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Note

Mass spectra of some di-D-fructose dianhydride derivatives

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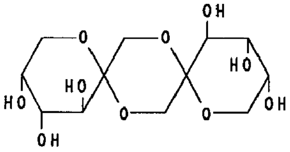
In the course of our studies of thermal treatments of sucrose, we had the need to separate and identify some di-D-fructose dianhydrides (DFDA's). It appears that the mass spectrometry of derivatives of such compounds has not previously been investigated. Our subsequent investigation of this mass spectrometry suggested some unusual fragmentation pattern which we now tentatively report, pending more definitive study.



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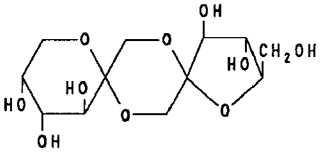

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Two of the DFDA's (**1** and **2**) have been investigated in the form of the fully substituted methyl (Me) and trimethylsilyl (Me_3Si) ethers. Their partial mass spectra are summarized in Tables I and II. The permethyl derivatives will be discussed first. The molecular ion ($M^+ = 408$) was not seen, but the base peaks *m/z* 88 and 101 were as expected from studies of simple fructosides. Karady and Pines[1] have shown that the ion 88 would be expected to predominate with fructopyranosides and that 101 would form predominantly from fructofuranosides, hence these are the base peaks from methylated **1** and **2** respectively. The other fragment ions (with the exception of those discussed below) were also as anticipated on the basis of the previous studies on fructosides[1]. However, the prominent ion *m/z* 277 seen in the spectra of methylated **1** and **2** is not so readily interpreted on the basis of previous studies. We interpret the formation of this ion (**3**) as shown in Scheme 1, which can be viewed as a special instance of formation of a J_1-type ion[2]. Successive losses of methanol from this ion would give rise to peaks at 245 and 213. A structure (**4**) for the ion 188 (postulated as forming by fragmentation of an

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TABLE I

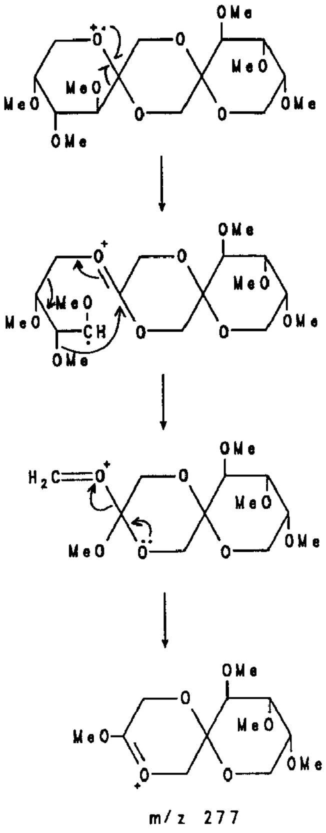
Partial mass spectra of methylated **1** and **2**

m/z	*Abundance (%)*		m/z	*Abundance (%)*	
	1	**2**		**1**	**2**
45	30.5	44.9	132	0.3	0.2
58	14.9	11.3	141	2.6	2.2
71	12.8	17.0	145	0.6	0.7
73	12.3	10.8	146	–	3.0
75	13.3	11.8	147	3.1	2.7
83	3.6	5.0	156	14.9	5.0
85	9.1	9.3	157	1.9	1.6
88	100.0	86.4	187	3.3	5.9
101	44.4	100.0	188	1.8	1.4
102	2.8	5.6	213	0.3	0.4
111	6.7	9.1	245	0.2	0.3
114	6.4	10.1	277	100.0	79.0
115	34.0	18.6	303	–	0.7
125	4.3	4.1	331	–	0.2
131	2.3	2.1			

TABLE II

Partial mass spectra of trimethylsilylated **1** and **2**

m/z	*Abundance (%)*	
	1	**2**
73	46.5	60.1
103	3.8	8.0
129	6.9	10.2
147	19.6	22.7
183	1.0	1.4
204	100.0	79.2
217	23.8	100.0
218	5.4	20.2
230	0.9	10.5
231	4.7	6.0
272	6.4	3.1
305	3.0	2.8
306	0.9	0.8
319	–	0.4
320	–	1.2
361	1.3	2.8
362	2.4	6.8
508	2.2	1.1
509	2.7	4.6



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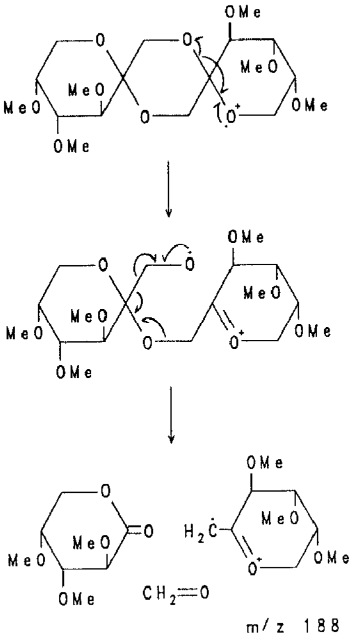
Scheme 1.

initial A_1 ion, Scheme 2) provides an explanation for *m/z* 156, and 125, by loss of methanol and methoxyl successively.

To confirm the above assignments the mass spectra of the perdeuteromethylated DFDA's were determined. These showed that the ions 88 and 101 were replaced by 94 and 107, respectively, as anticipated. The ion 277 was replaced by a dominant ion 289, thus confirming the presence of four methyl groups in ion structure **3**. Similarly the ion 188 was replaced by 197, confirming the presence of three methyl groups in ion structure **4**. All of the postulated fragment ions described above as being derived from **4** were observed with appropriate *m/z* values from the perdeuteromethylated products.

All of the foregoing comments can be applied to the Me_3Si derivatives (Table II). Ion 217 replaces 101 as the "pointer" to the presence of the furanose ring. The Me_3Si ion 509 corresponds to the ion 277 and is much less prominent, presumably because of the more facile fragmentation of the Me_3Si groups. The postulated Me ion (**4**) has its Me_3Si analogue at 362 and the subsequent fragmentation products are seen at 361, 272, and 183.



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Scheme 2.

EXPERIMENTAL

The dianhydrides **1** and **2** were prepared as described by Hilton[3], but purified by preparative l.c. on a Waters Delta-Pak 15-μm column eluted with water at 10 mL/min. The ratio of pyranose:furanose (**2**, elution time 9.85 min) to dipyranose product (**1**, 6.65 min) was 2:1. Methylation was carried out according to the procedure of Ciucanu and Kerek[4]. G.l.c.-m.s. was carried out with a Hewlett-Packard 5890A gas chromatograph fitted with an HP-1 fused-silica capillary column (25 m × 0.2 mm i.d.) connected via a capillary direct interface with a Hewlett-Packard 5970 series mass-selective detector at an ionizing potential of 70 eV.

ACKNOWLEDGMENTS

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