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MASS SPECTRA OF SOME PER-*O*-BENZOYLATED ALDOPYRANOSES AND ALDOFURANOSES

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ABSTRACT

Mass spectra by electron impact-ionization of penta-*O*-benzoyl derivatives of α-D-glucopyranose, β-D-glucopyranose, α-D-glucofuranose, α-D-galactopyranose, α-D-galactofuranose, β-D-galactofuranose, α-D-mannopyranose, and β-D-mannopyranose, and of tetra-*O*-benzoyl derivatives of α-D-xylopyranose, α-D-lyxopyranose, β-D-ribopyranose, and β-L-arabinopyranose are reported. Their fragmentation pattern is proposed and the fragments useful for diagnostic purposes are presented.

INTRODUCTION

Mass spectra of cyclic and acyclic monosaccharide derivatives have frequently been reported for acetylated derivatives, but benzoylated compounds have seldom been used for diagnostic purposes.

In an earlier paper, we reported the mass spectra of some benzoylated acyclic monosaccharide derivatives[1], and we now give the fragmentation scheme for some cyclic derivatives.

In the literature, there are several publications on the mass spectra of per-*O*-acetylated hexopyranoses[2–4] and hexofuranoses[3,4] and their characteristic fragmentation, which are useful for the differentiation of both types of cyclic derivative.

RESULTS AND DISCUSSION

The electron-impact, mass spectra of some per-*O*-benzoylated derivatives of cyclic aldohexoses and aldopentoses are reported, their fragmentation pattern is proposed, and the mass peaks that can be used for diagnostic purposes are presented.

In a previous paper, we used the characteristic fragments to ascertain the re-

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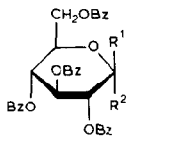

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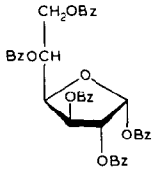

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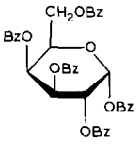

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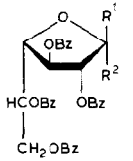
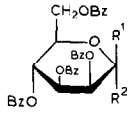
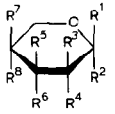


5 R^1 = H, R^2 = OBz
6 R^1 = OBz, R^2 = H



7 R^1 = H, R^2 = OBz
8 R^1 = OBz, R^2 = H

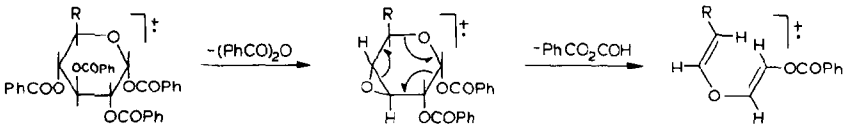


9 $R^1 = R^3 = R^6 = R^7 = H, R^2 = R^4 = R^5 = R^8 = OBz$
10 $R^1 = R^4 = R^6 = R^7 = H, R^2 = R^3 = R^5 = R^8 = OBz$
11 $R^2 = R^3 = R^5 = R^7 = H, R^1 = R^4 = R^6 = R^8 = OBz$
12 $R^1 = R^3 = R^6 = R^8 = H, R^2 = R^4 = R^5 = R^7 = OBz$

sults of other spectroscopic structure determinations[5]. We here present a general fragmentation pattern for compounds **1–12**.

As previously reported for the per-*O*-benzoylated derivatives[1], the base peak of these compounds is $[C_6H_5CO]^+$ (*m/z* 105), and for some, it is due to fragmentation thereof (*m/z* 77). Characteristic fragments of per-*O*-benzoylated compounds are also the peaks at *m/z* 331 $[(PhCO)_3O]^+$, *m/z* 227 $[(PhCO)_2OH]^+$, and *m/z* 122 $[PhCO_2H]^+$. The molecular ion is not found, and successive losses of benzoic acid or benzoic anhydride are observed. Several peaks of diagnostic value can be reported for the identification of the different cyclic structures and for differentiation of hexopyranoses from pentopyranoses.

For per-*O*-benzoylated pyranose derivatives, successive elimination of anhydride can be proposed, as similarly suggested by Biemann *et al.*[3] for acetylated derivatives, and shown in Scheme 1.

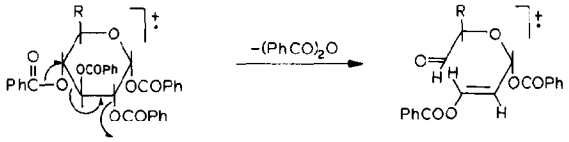


R = CH_2OCOPh (for hexopyranoses)
R = H (for pentopyranoses)

Scheme 1

The other possibility, the elimination of benzoic anhydride, with electron transfer, is proposed in Scheme 2; this is similar to that proposed by Heyns and Müller[2] for acetylated derivatives.

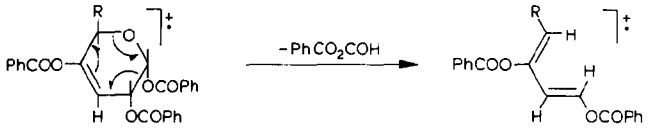
Important fragments derive from the loss of benzoic acid and the retro-Diels–



R = CH_2OCOPh (for hexopyranoses)
R = H (for pentopyranoses)

Scheme 2

Alder reaction, with successive splitting of the mixed anhydride of benzoic and formic acid; this is presented in Scheme 3.



R = CH_2OCOPh (for hexopyranoses)
R = H (for pentopyranoses)

Scheme 3

A general fragmentation pattern proposed for penta-*O*-benzoylaldohexopyranoses is presented in Scheme 4, and is exemplified for penta-*O*-benzoyl-α-D-glucopyranose (**1**). The same scheme is observed for other penta-*O*-benzoylpyranoses, having the β-D-*gluco* (**2**), α-D-*galacto* (**4**), α-D-*manno* (**7**), and β-D-*manno* (**8**) configurations. For these compounds, the molecular ion was not detected; the base peak is due to *m/z* 105 $[C_6H_5CO]^+$.

The chain fission of the exocyclic part $[PhCO_2CH_2\cdot]$ is observed for most of them, but with low relative abundance. Successive losses of benzoic acid or benzoic anhydride occur, with high relative abundance, as, for example, *m/z* 428, 335, 323, and 306. The assignments for the significant ions noted are listed in Table I.

A general fragmentation pattern is proposed for penta-*O*-benzoylaldohexofuranoses; this is presented in Scheme 5, and exemplified for penta-*O*-benzoyl-α-D-glucofuranose (**3**). The same scheme is applicable to penta-*O*-benzoyl-α-D-galactofuranose (**5**) and penta-*O*-benzoyl-β-D-galactofuranose (**6**). The molecular ion is not observed, and the base peak is *m/z* 105 $[C_6H_5CO]^+$.

The characteristic chain-fission of the C-4–C-5 linkage gives rise to the fragments of the cyclic part, *m/z* 431, and that of the exocyclic part, *m/z* 269, which are present in good relative abundance in the spectra of the three compounds.

For the furanoses, the successive losses of benzoic acid and benzoic anhydride give rise to the different ions listed in Table I with their assignments. In this case, the ions have a lower relative abundance than for the pyranose derivatives, as the stabilization due to cyclic, resonance-stabilized structures has a lower probability.

For the tetra-*O*-benzoylaldopentopyranoses, the fragmentation pattern pro-

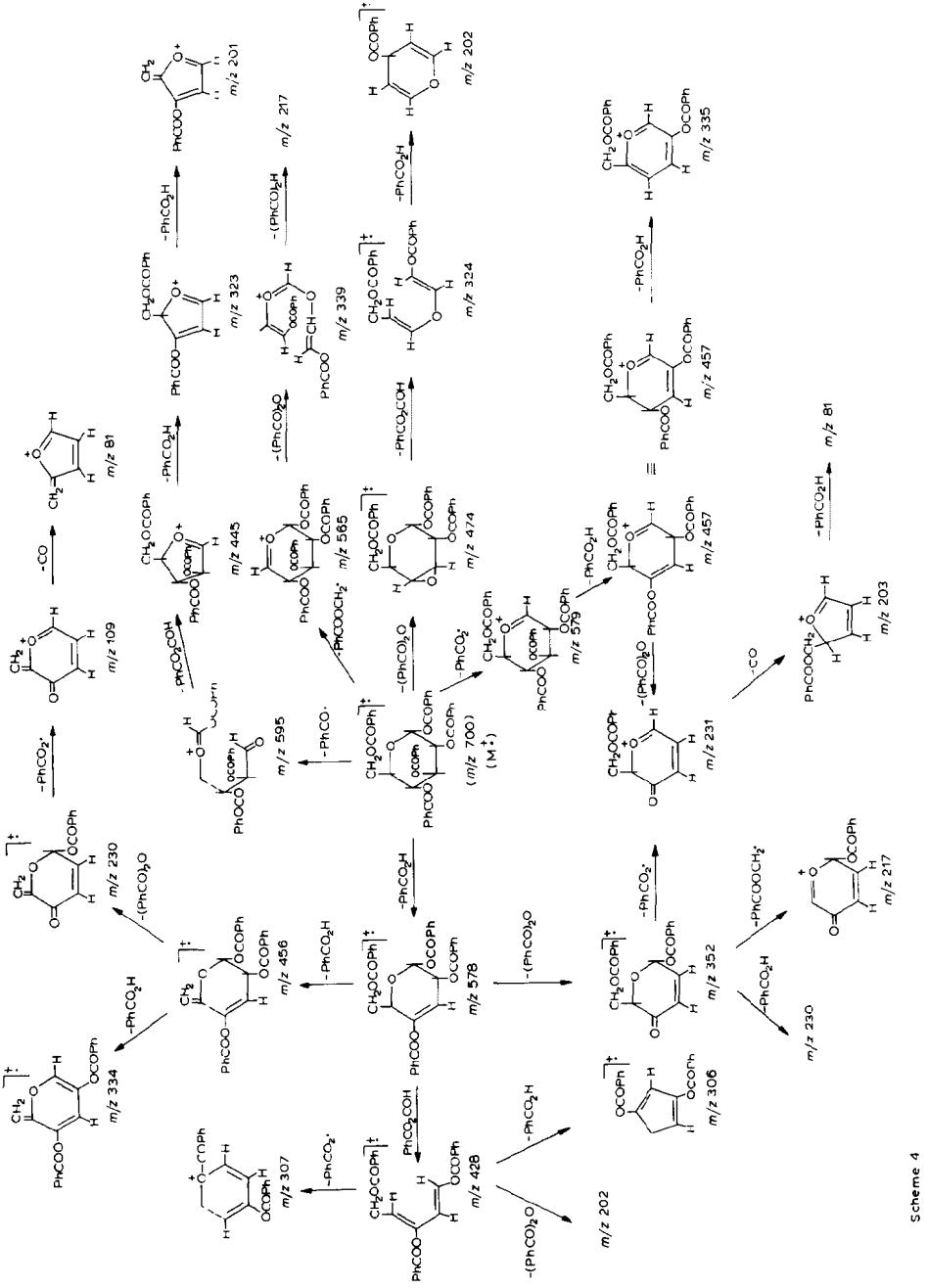
TABLE I

MAJOR FRAGMENTS RESULTING FROM ELECTRON-IMPACT IONIZATION OF PENTA-*O*-BENZOYL-α-D-GLUCOPYRANOSE (**1**), PENTA-*O*-BENZOYL-β-D-GLUCOPYRANOSE (**2**), PENTA-*O*-BENZOYL-α-D-GLUCOFURANOSE (**3**), PENTA-*O*-BENZOYL-α-D-GALACTOPYRANOSE (**4**), PENTA-*O*-BENZOYL-α-D-GALACTOFURANOSE (**5**), PENTA-*O*-BENZOYL-β-D-GALACTOFURANOSE (**6**), PENTA-*O*-BENZOYL-α-D-MANNOPYRANOSE (**7**), AND PENTA-*O*-BENZOYL-β-D-MANNOPYRANOSE (**8**)[a,b]

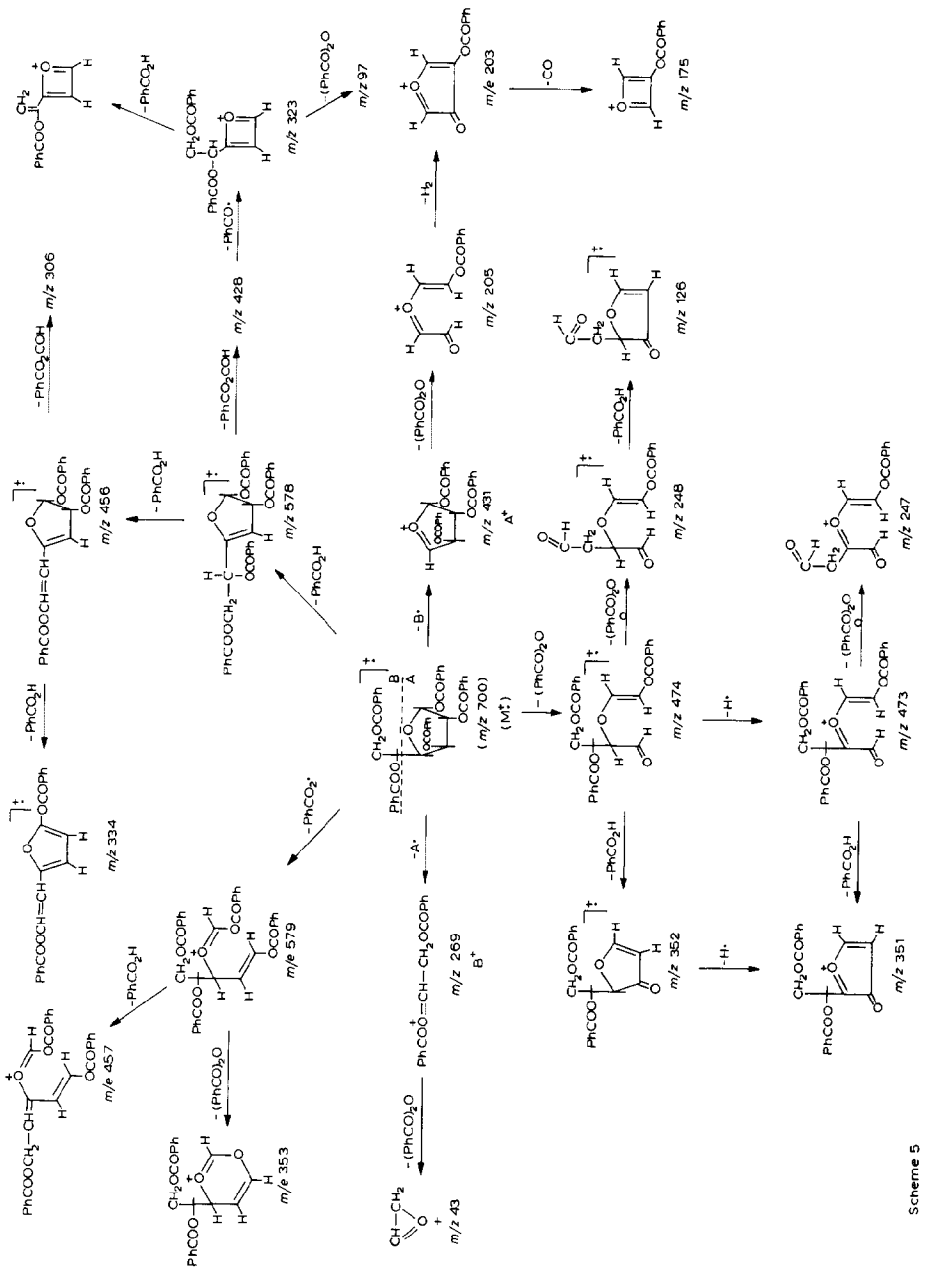
m/z	**1** *Int. (%)*	**2** *Int. (%)*	**4** *Int. (%)*	**7** *Int. (%)*	**8** *Int. (%)*	**3** *Int. (%)*	**5** *Int. (%)*	**6** *Int. (%)*	*Assignments*[c]
595	1.4	1.7	—	—	1.0	0.9	—	—	$M^+ - PhCO\cdot$
579	2.9	3.6	0.2	1.1	1.4	3.7	0.4	0.8	$M^+ - PhCO_2\cdot$
578	—	0.4	0.2	—	0.8	0.8	—	—	$M^+ - PhCO_2H$
565	0.5	0.8	—	—	0.4	—	—	—	$M^+ - PhCO_2CH_2\cdot$
474	2.4	2.3	0.1	0.5	2.1	—	0.2	0.3	$M^+ - (PhCO)_2O$
473	—	—	—	—	—	0.6	0.6	1.0	$M^+ - (PhCO)_2O - H\cdot$
457	1.2	0.6	—	0.4	0.3	0.7	—	—	$M^+ - PhCO_2H - PhCO_2\cdot$
456	3.9	1.5	0.2	1.3	0.9	2.0	0.4	0.1	$M^+ - 2PhCO_2H$
432	—	—	—	—	—	1.9	0.7	0.8	$M^+ - PhCO_2C_2H_2CO_2Ph$
431	0.9[d]	0.8[d]	—	—	0.4[d]	6.8	2.4	2.5	A^+
430	3.4	4.0	0.4	0.8	2.4	—	—	—	$M^+ - PhCO_2C_2H_2CO_2Ph - H_2$
429	20.6	21.9	1.6	4.1	13.3	—	—	—	$M^+ - PhCO_2COH - PhCO_2\cdot$
428	62.8	70.1	4.0	13.2	45.0	0.8	—	0.1	$M^+ - PhCO_2H - PhCO_2COH$
369	1.4	1.2	0.4	0.4	0.8	1.3	0.2	0.1	$M^+ - (PhCO)_2O - PhCO\cdot$
353	0.8	1.0	—	—	—	3.9	0.6	0.5	$M^+ - (PhCO)_2O - PhCO_2\cdot$
352	1.8	2.9	0.2	0.5	0.6	16.3	2.4	1.5	$M^+ - (PhCO)_2O - PhCO_2H$
339	1.2	2.8	—	0.5	0.9	2.9	0.5	0.3	$M^+ - (PhCO)_2O - PhCO_2CH_2\cdot$
335	11.9	11.4	0.7	4.0	3.2	8.7	1.7	2.3	$M^+ - 2PhCO_2H - PhCO_2\cdot$
334	18.0	21.6	0.9	7.2	5.1	—	5.8	6.8	$M^+ - 3PhCO_2H$
332	5.9	7.3	0.7	1.4	3.6	—	0.4	0.3	$M^+ - 3PhCO_2H - H_2$
331	26.3	32.5	3.1	6.0	16.4	1.3	1.1	1.0	$(PhCO)_3O^+$
324	8.1	9.9	1.3	7.2	5.1	0.7	0.1	0.1	$M^+ - (PhCO)_2O - PhCO_2COH$
323	39.9	51.4	6.3	11.7	26.1	0.7	0.2	0.1	$M^+ - PhCO_2H - PhCO_2COH - PhCO\cdot$
321	14.1	18.1	0.8	4.9	3.9	—	—	—	$M^+ - 2PhCO_2H - PhCO_2CH_2\cdot$
307	1.7	1.9	0.5	0.7	1.2	—	—	—	$M^+ - PhCO_2H - PhCO_2COH - PhCO_2\cdot$
306	8.6	10.5	1.8	3.0	5.4	0.4	—	0.3	$M^+ - 2PhCO_2H - PhCO_2COH$
282	3.4	—	—	—	—	0.9	0.2	0.1	$M^+ - 2PhCO_2H - PhCO_2COH - H\cdot$
281	16.6	20.6	2.2	3.9	8.6	—	—	—	$(PhCO_2)_2C_3H_3^+$
	—	—	—	—	—	2.3	0.7	0.5	$A^+ - PhCO_2COH$

272	—	—	—	—	—	8.6	3.0	2.0	$C_{15}H_{12}O_5^+$
270	—	—	—	—	—	1.5	0.5	0.5	$PhCO_2C_2H_4CO_2Ph^+$
269	1.0[d]	0.9[d]	—	0.4[d]	0.4[d]	8.6	3.0	2.0	B^+
248	0.6	1.0	—	—	0.4	0.5	0.2	0.5	$M^+ - 2(PhCO)_2O$
247	—	—	—	—	—	2.6	0.9	0.5	$M^+ - 2(PhCO)_2O - H\cdot$
231	6.7	9.4	0.7	2.6	1.5	7.2	1.7	1.3	$M^+ - PhCO_2H - (PhCO)_2O - PhCO_2\cdot$
230	10.0	12.4	0.7	4.9	3.7	47.8	10.3	6.8	$M^+ - 2PhCO_2H - (PhCO)_2O$
227	1.2	2.1	0.4	0.4	0.8	4.4	1.2	0.6	$(PhCO)_2OH^+$
217	0.5	1.6	—	—	0.4	4.4	0.2	0.3	$M^+ - PhCO_2H - (PhCO)_2O - PhCO_2CH_2\cdot$
205	—	—	—	—	—	0.7	0.2	0.1	$A^+ - (PhCO)_2O$
203	1.7	3.6	0.5	0.9	1.1	0.8	0.2	—	$M^+ - (PhCO)_2O - PhCO_2COH - PhCO_2\cdot$
202	10.9	25.9	2.0	3.6	7.1	2.3	0.6	0.5	$M^+ - (PhCO)_2O - PhCO_2COH - PhCO_2H$
201	6.7	17.1	1.6	3.4	4.3	1.9	0.5	0.3	$M^+ - 2PhCO_2H - PhCO_2COH - PhCO_2\cdot$
188	0.6	1.1	—	—	—	1.9	0.7	0.6	$M^+ - 3PhCO_2H - PhCO_2C_2H$
181	0.6	8.9	0.3	0.2	0.4	0.6	0.4	0.2	$M^+ - (PhCO)_2O - PhCO_2H - PhCO_2COH - PhCO_2\cdot$
177	1.2	3.5	0.4	0.5	0.8	0.7	0.2	0.3	$M^+ - (PhCO)_2O - PhCO_2COH - C_2H_2 - PhCO_2\cdot$
175	0.5	1.8	0.2	0.3	0.4	0.5	0.2	0.3	$M^+ - (PhCO)_2O - PhCO_2COH - CO - PhCO_2\cdot$
126	0.6	1.6	0.3	—	0.5	1.3	0.5	0.3	$M^+ - 2(PhCO)_2O - PhCO_2H$
122	1.8	71.0	0.5	1.8	1.5	10.0	0.7	3.3	$PhCO_2H^+$
109	1.6	3.7	0.5	0.7	0.5	1.0	0.9	0.5	$M^+ - 2PhCO_2H - (PhCO)_2O - PhCO_2\cdot$
107	3.6	10.0	0.9	1.6	2.8	2.8	1.0	0.9	$M^+ - 3PhCO_2H - (PhCO)_2O - H\cdot$
106	64.7	99.9	11.9	26.1	50.1	52.6	13.6	11.3	$C_6H_6CO^+$
105	100	100	100	100	100	100	100	100	$C_6H_5CO^+$
97	1.0	2.6	0.6	0.4	0.6	1.2	1.5	0.8	$M^+ - PhCO_2H - (PhCO)_2O - PhCO_2COH - PhCO\cdot$
81	0.7	3.3	0.7	0.5	0.7	0.8	1.6	0.5	$M^+ - 2PhCO_2H - (PhCO)_2O - CO - PhCO_2\cdot$
78	1.7	12.2	1.0	1.7	2.5	3.4	1.1	1.0	$C_6H_6^+$
77	15.5	89.9	11.9	18.1	30.6	39.1	13.9	14.2	$C_6H_5^+$
69	7.4	0.4	0.4	—	—	—	1.8	0.7	$M^+ - 2PhCO_2H - (PhCO)_2O - PhCO_2COH - CO - PhCO\cdot$
57	—	—	0.8[d]	0.9[d]	—	2.0	2.8	1.3	$A^+ - PhCO_2H - (PhCO)_2O - C_2H_2$
55	—	—	—	—	—	0.4	1.5	0.6	$A^+ - PhCO_2H - (PhCO)_2O - CO$
52	—	4.4	—	—	0.3	3.2	0.1	0.3	$C_4H_4^+$
51	2.2	28.5	1.4	2.7	2.5	5.8	1.6	1.8	$C_4H_3^+$
44	0.6	3.2	0.4	0.6	—	1.9	0.9	0.5	$PhCO_2C_2H_4CO_2Ph^+ - (PhCO)_2O$
43	—	—	1.4[d]	0.5[d]	—	1.2	10.5	2.0	$B^+ - (PhCO)_2O$

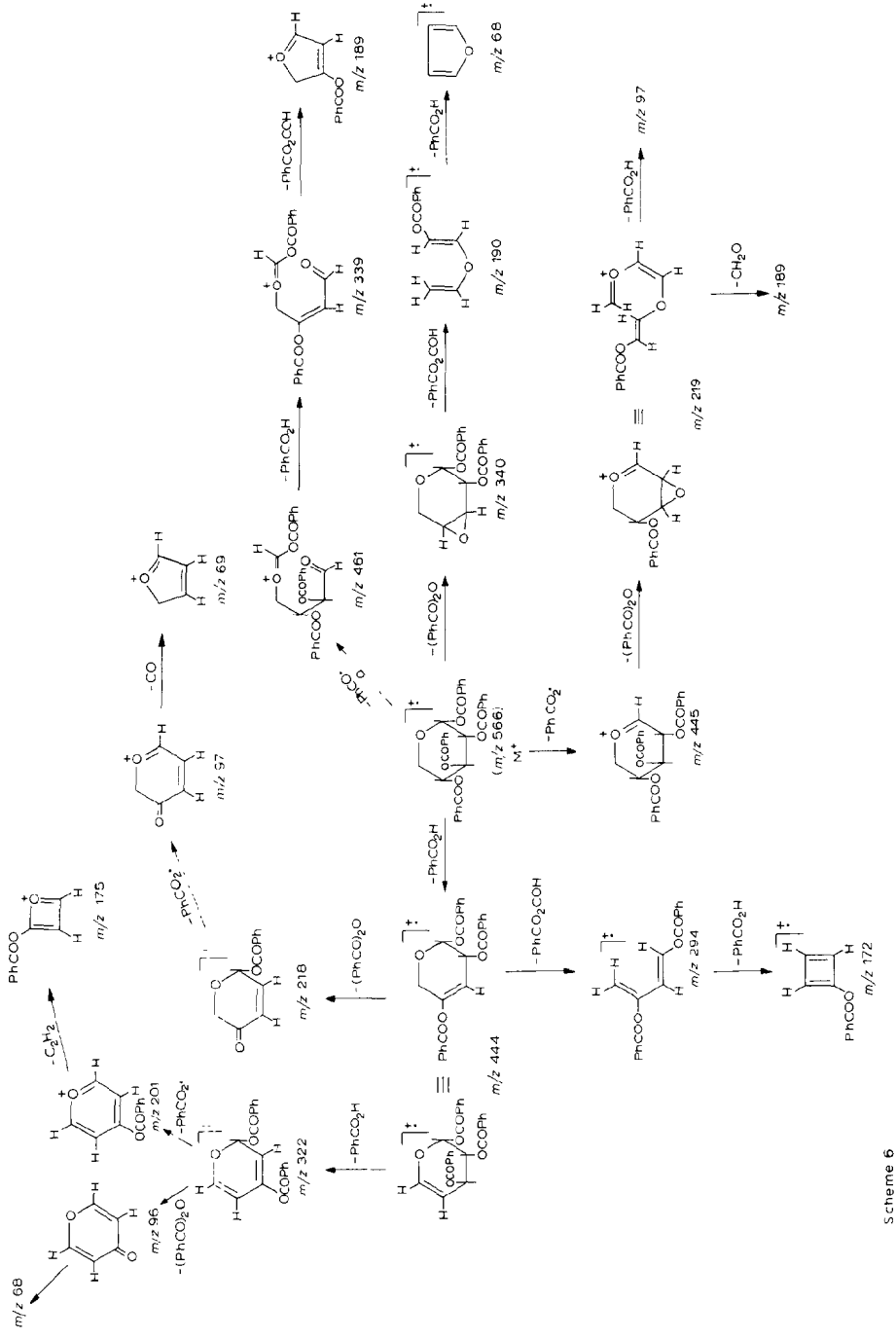
[a]Expressed as percent of the base peak. [b]For the fragmentation pattern, see Schemes 4 and 5. [c]Assignments are assumed. [d]Rearrangements in the spectrometer cannot be excluded.



Scheme 4



Scheme 5



Scheme 6

TABLE II

MAJOR FRAGMENTS OF ELECTRON-IMPACT IONIZATION OF TETRA-*O*-BENZOYL-α-D-XYLOPYRANOSE (**9**), TETRA-*O*-BENZOYL-α-D-LYXOPYRANOSE (**10**), TETRA-*O*-BENZOYL-β-D-RIBOPYRANOSE (**11**), AND TETRA-*O*-BENZOYL-β L-ARABINOPYRANOSE (**12**)[a,b]

m/z	**9** *Int. (%)*	**10** *Int. (%)*	**11** *Int. (%)*	**12** *Int. (%)*	*Assignments*[c]
461	0.8	0.9	—	—	$M^+ - PhCO\cdot$
460	2.6	—	—	0.4	$M^+ - PhCOH$
445	1.1	0.6	0.6	0.6	$M^+ - PhCO_2\cdot$
444	4.1	1.8	2.0	2.0	$M^+ - PhCO_2H$
340	4.7	3.0	1.0	2.9	$M^+ - (PhCO)_2O$
339	22.5	14.6	4.9	13.5	$M^+ - PhCO_2H - PhCO\cdot$ or $M^+ - (PhCO)_2O - H\cdot$
332	4.0	1.6	0.6	1.2	$(PhCO_2)_2CHPh^+$
331	17.7	7.0	2.6	5.6	$(PhCO)_3O^+$
323	2.4	0.8	—	0.9	$M^+ - PhCO_2H - PhCO_2\cdot$
322	2.0	0.8	0.6	—	$M^+ - 2PhCO_2H$
296	4.1	2.1	0.7	1.8	$M^+ - 2PhCO_2H - C_2H_2$
295	30.4	15.7	4.9	13.9	$M^+ - PhCO_2COH - PhCO_2\cdot$
294	96.0	73.9	24.1	66.1	$M^+ - PhCO_2COH - PhCO_2H$
281	3.7	1.4	0.5	1.2	$M^+ - PhCO_2COH - CH_2O - PhCO\cdot$
254	2.2	0.4	—	0.3	$M^+ - (PhCO_2)_2C_2H_2 - CO_2$
238	0.8	1.0	—	0.8	$M^+ - 2PhCO_2H - CH_2O - C_2H_2 - CO$
227	0.3	—	—	—	$(PhCO)_2OH^+$
219	0.8	0.6	—	—	$M^+ - (PhCO)_2O - PhCO_2\cdot$
218	2.9	2.5	0.4	0.4	$M^+ - (PhCO)_2O - PhCO_2H$
202	2.7	0.7	0.4	1.1	$M^+ - (PhCO)_2O - PhCOH - CH_2O - H_2$
201	10.6	2.6	1.9	4.8	$M^+ - 2PhCO_2H - PhCO_2\cdot$
190	0.4	0.3	—	—	$M^+ - (PhCO)_2O - PhCO_2COH$
189	1.2	1.4	—	1.1	$M^+ - (PhCO)_2O - CH_2O - PhCO_2\cdot$
175	2.3	1.8	0.4	1.6	$M^+ - 2PhCO_2H - C_2H_2 - PhCO_2\cdot$
172	0.8	0.9	—	0.8	$M^+ - 2PhCO_2H - PhCO_2COH$
122	2.5	23.0	0.5	0.8	$PhCO_2H^+$
106	94.2	43.1	20.9	43.5	$C_6H_6CO^+$
105	97.2	100	100	100	$C_6H_5CO^+$
97	2.0	0.4	—	0.5	$M^+ - PhCO_2H - (PhCO)_2O - PhCO_2\cdot$
96	1.0	—	—	—	$M^+ - 2PhCO_2H - (PhCO)_2O$
81	2.7	0.4	0.4	0.5	$M^+ - (PhCO)_2O - PhCO_2H - CH_2O - PhCOH - H\cdot$
78	18.5	2.8	1.4	2.7	$C_6H_6^+$
77	100	30.5	19.6	34.4	$C_6H_5^+$
69	2.2	—	—	—	$M^+ - PhCO_2H - (PhCO)_2O - CO - PhCO_2\cdot$
68	1.4	0.3	—	0.3	$M^+ - (PhCO)_2O - 2PhCO_2H - CO$
51	27.9	6.3	1.5	2.2	$C_4H_3^+$
50	4.8	1.4	—	0.6	$M^+ - 3PhCO_2H - PhCO_2COH$

[a]Expressed as percent of the base peak. [b]For the fragmentation pattern, see Scheme 6. [c]Assignments are assumed.

posed in Scheme 6 is exemplified for tetra-*O*-benzoyl-α-D-xylopyranose (**9**). The same scheme is applicable to the other tetra-*O*-benzoylpyranoses having the α-D-*lyxo* (**10**), β-D-*ribo* (**11**), and β-L-*arabino* (**12**) configurations. The molecular ion is not observed, and the base peak is *m/z* 105 $[C_6H_5CO]^+$ or *m/z* 77 $[C_6H_5]^+$. The fragmentation of these compounds is similar to those observed for the

TABLE III

CHARACTERISTIC FRAGMENTS OF ELECTRON-IMPACT IONIZATION OF PER-*O*-BENZOYLATED ALDOHEXOPYRANOSES, ALDOHEXOFURANOSES, AND ALDOPENTOPYRANOSES, USEFUL FOR THEIR IDENTIFICATION

Per-O-benzoylated compounds	m/z						
Aldohexopyranose	565	—	—	429	428	—	[a]
Aldohexofuranose	—	—	431	—	[a]	—	269
Aldopentopyranose	—	444	—	—	—	295	—

[a]Present in relatively low abundance.

hexopyranoses, and the fragments *m/z* 339 and 294 appear in the region of higher relative abundance. The significant ions are assigned and listed in Table II.

From comparison of the fragments from penta-*O*-benzoyl-aldohexopyranoses and -aldohexofuranoses, the ions of diagnostic value can be selected, as seen from Table I. Even so, in the mass spectrometer, there might be a rearrangement of the cyclic structures, but these fragments should appear with very low abundance, compared to the other ions present, and so we can propose the fragments that can be used to differentiate the two types of structure; these are listed in Table III.

The ions of *m/z* 429 and 428 are present in much higher relative abundance for the hexopyranoses, due to the possible stabilization of these ions by resonance.

Interpretation of the mass spectra of per-*O*-benzoylated derivatives of cyclic hexoses and pentoses has been shown to be useful, as characteristic splitting fragments could be found for each group of compounds; these are shown in Table III. Their use could also be convenient for interpretation of the mass spectra of benzoylated disaccharides or more-complex structures.

EXPERIMENTAL

The compounds studied were prepared by methods described in the literature: penta-*O*-benzoyl-α-D-glucopyranose[6] (**1**), penta-*O*-benzoyl-β-D-glucopyranose[7] (**2**), penta-*O*-benzoyl-α-D-glucofuranose[8] (**3**), penta-*O*-benzoyl-α-D-galactopyranose[9] (**4**), penta-*O*-benzoyl-α-D-galactofuranose[5] (**5**), penta-*O*-benzoyl-β-D-galactofuranose[5] (**6**), penta-*O*-benzoyl-α-D-mannopyranose[6] (**7**), penta-*O*-benzoyl-β-D-mannopyranose[10] (**8**), tetra-*O*-benzoyl-α-D-xylopyranose[11] (**9**), tetra-*O*-benzoyl-α-D-lyxopyranose[12] (**10**), tetra-*O*-benzoyl-β-D-ribopyranose[13] (**11**), and tetra-*O*-benzoyl-β-L-arabinopyranose[14] (**12**).

The mass spectra of compounds **1–3** and **7–12** 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°), and those of compounds **4–6** were recorded with a Varian Mat-112-S mass spectrometer operated in the same way. The intensities, expressed as percentage of total ionization, are listed in Tables I and II.

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