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MASS-SPECTRAL FRAGMENTATIONS OF PERMETHYLATED DIALDOSE DIANHYDRIDES*

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ABSTRACT

Mass spectra of permethylated dialdose dianhydrides were measured. Two intense peaks which belonged to A-type fragment-ions were observed at *m/z* 203 and 187. The fragment ions belonging to the D, F, and J types had only low intensities.

INTRODUCTION

Recently, the isolation and elucidation of the structures of novel disaccharides, dialdose dianhydrides, were reported[2,3]. These compounds were 1,2′:1′,2-dianhydrides of β-L-rhamnopyranose and methyl α-D-galactopyranuronate or α-D-galactopyranose. A mass-spectrometric study of their peracetates revealed that several pathways were present, and the detection of 1,2′:1′,2-dianhydride was made possible by analysis of the spectra[1a]. However, only a few reports are available on the spectra of peracetylated oligosaccharides and, hence, the generalization of these fragmentation pathways is difficult. On the other hand, extensive studies have been conducted on the spectra of permethylated oligosaccharides[4–6], and these revealed that several, common pathways, which could be denoted with alphabetical symbols, were present. Therefore, the mass spectra of permethylated dialdose dianhydrides proved very useful for the analysis of the fragmentation pathways.

In this article, we deal with the analysis of the fragmentation pathways and the structures of the fragment ions.

RESULTS AND DISCUSSION

Because of the instability of methyl esters of uronic acids in methylation reactions[7], the 1,2′:1′,2-dianhydride (**1**) of 3,4-di-*O*-methyl-β-L-rhamnopyranose and 3,4,6-tri-*O*-methyl-α-D-galactopyranose was examined, instead of the permethyl-

*Mass Spectrometry of Dialdose Dianhydrides, Part III. For Part II, see ref. 1*b*.

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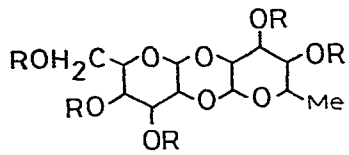


1 R = CH_3

2 R = CD_3

ated derivative of the 1,2′:1′,2-dianhydride of β-L-rhamnopyranose and methyl α-D-galactopyranuronate. The per(deuteriomethyl)ated derivative (**2**) of **1** was also examined, for a comparative study of the fragmentation pathways.

The mass spectra of **1** and **2** are given in Fig. 1. Compounds **1** and **2** have no reducing end, and so the symbols employed by Kochetkov and Chizhov[4] could not be used in their original form; the symbols a and b are used here as those which represent the rhamnose residue and the galactose residue, respectively. The formulas

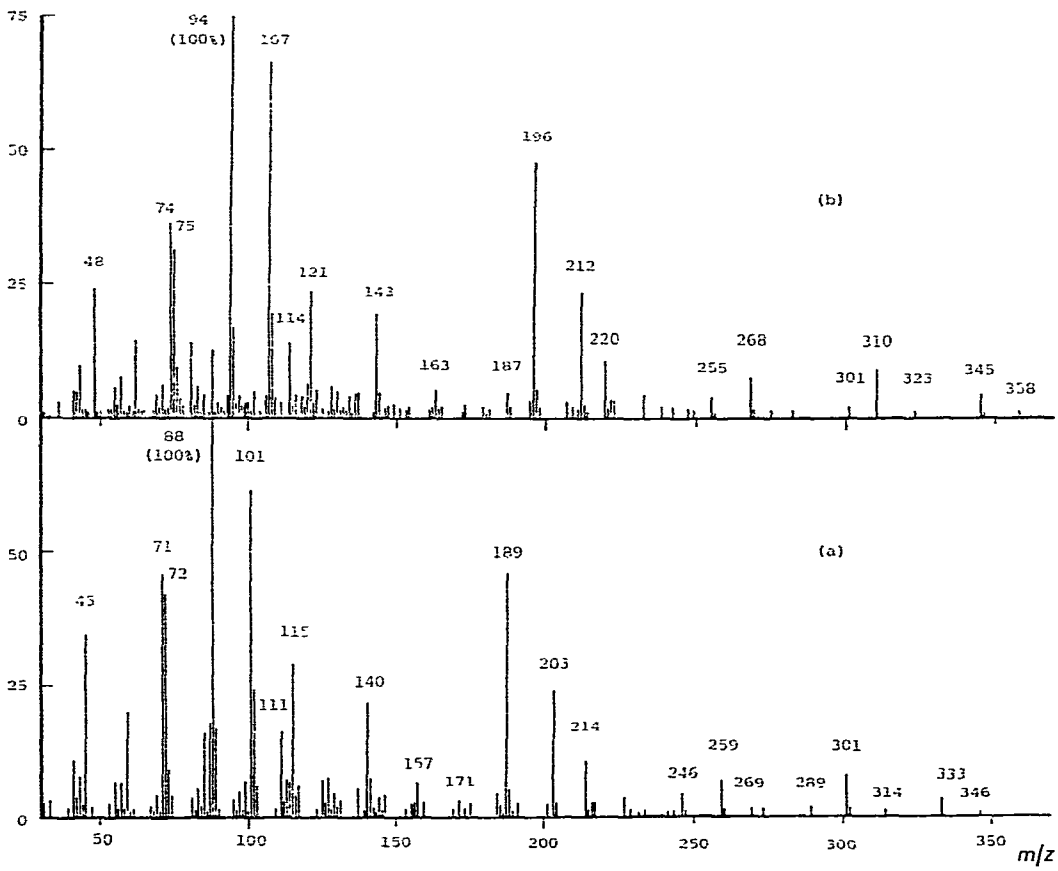
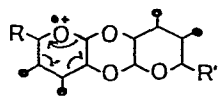


Fig. 1. Mass spectra of (a) **1** and (b) **2**.

of the fragment ions are written in planar forms in the Schemes, because the configurations of sugars have little influence on the spectra. The numbers given in the upper and the lower lines represent the values of *m/z* of the fragment ions formed by the degradations of the a ring and the b ring respectively, of **1**. The numbers in the parentheses represent the values of *m/z* in the spectrum of **2**. R and R′ indicate CH_3 and CH_2OCH_3, respectively, but they can be used interchangeably. The symbol (—●) represents OCH_3.

Peaks for the molecular ion (M^+) and the ($M^+ + 1$) ion were observed. The intensity of the ($M^+ + 1$) ion (0.091 %) was greater than that of the M^+ ion (0.089 %) at an ionizing potential of 20 eV, but the ratio was reversed at 70 eV (M^+, 0.089 %; $M^+ + 1$, 0.081 %).

The low-mass region of the spectrum of **1** was similar to that of those of permethylated hexopyranosides[4,5], which constitute one of the components of **1**.



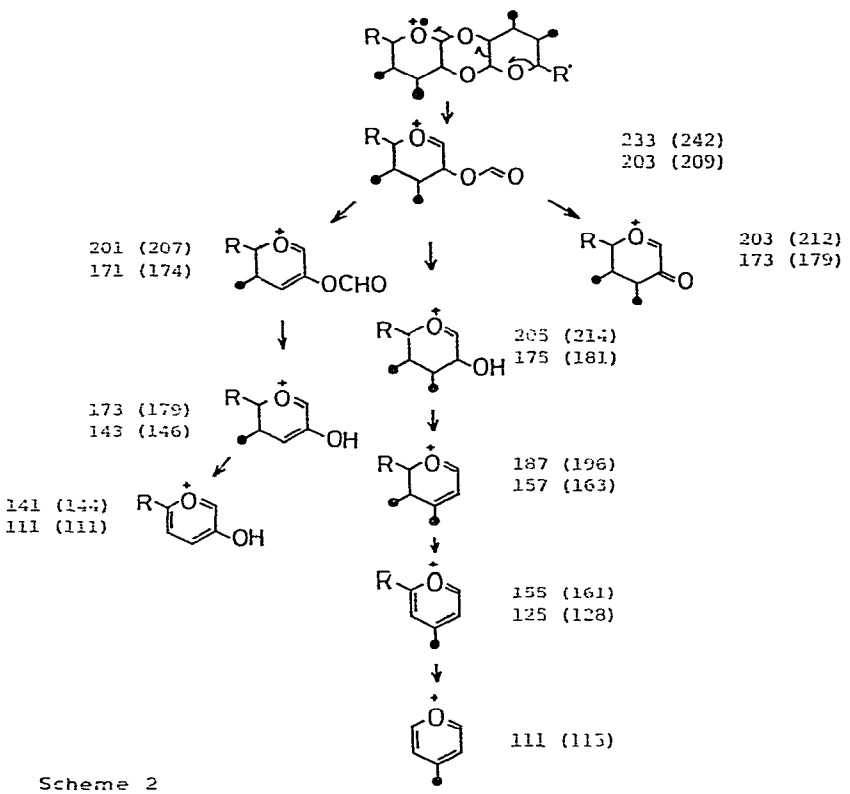
$\longrightarrow$ $\cdot MeO{\cdot}CH{=}CHOMe^{+\cdot}$ 88 (94)

Scheme 1

The base peak at *m/z* 88 corresponded to the H_1 ion ($MeO \cdot CH{=}CH \cdot OMe^{+}$; see Scheme 1) from permethylated hexopyranosides, and this was generated from both the a and the b residues; this fragment is common to various kinds of permethylated saccharides[4]. The elimination of the $\dot{C}H_3$ radical from the H_1 ion gave the ion of *m/z* 73. This ion generally has a relatively high intensity, but it was weak in the spectrum of **1**. The structures of the ions for the peak at *m/z* 101 were considered to be the same as the F_1 ($MeO \cdot CH{=}CH \cdot CH{=}O^{+}Me$) and G_1 ($MeO \cdot \underset{\llcorner CH \lrcorner}{CH} \cdot CH \cdot OMe^{+}$) ions. However, as the hydroxyl group at C-2 was not methylated, but glycosylated, these ions were not produced by the F type fragmentation. The pathway of the fragmentation of this ion was unclear. The peak at *m/z* 45, with a high intensity, was also observed, but that at *m/z* 75, which is one of the prominent peaks in the spectra of permethylated hexopyranosides, was not detected, because of the presence of the dianhydride structure; that is, the foregoing D_1 fragment was not formed because the 1- and 2-hydroxyl groups were combined *via* the dianhydride structure, and splitting of the C-1–C-2 bond did not eliminate any fragment ion that could be degraded by electron transfer.

Two characteristic peaks having high intensities, not present in the spectra of permethylated disaccharides, were observed at *m/z* 115 and 140. The mass spectrum of **2** showed that the former ion contained two methoxyl groups. Therefore, the structure of the ion for the peak at *m/z* 115 was presumed to be $MeOCH_2 \cdot CH{=}CH{=}O^{+}Me$. This ion was derived from C-3–C-6 of the b ring. The spectrum of **2** showed that the peak at *m/z* 140 contained only one methoxyl group, but the structure of this ion was not clear.

The spectrum of **1** was different, to a greater degree, from those of permethylated disaccharides in all regions, except that for the low-mass units. Cleavage of the molecule into halves was observed. Successive radical-transfer caused by the radical fission of one of the glycosidic linkages gave two kinds of fragment ions, of abA

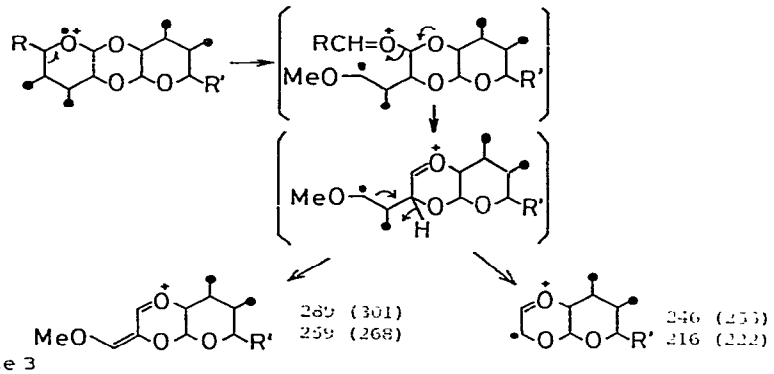


Scheme 2

and baA type (see Scheme 2). The abA_1 ion (*m/z* 233) was degraded by the loss of 46 mass units (CO and H_2O), to give an intense peak at *m/z* 187. This fragment ion had *m/z* 196 in the spectrum of **2**, showing the presence of three methoxyl groups. The structure of the fragment ion of *m/z* 187 is shown in Scheme 2; this ion was degraded by the loss of methanol, to give the ion of *m/z* 155, which generated the *m/z* 111 ion by loss of ethylene oxide.

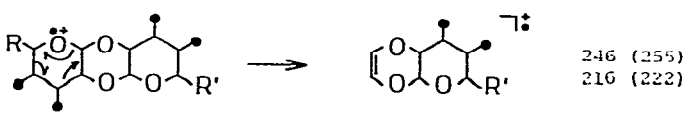
The spectrum of **2** showed that the contribution of this ion to the intensity of the *m/z* 111 ion was ~15%, and the ion corresponding to the residual 85% was an E-type ion. The different order of the eliminations of 46, 44 and 32 mass units gave the ions of *m/z* 201, 173, 141, and 97. The fragment ions included in this class had relatively high intensities. It was considered that A-type fragmentation of the rhamnose residue formed the main pathway of the fragmentation. The fragment ion of *m/z* 203 had a high intensity, and, from the spectrum of **2** (*m/z* 212), was found to contain three methoxyl groups, showing that this ion was not a baA_1 ion, but the ion generated

from the abA_1 ion by the elimination of CH_2O. The same reaction took place on the b ring of the dialdose dianhydride, but the intensities of the series of baA ions were low, compared to those of the abA ions. Therefore, the A type of fragmentation took place more easily on an a ring than on a b ring. These results were in good agreement with those for the mass spectra of the peracetates of dialdose dianhydrides[1a].

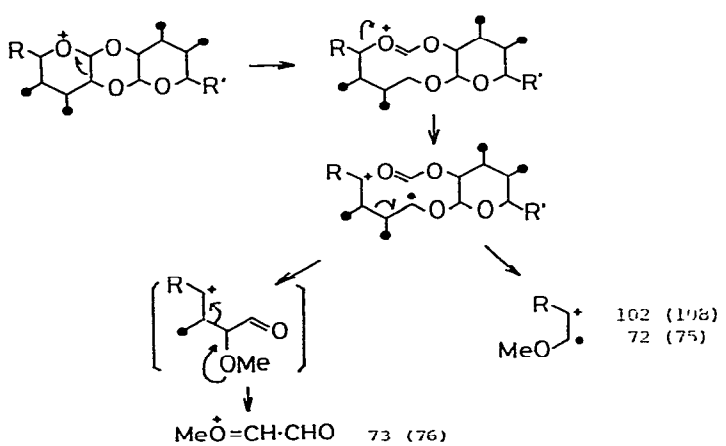


Scheme 3

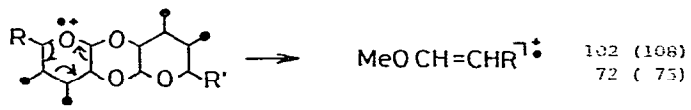
The formation of abB (*m/z* 289, 246) and baB (*m/z* 259, 216) ions was observed (see Scheme 3). The abB ion of *m/z* 289 had an intensity of 7.5%, and this was one of the major peaks in the high-mass region. The ions of *m/z* 246 and 216 were also generated from the molecular ion by H-type fragmentation (see Scheme 4). This observation was in good agreement with results reported by Kochetkov and Chizhov[8].



Scheme 4



Scheme 5



Scheme 6

The spectrum of **2** showed that this ion had three methoxyl groups, and that the structure given in the Schemes was reasonable.

Both the C (Scheme 5) and K (Scheme 6) types of fragmentation on the a and b rings gave the same fragment-ions, of *m/z* 102 for a, and 72 for b. The structures of these fragment-ions were determined to be $MeO \cdot CH=CH \cdot CH_2OMe^{+\cdot}$ and $MeO \cdot CH=CH \cdot CH_3^{+\cdot}$ by the aid of the spectrum of **2**. These two fragment-ions were not detected in the spectra of permethylated disaccharides, and are characteristic for the dialdose dianhydrides.

The elimination of the side chain of the b ring generated an intense peak of baE_1 (*m/z* 333). The successive elimination of methanol molecules gave a series of baE fragment-ions (*m/z* 301, 269). These ions were of remarkable intensities in the high-mass region. As the backbone structure of a 1,2′:1′,2-dianhydride is tight, and difficult to break down, the elimination of the side chain would be stressed. The elimination of a methyl radical from the 6-deoxyhexopyranose ring was not detected.

The fragmentations of the D, F, G, and J types were presumed to generate the same ions, of *m/z* 188 and 158. These ions should have three, and two, methoxyl groups, respectively, but the intensities of the ions of *m/z* 197 and 164 in the spectrum of **2** were less than 5%; this was in marked contrast to the fact that the ions belonging to these classes are abundant in the mass spectra of permethylated disaccharides.

Another fragmentation pathway was also observed. The molecular ion was degraded by the successive eliminations of methanol, to give the ions of *m/z* 346 and 314. These ions had only low intensities, but retro-Diels–Alder reactions on the a or b rings of the ion of *m/z* 314 gave the intense peaks of *m/z* 214 (11%) or 184 (5%), respectively. The second, retro-Diels–Alder reaction, on the dioxane ring of the ions of *m/z* 214 or 184, gave the ions of *m/z* 156 or 126. The eliminations of the side chain from the series of ions generated the ions of *m/z* 333, 301, 269, and 111. These fragmentation pathways, and the structures of these ions, were supported by the mass spectrum of **2**.

EXPERIMENTAL

*1,2′:1′,2-Dianhydride of 3,4-di-*O*-methyl-β-*L*-rhamnopyranose and 3,4,6-tri-*O*-methyl-α-*D*-galactopyranose* (**1**). — The 1,2′:1′,2-dianhydride of 3,4-di-*O*-acetyl-β-L-rhamnopyranose and 3,4,6-tri-*O*-acetyl-α-D-galactopyranose (2 mg) in dimethyl sulfoxide (1 mL) was mixed with 2M methylsulfinyl carbanion (1 mL). The mixture was kept for 30 min at 25–30°, and then methyl iodide (0.1 mL) was added. After 15 min at room temperature, the reaction was stopped by the addition of water. The

solution was twice extracted with chloroform (2 mL), dried (sodium sulfate), and evaporated. The residual syrup was subjected to g.l.c.–m.s.

*1,2′:1′,2-Dianhydride of 3,4-di-*O*-methyl-*d_3*-β-*L*-rhamnopyranose and 3,4,6-tri-*O*-methyl-*d_3*-α-*D*-galactopyranose* (**2**). — Compound **2** was prepared as for the preparation of **1**, except that methyl-d_3 iodide was used instead of methyl iodide.

Mass spectrometry. — The mass spectra of **1** and **2** were recorded by the g.l.c.–m.s. system of a Hitachi M70 spectrometer. The column (1 m) used in this experiment contained 3% of OV-1 on Chromosorb W. The ionizing potential was 20 eV, and the temperature in the ionizing chamber was in the range of 180 to 200°. The intensities of the peaks in the spectra are expressed relative to the intensity of the base peak.

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