Preliminary communication

Gas–liquid chromatography and mass spectrometry of aldononitrile acetates and partially methylated aldononitrile acetates

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Application of g.l.c.–m.s. in polysaccharide structure investigation requires alditol acetates or their partially methylated derivatives. The chromatographic separation[1,2] and the main electron-impact fragmentation patterns[3,4] of these compounds have been studied in detail. The method has one limitation caused by the symmetry of the alditol molecule which necessitates the use of sodium borodeuteride for reduction of the aldoses obtained on degradation of polysaccharides.

We now report on the g.l.c.–m.s. of aldononitrile acetates derived from pentoses, hexoses, heptoses, 6-deoxyhexoses, and their methyl ethers.

In contrast to the published data[5,6], we have found that the time required for preparation of aldononitrile acetates can be considerably decreased and that excellent separations of these compounds by g.l.c. can be achieved on readily available, polyester stationary phases. The separation of the aldononitrile acetates from nine monosaccharides is represented in Fig. 1.

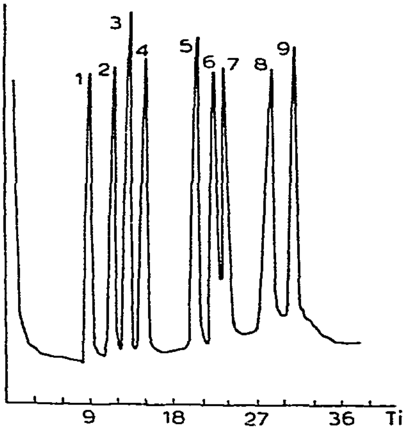


Fig. 1. The separation of a mixture of monosaccharides in the form of their aldononitrile acetates; 1, L-rhamnose; 2, D-ribose; 3, L-arabinose; 4, D-xylose; 5, D-mannose; 6, D-glucose; 7, D-galactose, 8, L-*glycero*-D-*manno*-heptose; 9, D-*glycero*-D-*gulo*-heptose. The separation was performed on a glass-spiral column (1 m × 3 mm) packed with 3% poly(neopentyl glycol succinate) on Chromosorb W (60–80), fitted in a LCM-8-MD gas-chromatograph, with flame-ionisation detector, a programmed temperature range of 160–230° (2°/min), and a nitrogen flow-rate of 50 ml/min.

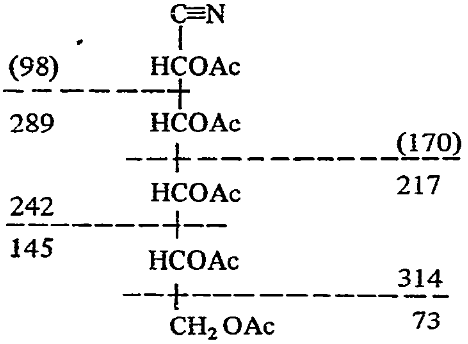
TABLE I

THE INTENSE PEAKS IN THE MASS SPECTRA[a] OF METHYLATED ALDONONITRILE ACETATES

Parent sugar	m/e																																
	45	83	85	87	88	89	96	99	101	112	113	115	117	127	129	131	142	145	154	158	159	161	173	175	186	189	197	205	212	214	217	233	261
3-Me-D-Glc		+	+					+				+		+			+				+										+		+
4-Me-D-Gal				+						+					+				+							+				+			
6-Me-D-Glc	+			+									+		+						+						+		+				
2,3,4-Me$_3$-D-Glc				+	+			+			+				+					+			+			+						+	
2,3,6-Me$_3$-D-Glc	+			+	+			+			+				+	+							+			+						+	
3,4,6-Me$_3$-D-Glc	+			+					+						+							+											
2,4,6-Me$_3$-D-Glc	+			+					+	+					+				+			+			+							+	
2,3,4,6-Me$_4$-D-Glc	+			+	+				+						+			+				+						+					
2,3,4-Me$_3$-L-Rha						+	+					+		+		+				+				+									

[a] The spectra were recorded with a Varian CH-6 instrument at an inlet temperature of 30–80°, ionizing potential of 70 eV,and an ion-source temperature of 180°.

The mass spectra of aldononitrile acetates contain characteristic peaks and are easy to interpret. Although none of the derivatives yields the molecular ion, all give ions at *m/e* M −73 and M −98, corresponding to the loss of $-CH_2OAc$ and $-CHOAcCN$ moieties, respectively. Both ions, as well as the ions formed by fission of other C—C bonds, are the primary fragments (1) that give series of more-intensive, secondary fragments by single or consecutive eliminations of acetic acid (−60) and ketene (−42), as described for the fragmentation of alditol acetates[4].



(1)

In almost all the recorded spectra, the base peak was *m/e* 43 (CH_3CO^+) and the prominent peaks were (for hexose derivatives) *m/e* 157 (217 − 60), 145 (289 − 60 − 2 × 42), 115 (157 − 42), and 103 (145 − 42) derived from fragments which do not carry the nitrile group. None of the spectra contain ions from the C-1—C-2 (98) and C-1—C-2—C-3 (170) moieties.

The fragmentation of the molecules of partially methylated aldononitrile acetates is analogous to that described for methylated alditol acetates, *i.e.* the fission takes place mainly between carbon atoms carrying vicinal methoxyl groups. The primary fragments formed eliminate molecules of acetic acid, ketene, methanol, or formaldehyde to yield more-intensive, secondary fragments. The *m/e* values of the intense peaks in the mass spectra of partially methylated aldononitrile acetates are listed in Table I. An inspection of the data in Table I indicates that unambiguous characterisation of methylated monosaccharides is possible. The intensities of certain peaks suggest that these may be useful for identification purposes. Thus, the ratio of intensities of peaks at *m/e* 205 and 161 in the mass spectrum of 5-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-gluconitrile is 1:7, whereas in the case of the 3,4,6-tri-*O*-methyl-D-glucose derivative it is 1:60.

All the aldononitriles investigated were obtained in a chromatographically homogeneous state. The parent monosaccharides were treated with hydroxylamine hydrochloride in dry pyridine followed by acetic anhydride, in accordance with the procedure described[5,6], except that the reaction time was reduced to 15 min.

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