BRIEF COMMUNICATIONS*

GAS-LIQUID CHROMATOGRAPHY AND MASS SPECTROMETRY OF ACETATES OF ALDONONITRILES OF PARTIALLY METHYLATED XYLOPYRANOSE AND ARABINOPYRANOSE

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The advantage of using the acetates of aldononitriles (AcCN) of partially methylated monosaccharides [1] over the use of alditols [2] and TMS ethers [3] for the determination of the position of OMe groups in a molecule from mass spectra (MS) has recently been shown.

We report GLC and MS information on the AcCNs of partially methylated D-Xylp and L-Arap (Tables 1 and 2). On considering the mass spectra, the pattern of methylation is determined already by the ratio of the intensities of the peaks of the ions B_3 and A_4. A distinction of similarly substituted stereoisomers can be made by means of the T values.

When the GLC peaks overlap (Id and If; IIa and IIc), the assignment is made either by the method of varied acceleration voltage or by deducting from the combined mass spectrum the component calculated from Table 2 and the relative intensity of the characteristic peak of the primary ion. Thus, for (IIc) this

TABLE 1. Relative Retention Times (T) of the AcCNs of Methylated D-Xylp and L-Arap

Initial sugar	Type of column	
	A	B
II g 2, 3, 4—OMe_3Ara	23	39
I g 2, 3, 4—OMe_3Xyl	31	47
I e 2, 4—OMe_2Xyl	40	57
II e 2, 4—OMe_2Ara	43	61
I d 2, 3—OMe_2Xyl	45	60
I f 3, 4—OMe_2Xyl	45	60
II d 2, 3—OMe_2Ara	46	63
I a 2—OMeXyl	53	67
II a 2—OMeAra	61	73
II c 4—OMeAra	61	73
I b 3—OMeXyl	64	75

TABLE 2. Mass Spectra of AcCNs of Partially Methylated Pentapyranoses

Type of ion*	m/e	Position of the OMe groups						
		2†	3	4	2, 3†	2, 4†	3, 4	2,3,4 †
B_3	217	1,00	—	—	—	—	—	—
A_4	214	1,3	0,05	2,4	—	—	—	—
B_3	189	—	1,00	1,00	1,00	1,00	—	—
A_4	186	—	—	—	0,1	3,3	3,8	—
B_3	161	—	—	—	—	—	1,00	1,00
A_4	158	—	—	—	—	—	—	0,5
B_2	145	2,1	1,7	—	0,9	—	—	—
A_3	142	—	2,3	1,0‡	—	—	1,5	—
B_2	117	6,3‡	—	11,0	0,5	30	80	1,3
A_3	114	—	—	—	0,8	—	—	—

*A represents an ion including the C atoms of the molecule starting from the first, and B from the last. The subscript figure represents the number of C atoms in the ion.

†Average values for the MS of the D-Xylp and L-Arap derivatives.

‡The reason for the relatively high intensity of these peaks is obscure.

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is the peak with m/e 189. The relative intensities of the peaks of the secondary ions depend on the conditions of obtaining the mass spectra more strongly than in the case of the primary ions.

The mass spectra were obtained on an LKB-9000 apparatus (70 V, 1.5 m × 3.4 mm, PNPGS, 5%). The T values were determined by using columns A (see [1], 120-220°C, 2°C/min) and B (steel, 1 m × 2 mm, BDS, 15%, 100-220°C, 5°C/min). The AcCN of Gal was used as internal standard (1.00). A mixture of the AcCNs of the partially methylated D-Xylp and L-Arap was obtained from the corresponding sets of methylated β-D-xylopyranoses and β-L-arabinopyranoses. The latter were synthesized by selecting the appropriate conditions for methylating the initial glycosides.

LITERATURE CITED

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3. G. Petersson et al., Svensk Papperstidning, 71, 77, 731 (1968).