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THE MASS SPECTRA OF SOME PER-*O*-ACETYLALDONONITRILES

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ABSTRACT

The mass spectra of some per-*O*-acetylaldono- and per-*O*-acetyldeoxyaldononitriles have been recorded. The major fragmentation-pathways are discussed in terms of the application of electron-impact mass-spectrometry to structural studies of aldoses. Both acetyl and deuterium-labelled acetyl derivatives are included. The spectra are useful in verifying the position of the deoxy group(s) of deoxyaldoses.

INTRODUCTION

Per-*O*-acetylaldononitriles are useful derivatives for the separation of mixtures of aldoses by gas–liquid chromatography (g.l.c.), both with packed columns[1–4] and with open, capillary, tubular columns[5]. In one application, human urinary alditols and aldoses have successfully been analyzed as acetyl and cyanoacetyl derivatives[6]; these compounds are volatile, thermally stable, and well suited for gas-phase analysis. As they retain terminal dissymmetry as open-chain structures, these derivatives are suitable for analyses of biological interest by gas–liquid chromatography–mass spectrometry (g.l.c.–m.s.).

Other derivatives of acyclic carbohydrates have been studied. The literature contains mass-spectral data on diethyl dithioacetal acetates[7,8], aldehydo acetates[9], alditol acetates[10], alditol trifluoroacetates[11], acetates of monosaccharide *N*-phenylosotriazoles[12], and deoxyfluoroalditol acetates[13]. The work reported here deals with studies of aldoses and deoxyaldoses as per-*O*-acetylaldononitriles and per-*O*-acetyldeoxyaldononitriles by electron-impact mass-spectrometry (e.i.–m.s.).

RESULTS AND DISCUSSION

Mass spectral data (*m/e* values and relative intensities) for the compounds studied are given in Table I.

Mass spectra of per-*O*-acetylaldononitrile derivatives[14] of aldoses show fragmentation pathways similar to those of per-*O*-acetylpolyols[10]. Direct cleavage of chain C–C bonds, followed by the loss of ketene (*m/e* 42), acetate radical (*m/e* 59),

TABLE I

MASS SPECTRA OF SOME PER-*O*-ACETYLALDONONITRILES AND PER-*O*-ACETYLDEOXYALDONONITRILES[1,15]; *m/e* VALUES AND RELATIVE INTENSITIES (IN PARENTHESES)

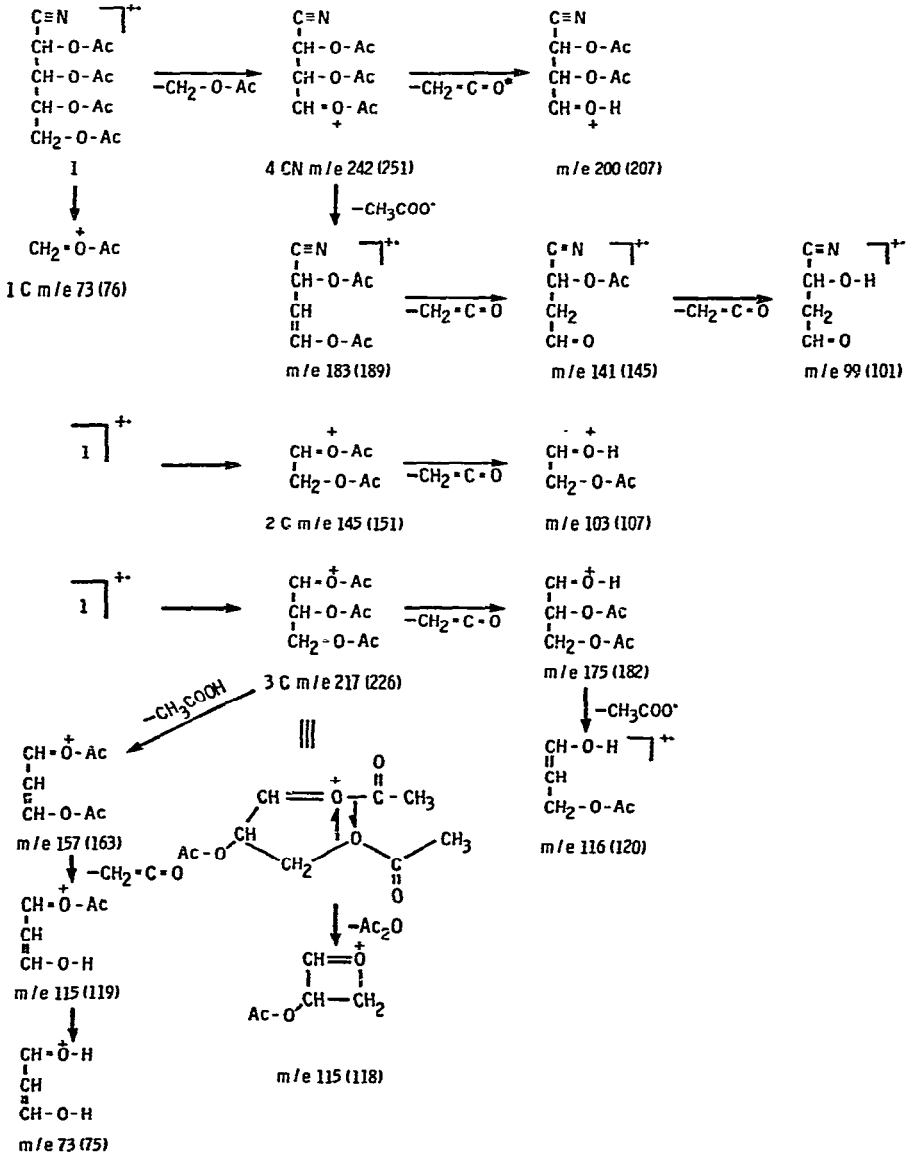
1	2	3	4	5	6	7	8	9	10	11	12
256(1)	265(1)	328(1)	340(2)	400(2)	415(5)	198(2)	204(1)	242(2)	251(2)	211(2)	218(1)
243(2)	252(3)	314(16)	326(20)	386(6)	402(3)	197(2)	203(1)	231(4)	240(6)	210(1)	217(1)
242(18)	251(25)	289(2)	301(4)	361(3)	401(16)	184(12)	190(20)	225(2)	235(1)	184(6)	190(5)
217(9)	250(2)	285(1)	293(2)	315(3)	400(3)	167(10)	182(1)	212(3)	234(4)	170(3)	174(1)
213(6)	226(15)	284(1)	282(4)	314(18)	376(6)	157(2)	173(14)	210(1)	233(1)	169(16)	173(14)
201(2)	220(8)	272(5)	276(1)	297(5)	368(3)	156(2)	161(5)	200(2)	232(1)	168(5)	172(1)
200(16)	207(18)	242(12)	251(18)	289(8)	327(7)	155(12)	159(13)	189(3)	219(1)	167(11)	171(1)
183(5)	190(9)	226(4)	238(2)	285(5)	326(38)	154(7)	157(11)	185(2)	218(5)	160(3)	166(2)
180(2)	189(4)	225(14)	232(16)	284(32)	307(6)	146(7)	154(69)	184(2)	216(2)	159(37)	165(27)
175(9)	183(5)	217(19)	231(7)	272(4)	306(6)	145(100)	151(96)	183(16)	207(3)	154(5)	164(3)
171(4)	182(11)	213(3)	226(23)	260(3)	301(17)	142(16)	150(4)	167(7)	197(1)	153(2)	157(3)
170(2)	176(5)	212(36)	219(7)	259(18)	294(10)	138(13)	146(16)	159(19)	196(2)	152(16)	156(2)
158(3)	163(32)	200(8)	218(45)	255(5)	293(60)	137(7)	141(15)	146(7)	191(2)	151(5)	155(13)
157(20)	157(15)	188(4)	217(3)	242(7)	282(5)	128(3)	140(13)	145(100)	190(12)	146(11)	154(100)
154(4)	156(15)	187(36)	207(6)	238(4)	269(8)	126(9)	130(8)	142(4)	189(7)	145	153(12)
153(13)	154(63)	183(18)	194(14)	237(4)	268(28)	125(100)	129(100)	141(40)	177(4)	142(8)	152(1)
146(7)	151(100)	175(7)	193(38)	225(4)	251(9)	124(3)	128(11)	140(3)	172(2)	136(4)	146(2)
145(100)	150(7)	170(5)	190(16)	218(5)	250(6)	122(9)	122(14)	130(5)	171(6)	130(1)	136(2)
141(16)	145(22)	166(5)	189(4)	217(40)	227(8)	116(3)	118(22)	129(36)	170(4)	129(16)	133(2)
140(5)	143(6)	165(6)	188(13)	213(3)	226(76)	115(17)	115(25)	125(6)	166(3)	127(7)	132(10)
129(5)	134(6)	158(5)	182(7)	212(22)	225(8)	113(6)	110(52)	117(19)	165(22)	126(12)	130(4)
126(3)	129(8)	157(22)	169(6)	200(4)	218(38)	112(15)	109(10)	104(2)	164(3)	125(100)	129(39)
116(7)	120(8)	156(4)	168(7)	199(8)	207(5)	104(5)	108(4)	103(51)	163(4)	118(4)	128(17)
115(86)	119(40)	153(10)	163(29)	195(8)	206(10)	103(79)	107(55)	100(3)	156(2)	117(63)	127(2)
113(2)	118(100)	152(4)	157(19)	187(30)	199(10)	96(8)	97(7)	99(13)	155(7)	112(7)	121(42)
112(7)	116(12)	145(100)	155(10)	183(5)	194(8)	95(9)	96(8)	98(6)	154(100)	110(13)	120(3)
111(5)	110(77)	144(16)	154(42)	178(5)	193(47)	86(14)	95(5)	87(10)	153(11)	109(21)	115(3)
104(4)	107(48)	140(5)	153(7)	175(11)	190(6)	85(4)	92(10)	85(4)	146(7)	104(5)	111(8)
103(82)	101(9)	138(8)	152(7)	170(5)	189(1)	84(9)	89(11)	71(3)	145(41)	103	110(72)
102(4)	86(7)	128(6)	151(100)	164(22)	183(6)	83(82)	85(80)	70(2)	134(5)	102(3)	109(10)
99(7)	85(16)	127(16)	150(15)	158(13)	182(18)	82(5)	79(18)	69(6)	133(15)	101(4)	103(16)
94(2)	76(7)	126(6)	145(15)	157(62)	181(10)	73(21)	78(7)	60(9)	132(37)	100(27)	94(3)

TABLE I (*continued*)

1	2	3	4	5	6	7	8	9	10	11	12
93(2)	75(9)	123(15)	141(10)	153(12)	180(6)	68(6)	76(21)	45(6)	128(2)	94(5)	92(3)
86(6)	72(8)	116(8)	130(25)	152(5)	176(6)	61(8)	63(29)	44(6)	127(5)	92(3)	90(23)
85(5)	63(30)	115(57)	129(16)	146(5)	167(44)	60(38)	52(26)	43	126(4)	88(3)	89(4)
84(4)	55(8)	111(7)	124(20)	145(75)	164(20)	59(3)	51(24)	42(7)	121(23)	87(42)	85(30)
79(7)	48(9)	107(3)	120(9)	141(8)	163(90)	55(10)	48(10)		116(5)	85(7)	84(7)
73(10)	47(44)	106(6)	119(49)	139(28)	162(9)	54(5)	47(50)		111(4)	84(10)	69(8)
71(2)	46	103(72)	118(52)	136(5)	161(10)	53(6)	46		110(66)	83(100)	65(6)
70(4)	45(75)	99(6)	113(16)	135(9)	157(14)	52(16)	45(75)		109(7)	82(11)	64(8)
61(3)	44(55)	97(8)	110(69)	128(7)	155(14)	51(8)	44(30)		108(5)	81(5)	63(2)
60(11)	43(23)	86(8)	107(42)	127(14)	154(38)	45(71)			107(4)	80(6)	59(9)
55(4)		85(17)	106(19)	126(7)	151(90)	44(85)			106(4)	70(5)	48(6)
52(5)		84(7)	98(15)	122(6)	142(52)	43			103(5)	69(10)	47(27)
51(3)		73(11)	86(28)	116(13)	137(9)	42(44)			102(5)	61(10)	46
45(7)		69(6)	85(20)	115(100)	136(19)				101(12)	60(32)	45(52)
44(25)		68(9)	79(10)	110(7)	132(10)				90(12)	58(11)	44(13)
43		61(5)	76(14)	103(64)	130(22)				89(8)	55(11)	43(12)
42(14)		60(55)	75(14)	97(14)	129(14)				72(7)	45(50)	
		55(8)	69(10)	86(8)	123(10)				69(9)	44(50)	
		54(14)	68(10)	85(15)	120(18)				63(8)	43	
		53(8)	63(95)	73(13)	119(100)				53(8)	42(35)	
		52(7)	55(10)	60(22)	118(82)				47(23)		
		51(11)	54(19)	55(8)	111(15)				46		
		50(8)	53(14)	45(36)	110(61)				45(42)		
		45(83)	52(17)	44(26)	109(12)						
		44(41)	51(19)	43	107(35)						
		43	50(12)	42(23)	106(10)						
		42(67)	47(70)		98(16)						
			46		86(19)						
					75(15)						
					63(53)						
					55(15)						
					47(41)						
					46						

and acetic acid (*m/e* 60) or acetic anhydride (*m/e* 102), occurs for all members of the class. A related type of fragmentation arises from loss of the same groups from the molecular ion.

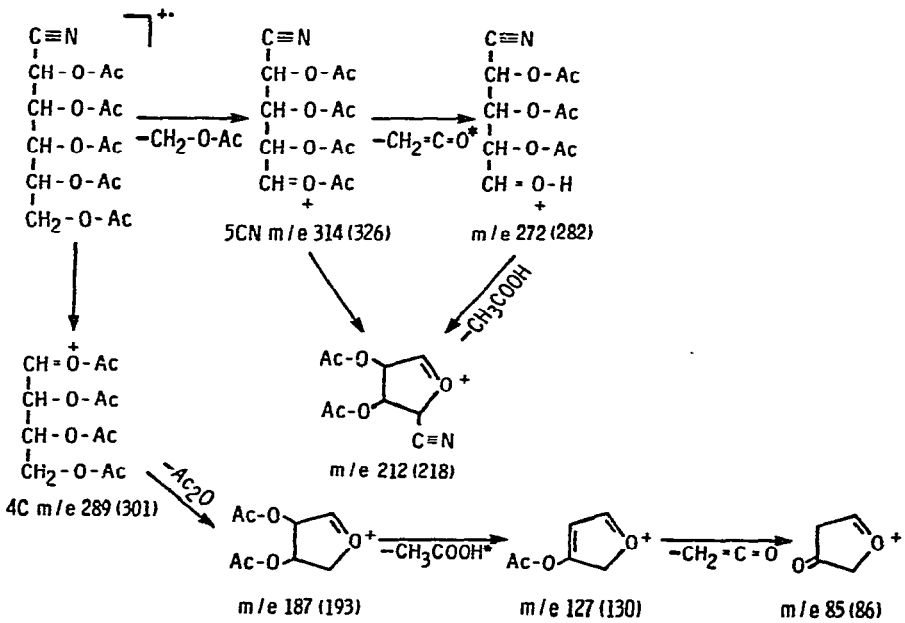
For all of the compounds studied, the cyano group protects the derivative from undergoing C-1–C-2 bond cleavage. The mass spectrum of per-*O*-acetylarabinononitrile shows a fragmentation pattern giving a 4CN, 3CN, 2CN, 3C, 2C, and 1C series



Scheme I

of ions (see Scheme 1). [Generally, the series of ions is designated in a fragmentation scheme with numbers corresponding to the number of carbon atoms in the chain[10]. Because a terminal C≡N group is sometimes present, the letter "N" is conveniently used to distinguish between ions containing (for example, 3CN) and not containing (for example, 3C) this moiety.] The most abundant ions observed are 242, 200 (4CN series), 157, 115 (3C series), and 145 (2C series). Most of the ions of the C series are found in the spectra of similar compounds, but an explanation of the ions *m/e* 115 is necessary. The mass spectra of labelled compounds indicates that two different ions, with *m/e* 115(118) and 115(119), are present. The structure of the latter ion is known; the ion of *m/e* 115(118) may arise from ion *m/e* 217(226) by expulsion of acetic anhydride (see Scheme 1).

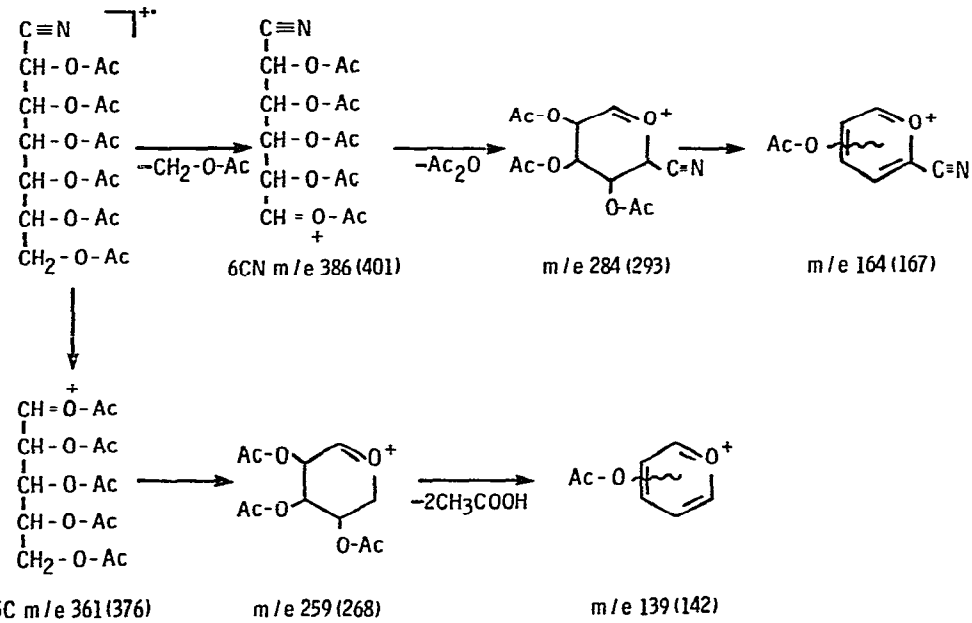
A similar fragmentation occurs for per-*O*-acetyl-D-gluconononitrile. In addition to the ions mentioned for the previous compound, the mass spectrum shows *m/e* 272(282), 212(218) (of 5CN species), 289(301), 187(193), 127(130), and 85(86) (of 4C species) (see Scheme 2).



Scheme 2

The mass spectrum of per-*O*-acetyl-D-*glycero*-D-*gulo*-heptononitrile gives additional fragments of the 6CN and 5C species, due to the additional carbon atom in the chain and to the additional acetoxyl group (compared to the corresponding D-glucose derivative) (see Scheme 3). The fragmentation of 5CN, 4C, 6CN, and 5C primary ions proceeds with expulsion of acetic anhydride, and leads to an abundance

of cyclic ions. This process appears to be much faster than the competitive loss of ketene from 6CN and 5C ions.



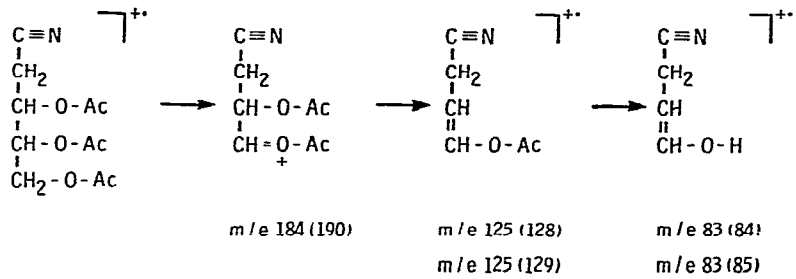
Scheme 3

A disadvantage inherent in the mass spectra of per-*O*-acetylaldononitriles is the lack of molecular ions, but molecular weights may readily be deduced from M − 59 (–OAc) and M − 73 (–CH_2OAc) ions.

A useful feature of per-*O*-acetylaldononitriles is their terminal dissymmetry. In structural analyses of polysaccharides *via* methylation, the per-*O*-acetyl-*O*-methylalditol end-products may be indistinguishable by mass spectrometry[15]. Use of per-*O*-acetyl-*O*-methylaldononitriles (instead of per-*O*-acetyl-*O*-methylalditols) should facilitate such structural studies.

Fragment ions attributable to the direct loss of acetic acid, acetate radical, or ketene from molecular ions of per-*O*-acetylaldononitriles appear to be much less significant (see Table I) than pathways involving cleavage of the carbon chain.

Per-*O*-acetyldeoxyaldononitriles fragment similarly to per-*O*-acetylaldononitriles. With these compounds, there is no cleavage adjacent to the deoxy group. Neither 3C nor 2CN species ions were found in the spectrum of per-*O*-acetyl-2-deoxy-D-*erythro*-pentononitrile. The presence of two abundant ions having *m/e* 125 (4CN) and 145 (2C) (for labelled derivative, *m/e* 151) is characteristic of the derivative of 2-deoxy-D-*erythro*-pentose (see Table I), but the mass spectrum of the labelled derivative shows an abundant ion at *m/e* 129, instead of the predicted *m/e* 128 (see



Scheme 4

Scheme 4). To explain this, mass spectra were measured at lower ionizing potentials (see Table II). With ethyl esters[16,17], almost complete scrambling of the ethoxyl hydrogen atoms occurs. Ions 85 and 129 may originate from scrambling of deuterium from acetyl groups to the sugar skeleton; this would involve the elimination of an acetate radical as $\cdot OOCCD_2H$ instead of $\cdot OOCCD_3$. The degree of scrambling is dependent on the ionizing potential, but the data are insufficient to rule out firmly a scrambling mechanism in the case of loss of acetate radicals. Because the ratio of scrambling is different for these two ions, 85(84) > 129(128), there are evidently two paths that provide ion *m/e* 84.

TABLE II

VARIATION OF THE RATIOS OF IONS *m/e* 84(85) AND 128(129) WITH IONIZING POTENTIAL

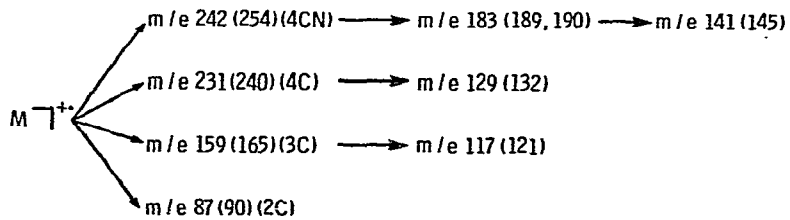
	7[a]		11[b]	
eV	*84:85*	*128:129*	*84:85*	*128:129*
70	6.5:100	9.8:100	24:100	48:100
20	7.2:100	8.5:100	25:100	49:100
17	7.5:100	9.7:100		
15	10:100	8.7:100	57:100	50:100
12	35:100	8.5:100		
11	57.5:100	11:100	101:100	60:100

[a]Compound 7 = tri-*O*-acetyl-2-deoxy-D-*erythro*-pentononitrile. [b]11 = tri-*O*-acetyl-2,6-dideoxy-D-*ribo*-hexononitrile.

The scrambling of deuterium from an acetyl group occurs not only for per-*O*-acetyldeoxyaldononitriles but also for derivatives of aldononitriles. The ion *m/e* 190 is more abundant than ion *m/e* 189 in the spectra of per-*O*-acetylaldononitriles.

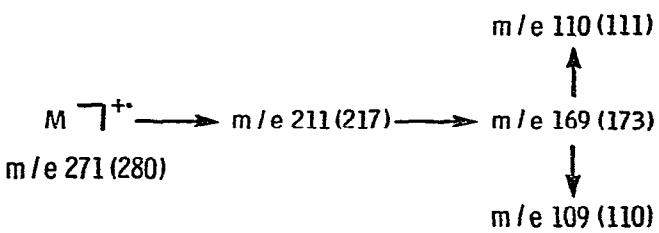
Major ions in the mass spectrum of tri-*O*-acetyl-2-deoxy-D-*erythro*-pentononitrile (see Table I) include *m/e* 73(76) (1C), 83(84,85) (4CN), 103(107) (2C), 112(115) (3CN), 125(128) (4CN), 145(151) (2C), and 184(190) (4CN). The ions of CN species are significant for the structural elucidation of any per-*O*-acetyl-2-deoxy-aldononitrile. Generally, the methylene carbon atom may be found from the 58

atomic mass unit (a.m.u.) shifts of the corresponding ions. For an ω-deoxyaldononitrile, *e.g.*, tetra-*O*-acetyl-6-deoxy-L-galactononitrile, any C-species ion is shifted by 58 a.m.u. The major fragmentation-pathways of tetra-*O*-acetyl-6-deoxy-L-galactononitrile are shown in Scheme 5. The fragmentation pathway of per-*O*-acetyldigitoxono-



Scheme 5

nitrile is a combination of the fragmentations of the derivatives of 2-deoxy- and 6-deoxy-aldoses. Besides abundant ions of 2C, 3C, and 4CN species, there are ions which arise from direct loss of acetic acid, ketene, or acetate radical according to Scheme 6; these ions are more prominent in spectra from derivatives of deoxyaldoses than in spectra from derivatives of aldoses.



Scheme 6

EXPERIMENTAL

Preparation of derivatives. — Reference aldoses and deoxyaldoses (Supelco, Inc., Bellefonte, Pa., U.S.A.) were converted into the corresponding per-*O*-acetyl-aldononitriles and per-*O*-acetyldeoxyaldononitriles by our published procedure[5]. The following compounds were studied: tetra-*O*-acetyl-L-arabinononitrile (**1**), tetra-*O*-(acetyl-d_3)-L-arabinononitrile (**2**), penta-*O*-acetyl-D-gluconononitrile (**3**), penta-*O*-(acetyl-d_3)-D-gluconononitrile (**4**), hexa-*O*-acetyl-D-*glycero*-D-*gulo*-heptononitrile (**5**), hexa-*O*-(acetyl-d_3)-D-*glycero*-D-*gulo*-heptononitrile (**6**), tri-*O*-acetyl-2-deoxy-D-*erythro*-pentononitrile (**7**), tri-*O*-(acetyl-d_3)-2-deoxy-D-*erythro*-pentononitrile (**8**), tetra-*O*-acetyl-6-deoxy-L-galactononitrile (**9**), tetra-*O*-(acetyl-d_3)-6-deoxy-L-galactononitrile (**10**),

tri-*O*-acetyl-2,6-dideoxy-D-*ribo*-hexononitrile (**11**), and tri-*O*-(acetyl-d_3)-2,6-dideoxy-D-*ribo*-hexononitrile (**12**).

Mass spectrometry. — Mass spectra were obtained with an LKB 9000 gas chromatograph–mass spectrometer fitted with a glass column (3 m × 4 mm) packed with 2% of SE-30 on Gas Chrom P (100–120 mesh, acid washed and silanized) at temperatures of 120 to 160°. Other conditions were: flash heater, 230°; molecular separator, 260°; ion source, 250°; and ionization potential, 70 eV, unless otherwise specified (see Table II).

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