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Mass Spectra of Some Per-*O*-benzoyl-alditols and -aldobiitols

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Electron impact mass spectra of some per-*O*-benzoyl-alditols and -aldobiitols are reported and the major fragmentation pathways are discussed.

INTRODUCTION

The mass spectra of acetylated cyclic[1] and acyclic[2] monosaccharide derivatives and those of benzoylated aldopyranoses and furanoses[3] have been reported. The reported mass spectra of acyclic benzoylated derivatives have been limited to aldononitriles having three to six carbon chains and to the related 5-(polybenzoyloxy alkyl) tetrazoles.[4] Thompson and Cory[5] reported only a few fragments of the mass spectra of some per-*O*-benzoylated alditols.

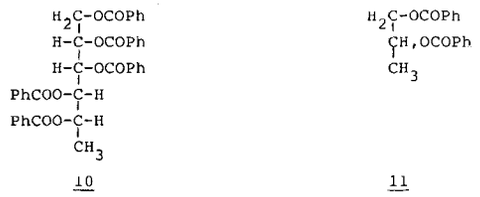
The fragmentation pathways proposed for penta-*O*-benzoylaldopyranoses[3] and per-*O*-benzoylalditols are now employed for the interpretation of the mass spectra of more complex molecules, such as the per-*O*-benzoyl-aldobiitols. These compounds show the fragmentation of the glycosidic bond and each of the fragments formed gives a characteristic fragmentation pattern.

RESULTS AND DISCUSSION

The electron impact ionization mass spectra (see Tables 1 and 2) were measured for the per-*O*-benzoylalditols shown in Fig. 1 (compounds **1–9**), the per-*O*-benzoyl-deoxyalditols shown in Fig. 2 (**10** and **11**) and for the per-*O*-benzoylaldobiitols shown in Fig. 3 (**12–17**).

The mass spectra of these substances, like those of other polybenzoylated compounds, do not show the molecular ion owing to the easy loss of benzoic acid. Successive losses of benzoic acid and benzoic anhydride are characteristic,[3,4] the base peak being the ion of *m/z* 105 $[PhCO]^+$. Also, intense peaks of *m/z* 331 $[(PhCO)_3O]^+$, *m/z* 227 $[(PhCO)_2OH]^+$, *m/z* 122 $[PhCO_2H]^+$ and *m/z* 106 $[C_6H_6CO]^+$ are common in the mass spectra of all the perbenzoylated compounds, and they are not of diagnostic value.

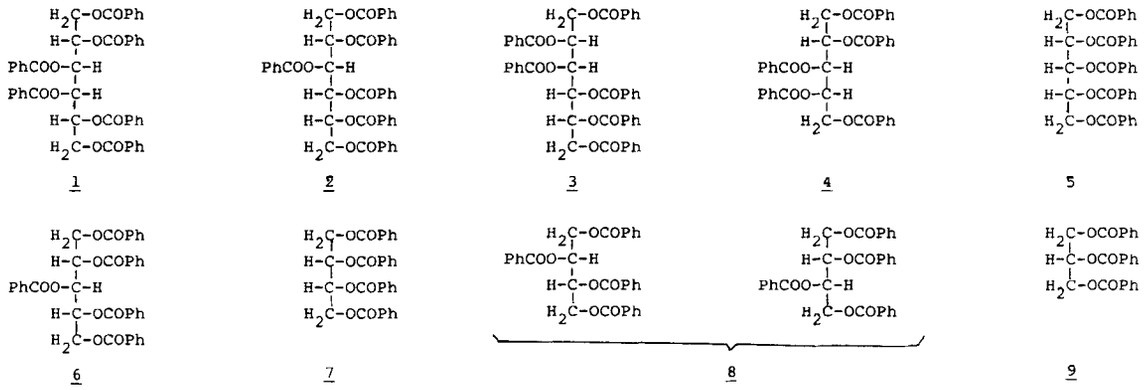
A general fragmentation pathway for the sugar chain allows the correlation between chains of different



10 11

10: penta-O-benzoyl-6-deoxy-L-mannitol.
11: 1,2(R,S)-di-O-benzoyl-propanediol.

Figure 2. Structures of compounds **10** and **11**.



1 2 3 4 5

6 7 8 9

1: hexa-O-benzoyl-D-galactitol; 2: hexa-O-benzoyl-D-glucitol; 3: hexa-O-benzoyl-D-mannitol;
4: penta-O-benzoyl-L-arabinitol; 5: penta-O-benzoyl-D-ribitol; 6: penta-O-benzoyl-D-xylitol;
7: tetra-O-benzoyl-D-erythrytol; 8: tetra-O-benzoyl-D,L-threitol; 9: tri-O-benzoyl-glycerol.

Figure 1. Structures of compounds **1–9**

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Table 1. Major fragments of electron impact ionization of per-*O*-benzoylalditols (1–11)[a]

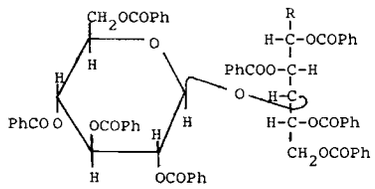
m/z	1	2	3	4	5	6	7	8	9	10	11	Assignments[b]
671	0.8	0.3	0.4									A_5^+
562	3.0	1.1	1.0									$M_h^{+\cdot} - 2\ PhCO_2H$
538	6.4	1.6	1.3									$M_t^{+\cdot}$
537	20.1	4.7	3.7			1.8						A_4^+
458	2.9	1.1	1.1									$M_h^{+\cdot} - (PhCO)_2O - PhCO_2H$
445	1.9	1.2	1.1									$A_5^+ - (PhCO)_2O$
416							0.6	15.9				$M_t^{+\cdot} - PhCO_2H$
415	1.0	0.3	0.3									$A_4^+ - PhCO_2H$
404	6.3	1.9	2.0				0.7	11.5				$M_g^{+\cdot}$
403	24.9	7.7	7.0			15.6	2.5	43.5				A_3^+
336	10.8	5.1	6.3									$M_h^{+\cdot} - 2\ PhCO_2H - (PhCO)_2O$
331	5.4	1.8	2.0	0.5	0.9	4.4	1.5	16.1	0.9			$[(PhCO)_3O]^+$
311	9.3	5.0	4.4									$A_4^+ - (PhCO)_2O$
294	7.9	3.2	3.3				31.9	31.9				$M_t^{+\cdot} - 2\ PhCO_2H$
293	1.3	0.4	0.5	0.4	0.9	0.6						$A_4^+ - 2\ PhCOH$
282									63.4			$M_g^{+\cdot} - PhCO_2H$
281	2.7	0.9	0.9	0.9	2.1	2.9	1.4	17.5	0.5	0.4		$A_3^+ - PhCO_2H$
270	3.6	1.4	1.4			3.1	4.9	100	2.1			$[PhCO_2CH_2CH_2OCOPh]^{+\cdot}$
269	21.3	8.8	9.1	0.4	1.0	18.1	29.8	65.8	12.5			A_2^+
214	9.4	5.4	5.4									$M_h^{+\cdot} - 3\ PhCO_2H - (PhCO)_2O$
201	3.4	2.0	2.0									$A_5^+ - 2\ PhCO_2H - (PhCO)_2O$
190							8.5	18.7				$M_t^{+\cdot} - PhCO_2H - (PhCO)_2O$
177	2.5	0.6		0.5	1.0	1.8	20.3	4.7	30.7			$A_3^+ - (PhCO)_2O$
163										0.4	0.5	$M_g^{+\cdot} - PhCO_2^{\cdot}$
160									19.6			$M_g^{+\cdot} - 2\ PhCO_2H$
149				3.2	10.3	1.0						$A_3^+ - (PhCO)_2O - CO$
149										0.5	1.3	A_6^+
147				0.4	1.2	0.4		0.4	0.3			$A_2^+ - PhCO_2H$
135				0.6	2.2		0.5	0.9	0.6	3.0		A_1^+
122	4.6	2.3	1.5	37.2	5.7	4.2	6.0	7.1	4.5	6.5	87.5	$[PhCO_2H]^{+\cdot}$
106	52.1	16.9	13.8	6.7	7.5	41.0	51.6	31.9	80.2	12.6	57.4	$[C_6H_6CO]^{+\cdot}$
105	100	100	100	79.4	100	100	100	31.9	100	100	100	$[PhCO]^+$
79				100	4.3	0.4	55.4	1.9				$[PhCO]^+ - C_2H_2$
77	25.7	7.7	5.8	58.8	67.9	40.3	67.0	65.8	95.2	89.3	97.3	$[C_6H_5]^+$
69										10.2		$A_8^+ - (PhCO)_2O - PhCO_2H$
57										10.7	0.8	$A_7^+ - (PhCO)_2O$
51	6.1	1.6	1.3	75.0	28.7	10.9	23.6	44.3	21.0	41.7	98.9	$[C_4H_3]^+$

[a] Intensities are expressed as a percentage of total ionization.

[b] $M_h = M_{hexa\text{-}O\text{-}benzoylhexitol}$; $M_p = M_{penta\text{-}O\text{-}benzoylpentitol}$; $M_t = M_{tetra\text{-}O\text{-}benzoyltetritol}$; $M_g = M_{tri\text{-}O\text{-}benzoylglycerol}$; $M_{g'} = M_{1,2\text{-}(R,S)\text{-}di\text{-}O\text{-}benzoylglycerol}$; A_1 = fragment of one carbon with its benzoyloxy group; A_2 = fragment of two carbons with their benzoyloxy groups; A_3 = fragment of three carbons with their benzoyloxy groups; A_4 = fragment of four carbons with their benzoyloxy groups; A_5 = fragment of five carbons with their benzoyloxy groups; A_6 = fragment of two carbons with one benzoyloxy group; A_7 = fragment of three carbons with two benzoyloxy groups; A_8 = fragmentof four carbons with three benzoyloxy groups.

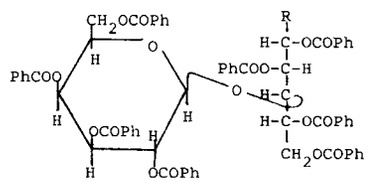
length. Thus, a similar fragmentation pattern is observed for hexitols and for other alditols with shorter chains. Therefore, we now propose a general nomenclature for the chain cuts: A_1 is a fragment of one carbon with its benzoyloxy group, A_2 is a fragment of two carbons with their benzoyloxy groups, and so on (see footnote to Table 1).

The chain cuts, which give rise to shorter fragments, are of interest for structural assignments. Thus $[A_4]^+$ (*m/z* 537) is important in the hexitol derivatives and it is



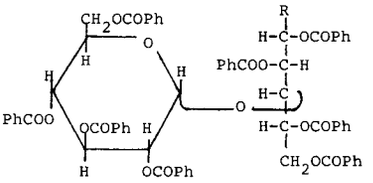
12 R : H

15 R : CH_2OCOPh



13 R : H

16 R : CH_2OCOPh



14 R : H

17 R : CH_2OCOPh

12: octa-O-benzoyl-3-O-(β-D-glucopyranosyl)-D-arabinitol;
13: octa-O-benzoyl-3-O-(β-D-galactopyranosyl)-D-arabinitol;
14: octa-O-benzoyl-3-O-(α-D-glucopyranosyl)-D-arabinitol;
15: nona-O-benzoyl-4-O-(β-D-glucopyranosyl)-D-glucitol;
16: nona-O-benzoyl-4-O-(β-D-galactopyranosyl)-D-glucitol;
17: nona-O-benzoyl-4-O-(α-D-glucopyranosyl)-D-glucitol.

Figure 3. Structures of compounds **12–17**.

Table 2. Major fragments of electron impact ionization of octa-*O*-benzoylaldobiitols[a]

m/z	12	13	14	Assignments[b]
672		0.1	0.4	$M_p^{+\cdot}$
579		0.1	3.1	$M^{+\cdot} - R_aO^{\cdot}$
551		0.1	0.2	$M^{+\cdot} - R'O^{\cdot}$
538	7.6	7.7	7.0	$M_t^{+\cdot}$
537	7.6	7.7	7.0	A_4^+
458	0.9	1.0	1.3	$M^{+\cdot} - PhCO_2OR_a$
429		1.2	0.6	$[R'OH]^{+\cdot} - HCO_2H - PhCO_2^{\cdot}$
428		0.1	1.6	$[R'OH]^{+\cdot} - HCO_2H - PhCO_2H$
404	2.3	2.8	2.6	$M_g^{+\cdot}$
403	8.9	10.0	10.5	A_3^+
336	3.1	5.0	4.1	$M^{+\cdot} - PhCO_2OR_a - PhCO_2H$
335	0.8	1.3	1.8	$M^{+\cdot} - 2\ PhCO_2H - R_aO^{\cdot}$
331	1.7	2.5	2.8	$[(PhCO)_3O]^+$
324		0.1	0.4	$M^{+\cdot} - (PhCO)_2O - HCO_2R_a$
294	2.4	3.3	4.3	$M_t^{+\cdot} - 2\ PhCO_2H$
282	1.2	1.4	1.7	$M_g^{+\cdot} - PhCO_2H$
281	0.9	1.3	1.7	$A_3^+ - PhCO_2H$
270	1.2	1.7	1.9	$[PhCO_2CH_2CH_2CO_2Ph]^{+\cdot}$
269	6.8	9.7	11.3	A_2^+
202		0.3	1.0	$M_p^{+\cdot} - 2\ PhCO_2H - (PhCO)_2O$
201	0.8	1.7	2.3	$A_5^+ - 2\ PhCO_2H - (PhCO)_2O$
177	0.6	1.1	1.7	$A_3^+ - (PhCO)_2O$
135		0.1	0.7	A_1^+
122	9.6	3.0	10.0	$[PhCO_2H]^{+\cdot}$
106	14.2	87.0	98.0	$[C_6H_6CO]^{+\cdot}$
105	100	100	100	$[PhCO]^+$
77	21.8	45.0	38.0	$[C_6H_5]^+$
51	4.7	43.4	23.6	$[C_4H_3]^+$

[a] Intensities are expressed as a percentage of the total ionization.
[b] Abbreviations as in Table 1; R′ = benzoylated cyclic part of the molecule; R_a = benzoylated acyclic part of the molecule.

also detected in some pentitols. The difference in the intensities of these fragments, 20.1% and 1.8%, cannot be explained by steric or structural considerations. Similar intensity differences are observed for *m/z* 403 $[A_3]^+$, which is present in hexitol, pentitol and tetritol derivatives with intensities from 43.5 to 2.5%, and for *m/z* 269 $[A_2]^+$, which is present in compounds **1**–**9** with intensities from 65.4 to 0.4%.

This general fragmentation pattern may be extended to the deoxy derivatives **10** and **11**. In this case, the chain cuts have the same nomenclature, but the deoxy parts have some additional fragments A_6–A_8 (for their structures, see the footnote to Table 1).

The mass spectra of perbenzoylated aldobiitols show the fragmentation of the glycosidic bond giving rise to two fragments, which correspond to the pyranoid and alditol units of the molecule. Each of these fragments undergoes characteristic fragmentations and the resulting ions appear, occasionally in low abundances. However, an oversaturated run allows the achievement of information of diagnostic value.

The more important splittings around the glycosidic linkage are exemplified for compound **12** in Schemes 1 and 2.

The per-*O*-benzoylaldobiitols show the loss of the acyclic part of the molecule and the formation of cyclic fragments, then following the pathways proposed for the penta-*O*-benzoyl aldopyranoses.[1]

Scheme 1 postulates first the loss of benzoic anhydride and then the splitting of the cyclic part, with loss of the acyclic fragment as a formyl ester. The ion of *m/z* 324 is present in the three compounds, and it gives further splittings, as shown previously.[3]

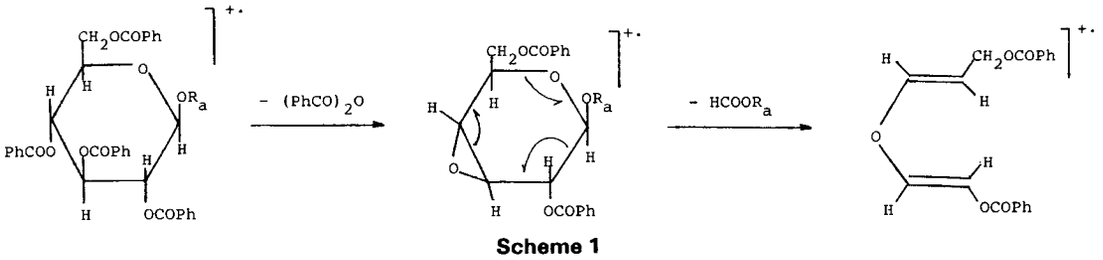
In Scheme 2 a splitting with rearrangement is proposed, which gives *m/z* 568, and the cyclic fragments formed from it. The migration of a benzoyl group from the cyclic part and the formation of the penta-*O*-benzoylpentitol is also proposed. We found several fragments corresponding to its further fragmentation.

The other possible mechanism is the migration and splitting of the acyclic part as an olefin, with formation of the cyclic ion at *m/z* 596, characteristic of benzoylated disaccharides.[6]

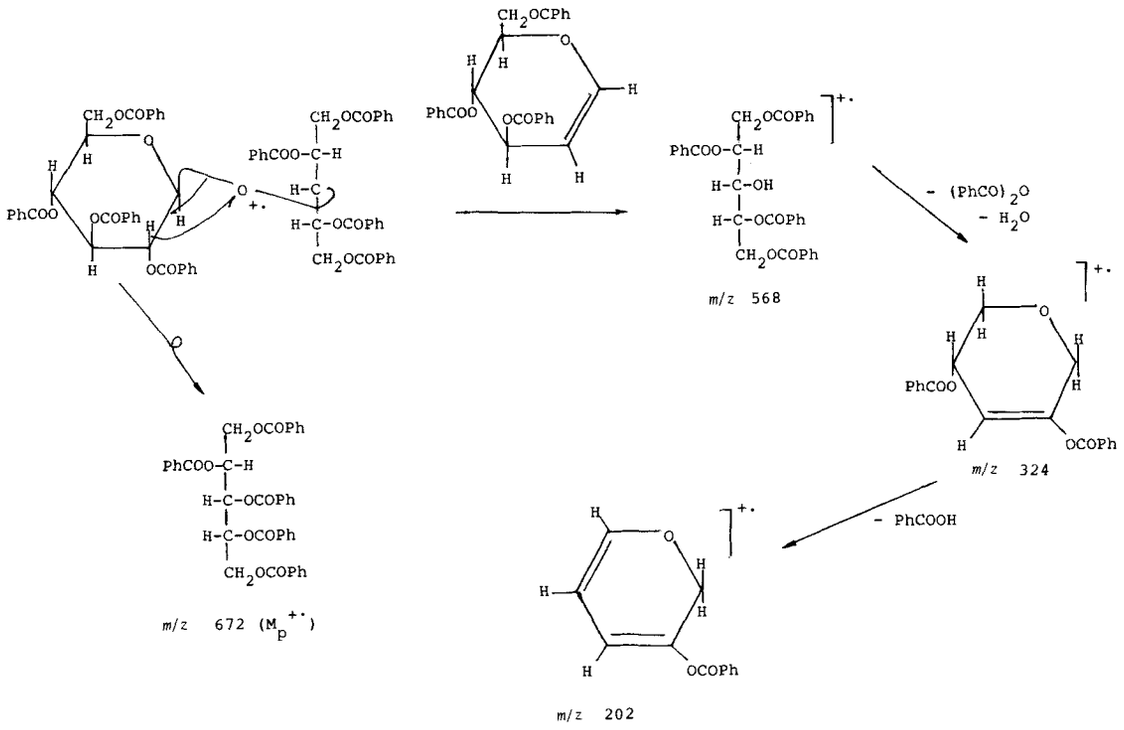
The mass spectra of nona-*O*-benzoylaldobiitols (**15**–**17**) show the expected fragments for the splitting of the glycosidic linkage giving *m/z* 579 (**15** 0.3%; **16** 2.0%; **17** 0.8%) and in Scheme 2 giving *m/z* 202 (**15** 0.5%, **16** 0.2%; **17** 0.1%). The formation of hexa-*O*-benzoylhexitols can be proposed by a rearrangement similar to that for the octa-*O*-benzoylaldobiitols. These fragments were not observed but we found those formed from them by the losses of benzoic acid and benzoic anhydride. Shorter chains and fragments from them are present, e.g. *m/z* 294 from M_t^+, *m/z* 284 from M_g^+, *m/z* 293 from A_4^+, *m/z* 201 from A_5^+ and *m/z* 281 and 177 from A_3^+.

In oversaturated runs, the characteristic fragments appear in high abundances, and they can be used for diagnostic purposes. These peaks are as follows: (i) for the cyclic part (tetra-*O*-benzoylhexo pyranosyl groups), *m/z* 579,[7] 429 and 428,[3], 324 and 202; (ii) for the acyclic part, hexa-*O*-benzoylhexitols, *m/z* 685, 684 and 578 and fragments corresponding to shorter chains; (iii) for the acyclic part of the shorter chains, the peaks mentioned under (ii) are absent, and for penta-*O*-benzoylpentitols *m/z* 672 and 537 are also absent.

This generalization allows one to extend the interpretation of the mass spectra to *O*-benzoylalditols of di- and tri-saccharides with different chain lengths and to other related structures.



Scheme 1



Scheme 2

EXPERIMENTAL

Mass spectra were obtained with a Varian MAT CH7-A mass spectrometer operated at 70 eV in the electron impact mode, coupled to a Varian MAT Data System 166 prepared for automatic subtraction, by the insertion technique (100–230 °C). The intensities, expressed as a percentage of the total ionization, are listed in Table 1.

Various compounds were prepared by methods described in the literature: hexa-*O*-benzoyl-D-galactitol (**1**),[8] hexa-*O*-benzoyl-D-glucitol (**2**),[9] hexa-*O*-benzoyl-D-mannitol (**3**),[10] penta-*O*-benzoyl-D-ribitol (**5**),[11] penta-*O*-benzoyl-D-xylitol (**6**),[12] tetra-*O*-benzoyl-D-erythritol (**7**),[13] tetra-*O*-benzoyl-D,L-threitol (**8**),[14] tri-*O*-benzoylglycerol (**9**),[15] penta-*O*-benzoyl-6-deoxy-L-mannitol (**10**),[16] 1,2-(*R*,S)-di-*O*-benzoylpropanediol (**11**),[16] octa-*O*-benzoyl-3-*O*-β-D-glucopyranosyl-D-arabinitol (**12**),[17] octa-*O*-benzoyl-3-*O*-β-D-galacto pyranosyl-D-arabinitol (**13**)[17] and octa-*O*-benzoyl-3-*O*-α-D-glucopyranosyl-D-arabinitol (**14**).[17]

For penta-*O*-benzoyl-L-arabinitol (**4**), L-arabinitol (3.5 g) was benzoylated with a mixture of 15 cm^3 of pyridine and 15 cm^3 of benzoyl chloride, adding the reagent in small portions and keeping the temperature between 60 and 80 °C. After 24 h at room temperature it was poured into ice–water to give compound **4** as a solid, which was recrystallized from methanol, (11.3 g, 72%), m.p. 145–146 °C, $[\alpha]_D$ − 15.3° (*c* 1, chloroform). Analysis: calculated for $C_{40}H_{32}O_{10}$, C 71.42, H 4.76; found, C 71.22, H 4.57%.

Synthesis of nona-*O*-benzoylaldobiitols

The disaccharide (1.2 g) was dissolved in 5 cm^3 of water and treated with sodium tetrahydroborate (0.22 g) in 3 cm^3 of water. After 3 h, Zeo Karb 225 (H^+) resin was added and the solution was filtered and evaporated several times with methanol. Purity was controlled by paper chromatography. The dry residue was dissolved in pyridine (15 cm^3) and benzoyl chloride (5 cm^3) was added, keeping the temperature between 60 and 80 °C. The reaction mixture was kept for 4 h at 60 °C, poured into ice–water and washed until a powder was obtained, which was recrystallized several times from acetone–water. Individual compounds were obtained as follows.

Nona-*O*-benzoyl-4-*O*-β-D-glucopyranosyl-D-glucitol (**15**) was obtained in 79.9% yield, m.p. 94–96°, $[\alpha]_D$ +10.8° (*c* 1, chloroform). Analysis: calculated for $C_{75}H_{60}O_{20}$, C 70.31, H 4.72; found, C 70.47, H 4.72%.

Nona-*O*-benzoyl-4-*O*-β-D-galactopyranosyl-D-glucitol (**16**) was obtained in 51% yield, m.p. 95–97°, $[\alpha]_D$ +57.0° (*c* 1, chloroform). Analysis: calculated for $C_{75}H_{60}O_{20}$, C 70.31, H 4.72; found, C 70.05, H 4.70%.

Nona-*O*-benzoyl-4-*O*-α-D-glucopyranosyl-D-glucitol (**17**) was obtained in 83.5% yield, m.p. 92–95 °C, $[\alpha]_D$ +80.5° (*c* 1, chloroform). Analysis: calculated for $C_{75}H_{60}O_{20}$, C 70.31, H 4.72; found, C 70.31, H 4.53.

Acknowledgements

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