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MASS SPECTROMETRY OF ALDITOL ACETATES: ORIGIN OF THE FRAGMENTS HAVING EVEN MASS NUMBERS

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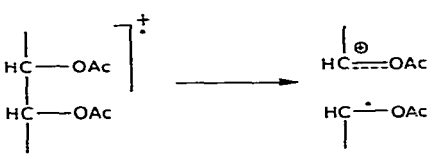
ABSTRACT

Most of the fragments formed during electron-impact mass spectrometry of alditol acetates have odd mass numbers, but fragments having even mass numbers are also formed. The origin of these fragments has been rationalized for fully acetylated 1-deoxyhexitols by using deuterated analogues and studying the metastable transitions. The previously known di-*O*-benzylidene-1-deoxy-L-gulitol was shown to be the 3,5 : 4,6-di-*O*-benzylidene derivative.

INTRODUCTION

During electron-impact mass spectrometry of alditol acetates, most fragments are obtained by cleavage of the alditol chain into an ion and a radical, as indicated below:



The primary fragments thus formed are further degraded, mainly by elimination(s)[1] of acetic acid (60) and ketene (42), to give fragments having odd mass numbers. However, fragments having even mass numbers are also obtained. Those of *m/e* 170 and 128 are the most prominent fragments of even mass for hexitol acetates (4% and 6% of the base peak, *m/e* 43, respectively) and are stronger in the mass spectra of 1(6)-deoxyhexitol acetates (8% and 11%, respectively).

In order to study the origin of these fragments, the mass spectra of 1-deoxyhexitol acetates and some specifically deuterated analogues have been investigated by studying metastable transitions.

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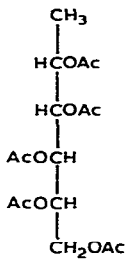
RESULTS AND DISCUSSION

Preparation of specifically deuterated derivatives

The penta-acetates of 1-deoxy-L-mannitol (**1**), 1-deoxy-L-galactitol-*1-d* (**2**), 1-deoxy-D-mannitol-*2-d* (**3**), and 1-deoxy-L-mannitol-*6-d* (**4**) were prepared by conventional methods.



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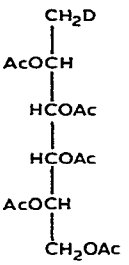

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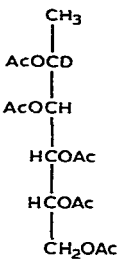

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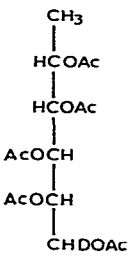

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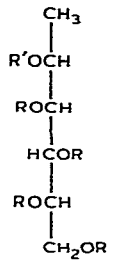
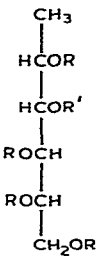
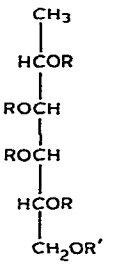
Two series of alditol acetates having trideuterioacetyl groups in specific positions (**5**, **5a**, **6**, **6a**, **7**, and **7a**) were prepared from di-*O*-benzylidene-1-deoxyhexitols. Two of these, 2,3:4,5-di-*O*-benzylidene-1-deoxy-D-galactitol and 2,5:4,6-di-*O*-benzylidene-1-deoxy-L-mannitol, had been characterized previously[2]. The third was the known di-*O*-benzylidene-1-deoxy-L-gulitol (di-*O*-benzylidene-6-deoxy-D-glucitol)[3], which, by analogy with 1,3:2,4-di-*O*-benzylidene-D-glucitol[4], should be 3,5:4,6-di-*O*-benzylidene-1-deoxy-L-gulitol (**8**). G.l.c.–m.s. of the product obtained after methylation, acid hydrolysis, and acetylation demonstrated the presence of a free hydroxyl group at C-2 in **8**. In the ^{1}H-n.m.r. spectrum of **8**, the signals for the benzylidene protons appeared at δ 5.61, demonstrating the presence of two 1,3-dioxane rings[5] and thereby confirming the expected structure.

The acetylated 1-deoxyhexitols (**5**, **6**, and **7**) having a trideuterioacetyl group on O-2, O-3, and O-6, respectively, were prepared from the foregoing di-*O*-benzylidene derivatives by trideuterioacetylation, followed by acetolysis. The corresponding analogues, **5a**, **6a**, and **7a**, containing trideuterioacetyl groups in all positions except

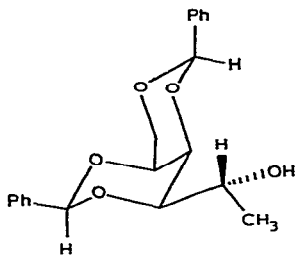






5 R = Ac, R′ = $COCD_3$ 6 R = Ac, R′ = $COCD_3$ 7 R = Ac, R′ = $COCD_3$

5a R = $COCD_3$, R′ = Ac 6a R = $COCD_3$, R′ = Ac 7a R = $COCD_3$, R′ = Ac



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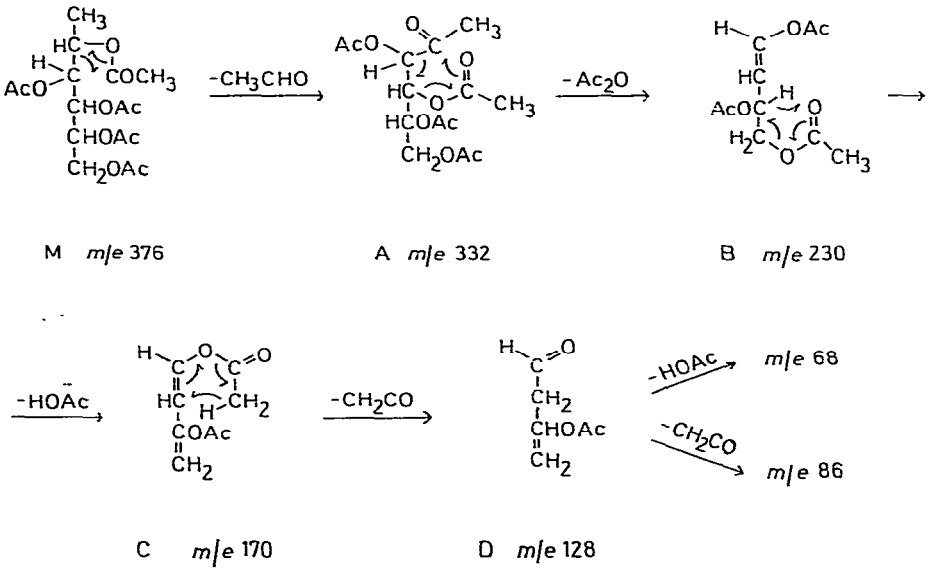
one (namely, O-2, O-3, and O-6, respectively) were prepared by acetylation of the di-*O*-benzylidene derivatives, followed by acetolysis with deuterated reagents. The mass spectra of **5**, **5a**, **6**, **6a**, **7**, and **7a** demonstrated that they had the expected substitution patterns and that no migration of *O*-acetyl groups had occurred during the preparations.

Mass spectrometry

The fact that the 1-deoxyhexitol derivatives studied (**1–7**) have different configurations (*manno-*, *galacto-*, or *gulo-*) should not complicate the results, as differences in mass spectra of stereoisomeric alditol acetates are insignificant.

Starting with *m/e* 128 in the mass spectrum of **1**, it was demonstrated that this ion is formed from *m/e* 170 by loss of 42 m.u., which suggests elimination of ketene. The ion *m/e* 170 is formed from *m/e* 230 by loss of 60 m.u., corresponding to elimination of acetic acid. More unexpectedly, it was found that the ion *m/e* 230 is formed



Scheme 1. Proposed fragmentation reactions in electron impact of a 1-deoxyhexitol penta-acetate (all the structures shown are ion radicals).

TABLE I

DEUTERIUM LABELLING IN IONS DERIVED FROM SPECIFICALLY DEUTERATED ANALOGUES OF 1-DEOXY-HEXITOL ACETATES

Substance	*D on C*	*$COCD_3$ on O*	*Number of deuterium atoms in ion*				
			M	*A*	*B*	*C*	*D*
1	—	—	0	0	0	0	0
2	1	—	1	0	0	0	0
3	2	—	1	0	0	0	0
4	6	—	1	1	1	1	1
5	—	2	3	3	0	0	0
5a	—	3,4,5,6	12	12	9	6	4
6	—	3	3	3	3	3	1
6a	—	2,4,5,6	12	12	6	3	3
7	—	6	3	3	3	0	0
7a	—	2,3,4,5	12	12	6	6	4

from *m/e* 332 by loss of 102 m.u., corresponding to elimination of acetic anhydride. Ions 42 or 60 m.u. larger than *m/e* 230 were not observed, indicating that acetic anhydride is eliminated as such in the formation of this ion.

The ion *m/e* 332 was too weak to be observed in the ordinary mass spectrum, and therefore its parent ion could not be determined. However, it is only 44 m.u. smaller than the molecular ion, *m/e* 376 (which was not observed), and is most probably formed therefrom by elimination of acetaldehyde. This reaction (M→A in Scheme 1) is analogous to the loss of formaldehyde from the molecular ion on electron impact of 1,2-diacetoxyethane[6].

Similar studies of the specifically deuterated analogues (Table I) gave more detailed information. That C-1 and C-2 are lost in the elimination of acetaldehyde (M→A) was indicated by the loss of the deuterium atom from both **2** and **3** in this step. In agreement with the assumed mechanism, no deuterium from *O*-trideuterioacetyl groups was lost in this step. The reaction is assumed to proceed as suggested by Sasaki *et al.*[6].

In the next step (A→B), acetic anhydride is eliminated. That all of the hydrogen atoms in the acetic anhydride are derived from acetyl groups is evident, *e.g.*, from the fragmentation of **6a**, from which 6 deuterium atoms were lost in this step. From the fragmentation of **5**, it is evident that the acetyl group originally linked to O-2 is lost in this step. The other acetyl group of acetic anhydride could not have been derived from the acetyl groups on O-3 or O-6, as the deuterium label in **6** and **7** was retained in fragment B, and consequently was derived from the acetyl group on O-4 or O-5. A McLafferty type reaction (Scheme 1), involving AcO-4, seems to be the most reasonable mechanism for this elimination, even if such rearrangements that do not involve a γ-hydrogen are uncommon.

The acetic acid lost in the next step (B→C) is derived from the acetyl group

on O-6, as shown by the fragmentation of **7**, from which the deuterium label was lost in this step. The mechanism is assumed to be a conventional McLafferty elimination.

The last step (C→D) is an elimination of ketene, also by a McLafferty elimination, in which one of the hydrogen atoms in the acetyl group is retained, as indicated in Scheme 1. Two of the three deuterium atoms in the acetyl group on O-3 in **6** were lost in this step, demonstrating that AcO-3 is involved in this elimination.

The ion D still contains one *O*-acetyl group, originally linked to C-5 in M. This was eliminated either as acetic acid or ketene, giving the fragments *m/e* 68 and 86 observed in the metastable spectrum of **1**.

Inspection of the figures in Table I shows that they are fully consistent with the assumed course of fragmentation. The formation of the fragments *m/e* 170 and 128 in the mass spectra of hexitol acetates indicates that elimination of acetoxyacetaldehyde initiates the fragmentation leading to these ions. However, elimination of acetoxyacetaldehyde from a 1-deoxyhexitol acetate seems to be insignificant, indicating that elimination of acetaldehyde is a favoured reaction. Elimination of formaldehyde as the first step seems to be even less important. Thus, *m/e* 170 and 128 are weak in the mass spectra of pentitol acetates. Fragmentations starting with the elimination of acetoxyacetaldehyde are more important, as shown by the fragments *m/e* 158 and 116 (2% and 3%, respectively, of the base peak, *m/e* 43). Assuming the elimination of an aldehyde from the molecular ion as the primary step, most even-mass fragments in the mass spectra of alditol acetates can be rationalized. These even-mass fragments are insignificant in the mass spectra of partially methylated alditol acetates[1], in which fission of the alditol chain at a methoxylated carbon atom is the most important reaction.

EXPERIMENTAL

General methods. — Mass spectrometry was conducted on a Varian MAT 311 double-focussing instrument. Normal spectra were run with an ionisation potential of 70 eV. For the recording of metastable decay processes, two methods were used. In the first method, the voltage of the electrostatic analyser was kept constant and the accelerating voltage varied, which allows the identification of the parent ions from a given daughter ion. The second method used the DADI-technique (direct analysis of daughter ions), in which the voltage of the electrostatic analyser was varied and the accelerating voltage was kept constant. This allows the identification of all the daughter ions derived from a parent ion.

N.m.r. spectra were recorded for solutions in deuteriochloroform (internal tetramethylsilane).

Methylation analysis and g.l.c. (with an OV-225 column) were performed as described earlier[7].

Preparation of deuterated sugars. — 1-Deoxy-L-galactitol-*1-d* penta-acetate (**2**) was obtained by reduction of 1,2:3,4-di-*O*-isopropylidene-6-*O*-*p*-tolylsulfonyl-α-D-galactose[9] with $LiAlD_4$, followed by hydrolysis, reduction ($NaBH_4$), and acetylation.

1-Deoxy-D-mannitol-*2-d* penta-acetate (**3**) was obtained from methyl 3,4,6-tri-*O*-benzyl-α-D-glucopyranoside. Oxidation[8] followed by reduction with sodium borodeuteride yielded a mixture of the *manno* and the *gluco* derivatives, for convenience referred to as the former. After hydrogenolysis, hydrolysis, and conversion into the diethyl dithioacetal, desulfuration with Raney nickel yielded **3**.

1-Deoxy-L-mannitol-*6-d* penta-acetate (**4**) was prepared by reduction of L-rhamnose with sodium borodeuteride, followed by acetylation.

Trideuterioacetylation of 3,5:4,6-di-*O*-benzylidene-1-deoxy-L-gulitol (see below), 2,5:4,6-di-*O*-benzylidene-1-deoxy-L-mannitol, and 2,3:4,5-di-*O*-benzylidene-1-deoxy-D-galactitol followed by acetolysis (acetic anhydride–acetic acid–sulfuric acid, 35:15:1; 16 h at room temperature) gave derivatives **5**, **6**, and **7**. The derivatives **5a**, **6a**, and **7a** were prepared by the alternative procedure, namely, acetylation followed by acetolysis with deuterated reagents. The mass spectra of the substances showed that no migration or hydrolysis had taken place.

*Characterization of 3,5:4,6-di-*O*-benzylidene-1-deoxy-*L*-gulitol.* — Methylation of di-*O*-benzylidene-1-deoxy-L-gulitol[3] gave, after hydrolysis and acetylation, the acetylated 2-*O*-methylhexitol derivative, as shown by g.l.c.–m.s.[7]. In the ^{1}H-n.m.r. spectrum, the signal for the benzylidene protons appeared as a singlet at δ 5.61.

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