M^+
308	—	—	2.19	$M^+ - CH_2O$
297	1.67	$M^+ + 2$	—	—
296[d]	13.14	$M^+ + 1$	0.38	$(M^+ + 1) - N_3H$
295[d]	68.80	M^+	2.49	$M^+ - N_3H$
268	0.37	$M^+ - CNH$	—	—
267	2.41	$M^+ - CNH - H$	—	—
265[d]	19.74	$M^+ - CH_2O$	1.10	$M^+ - N_3H - CH_2O$
238	0.75	$M^+ - CNH - CH_2O$	—	—
216	—	—	2.87	$M^+ - PhCO_2H$
174	4.43	$M^+ - PhCO_2$	—	—
173[d]	0.42	$M^+ - PhCO_2H$	2.35	$M^+ - N_3H - PhCO_2H$
122	0.56	$PhCO_2H^+$	4.25	$PhCO_2H^+$
106	14.06	$C_6H_6CO^+$	48.64	$C_6H_6CO^+$
105	100.	$PhCO^+$	100.	$PhCO^+$
77	43.14	Ph^+	99.80	Ph^+
69	—	—	2.78	CN_4H^+
51	12.89	$C_4H_3^+$	52.02	$C_4H_3^+$
43	—	—	1.07	N_3H^+

[a]For the fragmentation pattern, see Scheme 1. [b]Intensity, expressed as percent of the base peak. [c]Assignments are assumed. [d]Italicized *m/z* values are chain fragments common to both compounds.

case, the molecular ion appears in low relative abundance. The base peak is due to the ion $[C_6H_5CO]^+$. The ions formed are listed in Table I and those common to compounds **1** and **2** are italicized.

In the mass spectrum of 5-[1(*R*,*S*),2-dihydroxyethyl]tetrazole (**3**), a similar fragmentation of the heterocyclic part and of the chain is observed (see Scheme 2). The molecular ion appears in low relative abundance, and the base peak is $M^+ - CH_2O$ (*m/z* 100), as shown in Table II. The primary fragments formed by fission of C-1–C-2 (*m/z* 99 and 31) and C-het–C-1 (*m/z* 69 and 61) appear in different relative abundances due to their different stabilities.



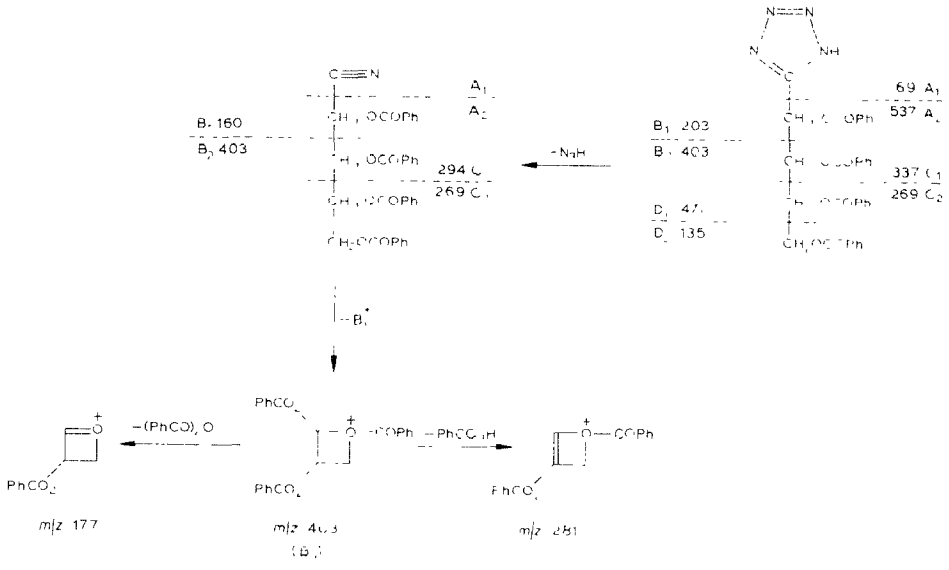
Scheme 2

TABLE II

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF 5-[1(*R*,*S*),2-DIHYDROXYETHYL]TETRAZOLE[a] (**3**)

m/z	*Int.* (%)[b]	*Assignments*[c]
130	0.79	$M^{+\cdot}$
112	0.91	$M^{+\cdot} - H_2O$
100	100.	$M^{+\cdot} - CH_2O$
99	9.91	B_1^+
71	29.44	$B_1^+ - N_2$
70	2.12	$M^{+\cdot} - N_2 - CH_3OH$
69	1.51	A_1^+
61	29.18	A_2^+
60	2.84	$M^{+\cdot} - CN_4H_2$
57	91.15	$M^{+\cdot} - N_3H - CH_2O$
56	8.34	$B_1^+ - N_3H$
55	5.62	$M^{+\cdot} - N_4H - CH_3OH$
45	6.64	$M^{+\cdot} - N_2 - CNH - CH_2O$
44	7.71	$B_1^+ - N_2 - CNH$
42	48.70	$M^{+\cdot} - 2N_2 - CH_3OH$
41	6.29	$A_1^+ - N_2$
31	91.29	B_2^+

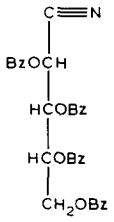
[a]For chain fragmentation, see Scheme 2. [b]Intensity, expressed as percent of the base peak. [c]Assignments are assumed.



Scheme 3

The mass spectra of tetra-*O*-benzoyl-D-arabinononitrile (**4**) and tetra-*O*-benzoyl-D-xylononitrile (**5**) show similar fragmentation. The molecular ion is not observed, and the base peak is respectively due to the $[C_6H_5CO]^+$ or $[C_6H_5]^+$ ion. The primary fragment produced by fission of the C-2–C-3 bond gives rise to a cyclic ion of *m/z* 403, which probably loses benzoic acid or benzoic anhydride, to afford other cyclic ions (see Scheme 1) similar to those proposed for acetylated aldononitriles[5,8]. Assignments for the ions observed are listed in Table III.

The mass spectra of 5-(tetra-*O*-benzoyl-D-*arabino*-tetritol-1-yl)tetrazole (**6**), and 5-(tetra-*O*-benzoyl-D-*xylo*-tetritol-1-yl)tetrazole (**7**) showed partial splitting of the heterocyclic moiety and good agreement with the nitrile fragmentation, as also observed in the case of compound **2**. The particular fragments from the chain fis-



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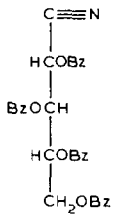

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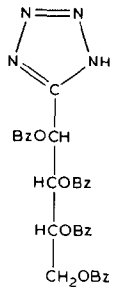

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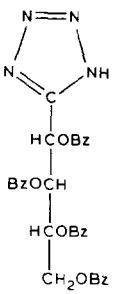

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TABLE III

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF TETRA-*O*-BENZOYL-D-ARABINONONITRILE[a] (**4**) AND OF TETRA-*O*-BENZOYL-D-XYLONONITRILE[a] (**5**)

m/z	**4** *Int. (%)*[b]	**5** *Int. (%)*[b]	*Assignments*[c]
441	2.09	3.26	$M^+ - PhCO_2H$
428	—	1.27	D_1^+
403	13.06	6.35	B_2^+
319	12.77	10.33	$M^+ - 2PhCO_2H$
294	—	2.63	C_1^+
281	—	39.86	$B_2^+ - PhCO_2H$
269	—	18.58	C_2^+
215	13.15	5.05	$M^+ - PhCO_2H - (PhCO)_2O$
188	0.82	0.41	$M^+ - CNH - PhCO_2H - (PhCO)_2O$
177	—	0.35	$B_2^+ - (PhCO)_2O$
122	21.15	8.42	$PhCO_2H^+$
106	93.74	93.79	$C_6H_6CO^+$
105	100.	99.37	$PhCO^+$
93	1.25	0.70	$M^+ - 2PhCO_2H - (PhCO)_2O$
77	96.75	100.	Ph^+
51	3.40	24.93	$C_4H_3^+$

[a]For the fragmentation pattern, see Scheme 3. [b]Intensity, expressed as percent of the base peak, [c]Assignments are assumed.

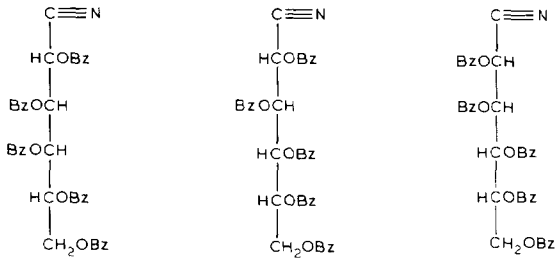
sion, and successive losses of nitrogenated or benzoyl fragments, are shown in Table IV. The ions in common with the nitriles are italicized.

TABLE IV

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF 5-(TETRA-*O*-BENZOYL-D-*arabino*-TETRITOL-1-YL)TETRAZOLE[a] (**6**) AND 5-(TETRA-*O*-BENZOYL-D-*xylo*-TETRITOL-1-YL)TETRAZOLE[a] (**7**)

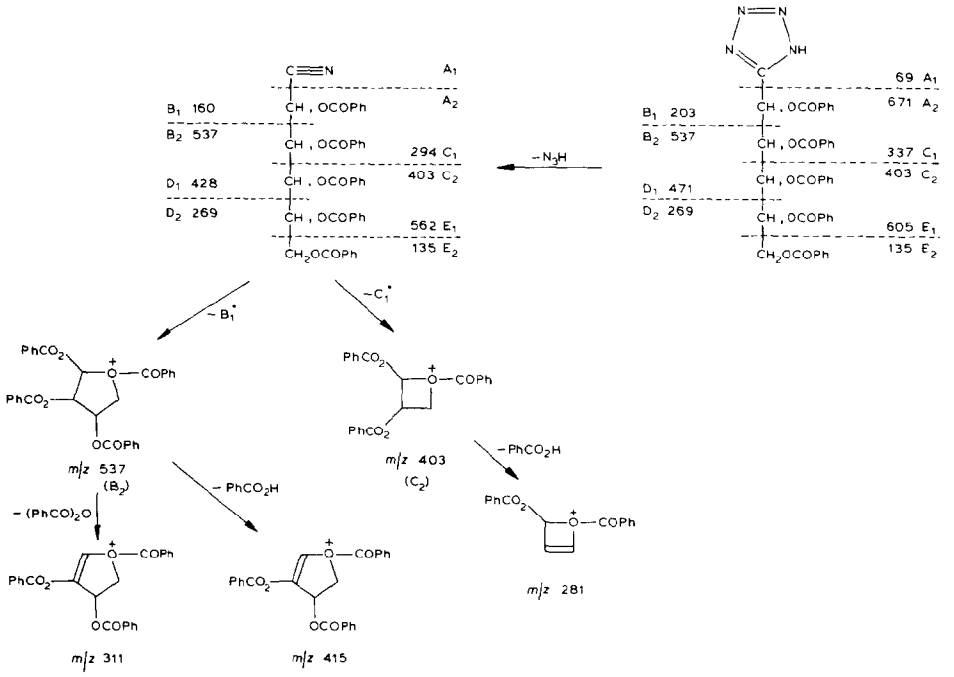
m/z	**6** *Int. (%)*[b]	**7** *Int. (%)*[b]	*Assignments*[c]
269[d]	0.57	—	C_2^+
177[d]	0.67	0.79	$B_2^+ - (PhCO)_2O$
148	0.68	6.16	$B_1^+ - N_2 - CNH$
136	—	1.47	$M^+ - 2PhCO_2H - (PhCO)_2O$
135	—	1.92	D_2^+
127	—	0.74	$M^+ - CNH - 2(PhCO)_2O$
123	1.25	6.44	$D_1^+ - PhCO_2H - (PhCO)_2O$
122	17.12	41.78	$PhCO_2H^+$
121	1.88	65.76	$D_1^+ - PhCO_2H - (PhCO)_2O - H\cdot$
111	—	1.10	$M^+ - N_3H - 2(PhCO)_2O$
109	—	1.32	$M^+ - CNH - 2PhCO_2H - (PhCO)_2O$
106	7.88	23.47	$C_6H_6CO^+$
105	100	21.99	$PhCO^+$
100	—	3.00	$M^+ - N_2 - 2(PhCO)_2O - CN\cdot$
99	—	1.36	$M^+ - N_2 - CNH - 2(PhCO)_2O$
98	1.47	7.13	$M^+ - 2N_2 - 2(PhCO)_2O$
94	0.40	1.79	$D_1^+ - N_2 - PhCO_2H - (PhCO)_2O$
91	0.41	3.25	$M^+ - CNH - 4PhCO_2H$
87	0.54	2.49	$A_2^+ - 2(PhCO)_2O$
85	0.37	2.60	$M^+ - 2(PhCO)_2O - CN_4H$
83	1.02	8.37	$M^+ - N_3H - CNH - 2(PhCO)_2O - H\cdot$
79	0.86	4.54	$M^+ - 2N_2 - 2PhCO_2H - (PhCO)_2O - H\cdot$
78	2.95	45.98	$D_1^+ - CNH - 3PhCO_2H$
77	40.53	52.24	Ph^+
			$D_1^+ - N_2 - 3PhCO_2H$
76	2.19	20.97	$M^+ - N_3H - 3PhCO_2H - PhCO_2\cdot$
75	1.11	13.13	$M^+ - N_3H - 4PhCO_2H$
74	2.19	20.07	$M^+ - N_3H - 4PhCO_2H - H\cdot$
70	0.44	3.55	$CN_4H_2^+$
69	0.35	3.72	A_1^+
66	3.57	4.31	$M^+ - N_3H - CNH - 2PhCO_2H - (PhCO)_2O$
65	0.42	8.59	$C_1^+ - N_2 - 2PhCO_2H$
56	—	8.17	$C_1^+ - N_2 - CNH - (PhCO)_2O$
54	0.76	5.97	$C_1^+ - N_2 - CNH - 2PhCO_2H$
			$B_1^+ - CNH - PhCO_2H$
53	—	7.89	$C_1^+ - 2N_2 - 2PhCO_2H$
51	16.92	100	$C_4H_3^+$
50	7.37	33.89	$C_1^+ - N_3H - 2PhCO_2H$
			$D_1^+ - N_2 - CNH - 3PhCO_2H$
49	0.43	5.37	$D_1^+ - 2N_2 - 3PhCO_2H$
43	1.57	33.42	N_3H^+

[a]For chain fragmentation, see Scheme 3. [b]Intensity, expressed as percent of the base peak. [c]Assignments are assumed. [d]Italicized *m/z* values are chain fragments in common with those of corresponding nitriles.



8 **9** **10**

The fragmentation pattern proposed for penta-*O*-benzoyl-D-galactononitrile (**8**), penta-*O*-benzoyl-D-gluconononitrile (**9**), and penta-*O*-benzoyl-D-mannononitrile (**10**) are shown in Scheme 4. The molecular ion was not detected. The base peak is due to the $[C_6H_5CO]^+$ ion. Two different cyclic ions might be formed by primary fission of C-2–C-3 (*m/z* 537) and C-3–C-4 (*m/z* 403), respectively, and subsequent formation of other cyclic ions is proposed, in the same way as for the acetylated derivatives[5,8]. The ions are listed in Table V.



Scheme 4

TABLE V

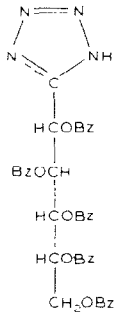
MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF PENTA-*O*-BENZOYL-D-GALACTONONITRILE[a] (**8**), PENTA-*O*-BENZOYL-D-GLUCONONITRILE[a] (**9**), PENTA-*O*-BENZOYL-D-MANNONONITRILE[a] (**10**), 5-(PENTA-*O*-BENZOYL-D-*gluco*-PENTITOL-1-YL)TETRAZOLE[a] (**11**), AND 5-(PENTA-*O*-BENZOYL-D-*manno*-PENTITOL-1-YL)TETRAZOLE[a] (**12**)

	8	**9**	**10**		**11**	**12**	
m/z	*Int.* (%)[b]	*Int.* (%)[b]	*Int.* (%)[b]	*Assignments*[c]	*Int.* (%)[b]	*Int.* (%)[b]	*Assignments*[c]
712	—	—	—	—	—	0.46	$M^+ - N_2$
617	—	—	—	—	—	2.72	$M^+ - PhCO_2H$
591	—	—	—	—	—	3.07	$M^+ - CNH - PhCO_2H$
590	—	—	—	—	—	7.07	$M^+ - N_2 - PhCO_2H$
576[d]	—	0.50	—	$M^+ - PhCO_2\cdot$	2.19	0.76	$M^+ - N_3H - PhCO_2\cdot$
575[d]	0.46	0.68	0.33	$M^+ - PhCO_2H$	4.46	1.08	$M^+ - N_3H - PhCO_2H$
563	—	—	—	—	1.89	1.55	$M^+ - N_2 - CNH - PhCO_2H$
562[d]	0.72	1.63	0.45	E_1^+	5.66	4.67	$E_1^+ - N_3H$ $M^+ - 2N_2 - PhCO_2H$
537[d]	0.61	0.99	0.36	B_2^+	3.56	1.48	B_2^+
471[d]	—	0.31	—	$M^+ - (PhCO)_2O$	0.47	0.39	$M^+ - N_3H - (PhCO)_2O$
455	—	—	—	—	3.88	1.70	$E_1^+ - N_2 - PhCO_2H$
454	—	—	—	—	14.61	1.48	$M^+ - N_3H - PhCO_2H - PhCO_2\cdot$
453[d]	7.43	10.92	4.08	$M^+ - 2PhCO_2H$	44.91	4.46	$M^+ - N_3H - 2PhCO_2H$
441	—	—	—	—	—	6.07	$M^+ - N_2 - CNH - 2PhCO_2H$
428[d]	1.09	2.04	0.44	D_1^+	7.56	0.66	$D_1^+ - N_3H$
426	—	—	—	—	0.23	0.43	$M^+ - N_3H - CNH - 2PhCO_2H$
415[d]	1.68	3.24	1.58	$B_2^+ - PhCO_2H$	13.57	1.01	$B_2^+ - PhCO_2H$
403[d]	2.43	2.67	0.96	C_3^+	10.67	82.58	C_2^+
350[d]	0.31	—	0.61	$M^+ - (PhCO)_2O - PhCO_2\cdot$	6.37	0.35	$M^+ - N_3H - (PhCO)_2O - PhCO_2\cdot$
349[d]	1.52	1.25	0.36	$M^+ - (PhCO)_2O - PhCO_2H$	3.72	0.78	$M^+ - N_3H - (PhCO)_2O - PhCO_2H$
333	—	—	—	—	1.52	2.32	$E_1^+ - N_2 - 2PhCO_2H$
331[d]	4.66	5.46	3.14	$M^+ - 3PhCO_2H$	26.93	3.72	$M^+ - N_3H - 3PhCO_2H$
318	—	—	—	—	—	4.95	$M^+ - 2N_2 - 3PhCO_2H$
311[d]	0.71	0.70	0.42	$B_3^+ - (PhCO)_2O$	3.92	2.12	$B_2^+ - (PhCO)_2O$
294	—	—	—	—	1.16	1.59	$C_1^+ - N_3H$
281[d]	2.04	2.53	1.40	$C_2^+ - PhCO_2H$	13.54	5.34	$C_2^+ - PhCO_2H$
270	—	—	—	—	9.59	2.13	$M^+ - 2PhCO_2H - (PhCO)_2O$
269[d]	13.18	9.67	5.98	D_2^+	56.97	10.45	D_2^+

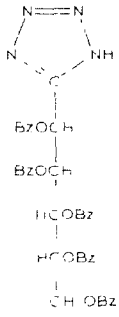
227[d]	0.33	—	—	$M^+ - 2PhCO_2H - (PhCO)_2O$	2.25	1.09	$M^+ - N_3H - 2PhCO_2H - (PhCO)_2O$
225	—	—	—	—	0.43	2.57	$M^+ - CNH - 4PhCO_2H$
215	—	—	—	—	—	7.05	$M^+ - N_2 - CNH - 2PhCO_2H - (PhCO)_2O$
214	—	—	—	—	—	20.74	$M^+ - 2N_2 - 2PhCO_2H - (PhCO)_2O$
196	—	—	—	—	—	6.28	$M^+ - 2N_2 - 4PhCO_2H$
181[d]	0.40	—	—	$M^+ - CNH - 4PhCO_2H - H\cdot$	2.35	2.97	$M^+ - N_3H - CNH - 4PhCO_2H - H\cdot$
177	—	—	—	—	0.72	17.84	$C_2^+ - (PhCO)_2O$
160	—	—	—	—	—	30.02	$B_1^+ - N_3H$
135	—	—	—	—	—	0.50	D_2^+
123	—	—	—	—	1.90	43.30	$M^+ - N_3H - PhCO_2H - 2(PhCO)_2O$
122	3.04	0.53	1.57	$PhCO_2H^+$	24.74	99.83	$PhCO_2H^+$
121	—	—	—	—	0.38	10.92	$PhCO_2^+$
106	32.50	13.78	17.84	$C_6H_6CO^+$	99.81	99.83	$C_6H_6CO^+$
105	100.	100.	100.	$PhCO^+$	99.98	99.72	$PhCO^+$
104	—	—	—	—	6.21	16.60	$M^+ - CNH - 4PhCO_2H - PhCO_2\cdot$
103	—	—	—	—	0.83	5.33	$M^+ - CNH - 5PhCO_2H$
94	—	—	—	—	0.80	20.81	$M^+ - N_2 - CNH - 2PhCO_2H - (PhCO)_2O - PhCO_2\cdot$
93	—	—	—	—	—	4.95	$M^+ - N_2 - CNH - 3PhCO_2H - (PhCO)_2O$
78	—	—	—	—	17.89	84.61	$M^+ - N_3H - CNH - 3PhCO_2H - (PhCO)_2O$
77	43.87	21.59	22.50	Ph^+	100.	99.77	Ph^+
76	—	—	—	—	8.50	60.85	$M^+ - N_2 - 5PhCO_2H - CN\cdot$
75	—	—	—	—	2.33	32.42	$M^+ - N_2 - CNH - 5PhCO_2H$
74	—	—	—	—	2.68	51.81	$M^+ - 2N_2 - 5PhCO_2H$
73	—	—	—	—	0.79	10 53	$M^+ - 2N_2 - 5PhCO_2H - H\cdot$
69	—	—	—	—	—	0 76	A_1^+
66	—	—	—	—	0 45	12.97	$C_1^+ - CNH - 2PhCO_2H$
65	—	—	—	—	0.92	21.72	$C_1^+ - N_2 - 2PhCO_2H$
63	—	—	—	—	0.47	9.56	$E_1^+ - N_3H - CNH - H_2 - 2PhCO_2H - (PhCO)_2O$
55	—	—	—	—	0.67	5.35	$C_2^+ - PhCO_2H - (PhCO)_2O$
51	6.10	2.37	2.93	$C_4H_3^+$	31.76	100.	$C_4H_3^+$
50	—	—	—	—	8.79	93.60	$D_1^+ - N_2 - 3PhCO_2H$
49	—	—	—	—	0.48	13.15	$D_1^+ - 2N_2 - 3PhCO_2H$
							$A_2^+ - 4PhCO_2H$
43	—	—	—	—	—	6.47	N_3H^+

[a]For chain fragmentation, see Scheme 4 [b]Expressed as percent of the base peak. [c]Assignments are assumed. [d]Italicized *m/z* values are chain fragments common to both types of compound.

The mass spectra of 5-(penta-*O*-benzoyl-D-*gluco*-pentitol-1-yl)tetrazole (**11**) and 5-(penta-*O*-benzoyl-D-*manno*-pentitol-1-yl)tetrazole (**12**) agree with those in Scheme 4. On the one hand, they lose hydrazoic acid and agree with the nitrile fragmentation, and on the other, they show their own splitting of the chain and successive losses of benzoyl fragments. The ions in common with the nitrile fragmentation are italicized and the most significant ions are listed in Table V.

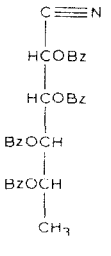


11

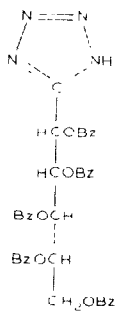


12

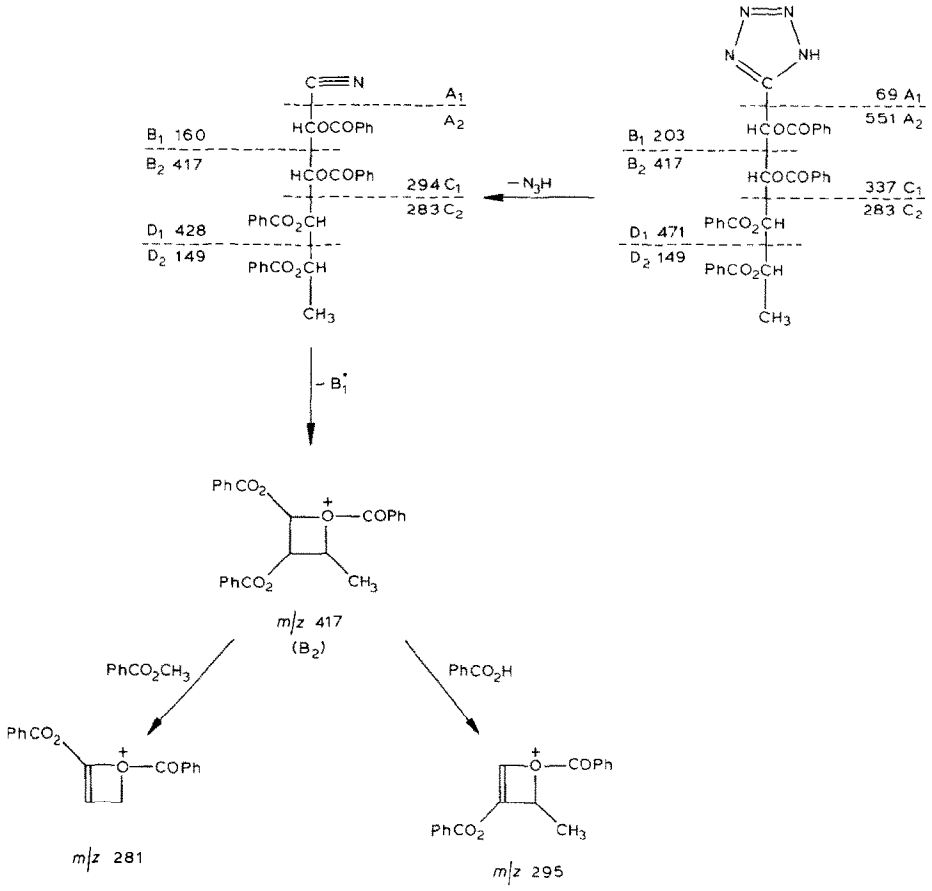
The mass spectra of tetra-*O*-benzoyl-6-deoxy-L-mannononitrile (**13**) and 5-(1,2,3,4-tetra-*O*-benzoyl-L-*manno*-pentitol-1-yl)tetrazole (**14**) have a pattern relationship similar to those of the former groups of compounds, with the difference of the 5-C-methyl (6-deoxy) group in **13**. Compound **14** gives rise to compound **13** by loss of hydrazoic acid, and from this ion, formation of a cyclic primary fragment (*m/z* 417) is proposed, as for the former groups of compounds. The further loss of methyl benzoate, or benzoic acid, probably again gives cyclic ions (see Scheme 5). The fragments are listed in Table VI, and the ions common to both compounds are italicized.



13



14



Scheme 5

Even though all of the ions formed could be rationalized, only the more significant ones are listed in Tables I-VI. The mass spectra of these benzoylated aldononitriles permit proposal of a fragmentation pattern that could prove useful. The fragmentation of 5-[poly(benzoyloxy)alkyl]tetrazoles by loss of hydrazoic acid agrees on the one hand with the scheme for the structurally related aldononitriles, and, on the other, shows its own pattern.

EXPERIMENTAL

The compounds studied were prepared by the methods described in the literature: 2,3-di-*O*-benzoyl-DL-glyceronononitrile[10] (**1**), 5-[1(*R,S*),2-dibenzoyloxyethyl]tetrazole[10] (**2**), 5-[1(*R,S*),2-dihydroxyethyl]tetrazole[10] (**3**), tetra-*O*-benzoyl-D-arabinononitrile[11] (**4**), tetra-*O*-benzoyl-D-xylononitrile[12] (**5**), 5-(tetra-*O*-benzoyl-D-*arabino*-tetritol-1-yl)tetrazole[11] (**6**), 5-(tetra-*O*-benzoyl-D-*xylo*-tetritol-1-

TABLE VI

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF TETRA-*O*-BENZOYL-6-DEOXY-L-MANNONONITRILE[a] (**13**) AND 5-(1,2,3,4-TETRA-*O*-BENZOYL-L-*manno*-PENTITOL-1-YL)TETRAZOLE[a] (**14**)

	13		**14**	
m/z	*Int.* (%)[b]	*Assignments*[c]	*Int.* (%)[b]	*Assignments*[c]
620	—	—	0.34	M^+
455[d]	0.50	$M^+ - PhCO_2H$	0.84	$M^+ - N_3H - PhCO_2H$
428	0.60	D_1^+	—	—
417[d]	1.01	B_2^+	1.23	B_2^+
411	1.57	$M^+ - PhCO_2H - CH_3CHO$	—	—
376	—	—	0.61	$M^+ - 2PhCO_2H$
349	—	—	1.56	$D_1^+ - PhCO_2H$
333	2.58	$M^+ - 2PhCO_2H$	—	—
331[d]	30.24	$M^+ - 2PhCO_2H - H_2$	0.64	$M^+ - N_3H - 2PhCO_2H - H_2$
307	6.76	$M^+ - 2PhCO_2H - CN\cdot$	—	—
295[d]	4.16	$B_2^+ - PhCO_2H$	0.36	$B_2^+ - PhCO_2H$
283[d]	1.95	C_2^+	1.96	C_2^+
281	0.58	$B_2^+ - PhCO_2CH_3$	—	—
229	4.05	$M^+ - PhCO_2H - (PhCO)_2O$	—	—
160	—	—	0.43	$B_1^+ - N_3H$

123	—	—	5.00	$M^+ - 2PhCO_2H - (PhCO)_2O - CNH$
122	7.58	$PhCO_2H^+$	7.22	$PhCO_2H^+$
				$M^+ - N_2 - 2PhCO_2H - (PhCO)_2O$
117	—	—	3.20	$E_1^+ - 4PhCO_2H$
106	64.98	$C_6H_6CO^+$	9.63	$C_6H_6CO^+$
105	100.	$PhCO^+$	100.	$PhCO^+$
104	—	—	0.81	$M^+ - N_2 - 4PhCO_2H$
88	—	—	5.96	$M^+ - N_2 - 3PhCO_2H - PhCO_2CH_3 - H_2$
86	—	—	42.69	$M^+ - N_3H - 4PhCO_2H - H_2 - H\cdot$
84	—	—	73.19	$C_1^+ - CNH - (PhCO)_2O$
79	—	—	4.25	$M^+ - N_3H - CNH - 2(PhCO)_2O$
78	—	—	3.36	$D_1^+ - CNH - 3PhCO_2H$
77	99.74	Ph^+	30.07	Ph^+
				$D_1^+ - N_2 - 3PhCO_2H$
76	—	—	1.75	$M^+ - N_3H - 3PhCO_2H - PhCO_2CH_3$
70	—	—	1.44	$CN_4H_2^+$
51	10.83	$C_4H_3^+$	9.26	$C_4H_3^+$
50	—	—	4.99	$C_1^+ - N_3H - 2PhCO_2H$
49	—	—	19.59	$D_1^+ - 2N_2 - 3PhCO_2H$
47	—	—	43.27	$E_1^+ - N_3H - CNH - 4PhCO_2H$
43	—	—	0.15	N_3H^+

[a]For chain fragmentation, see Scheme 5. [b]Expressed as percent of the base peak. [c]Assignments are assumed. [d]Italicized *m/z* values are chain fragments common to both compounds.

yl)-tetrazole[11] (**7**), penta-*O*-benzoyl-D-galactononitrile[13] (**8**), penta-*O*-benzoyl-D-gluconononitrile[13] (**9**), penta-*O*-benzoyl-D-mannononitrile[13] (**10**), 5-(penta-*O*-benzoyl-D-*gluco*-pentitol-1-yl)tetrazole[11] (**11**), 5-(penta-*O*-benzoyl-D-*manno*-pentitol-1-yl)tetrazole[11] (**12**), tetra-*O*-benzoyl-6-deoxy-L-mannononitrile[13] (**13**), and 5-(1,2,3,4-tetra-*O*-benzoyl-L-*manno*-pentitol-1-yl)tetrazole[11] (**14**).

The mass spectra were recorded with a Varian Mat CH7-A mass spectrometer, operated at 70 eV in the e.i. mode, coupled to a Varian Mat Data System 166 prepared for automatic subtraction, by the insertion technique (100–230°). The peak intensities, expressed as percentage of total ionization, are listed in Tables I–VI.

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