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G.L.C.–M.S. OF THE OXIDATION PRODUCTS OF PENTITOLS AND HEXITOLS AS *O*-BUTYLOXIME TRIFLUOROACETATES

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ABSTRACT

Chemical ionisation (c.i.) mass spectra of trifluoroacetylated *O*-butyloximes of 2- and 3-pentuloses, 2- and 3-hexuloses, and 2,5-hexodiuloses (products of the oxidation of the pentitols and hexitols with bromine) are reported. Small amounts of 2-pentosuloses and 2,3- and 2,4-pentodiuloses could be detected by using selected ion monitoring at *m/z* 579 (M + 1). The mass spectra comprise few signals, with those for (M + 1) or (M + 1 − 2 F_3C-COO) being the most intense.

INTRODUCTION

The separation of pentoses[1,2], hexoses[3,4], 2- and 3-pentuloses, 2- and 3-hexuloses, and 2,5-hexodiuloses[5] as *O*-butyl-, *O*-methyl-, and *O*-(2-methyl-2-propyl)-oxime derivatives by g.l.c. on OV-225 has been reported. We now present g.l.c.–m.s. data on trifluoroacetylated 2- and 3-pentulose, 2- and 3-hexulose, and 2,5-hexodiulose *O*-butyloxime derivatives which may be useful in the analysis of biological material[6] and of complex sugar mixtures arising in the formose reaction[7,8].

Trimethylsilylated and acetylated carbohydrate *O*-alkyloximes are acyclic[9,10], and *Z* (syn) and *E* (anti) isomers are formed. Diuloses may give up to four isomers[11,12].

EXPERIMENTAL

Materials. — D-*erythro*-2-Pentosulose and D-*threo*-2-pentosulose were obtained[13] by oxidation of D-ribose and D-xylose with Cu(II) acetate, and allitol, D-altritol, and D-iditol by conventional reduction of D-allose, D-talose, and D-idose, respectively, with borohydride. Other chemicals were commercial products.

Oxidation of alditols and derivatisation of products. — Oxidation was effected with bromine in the presence of calcium carbonate, acids were removed with an ion-exchange resin, and derivatisation was carried out as described previously[5].

G.l.c.–m.s. — An MAT 44S gas chromatograph–mass spectrometer equipped with a 50-m glass capillary column, wall-coated with OV-225, was used. G.l.c. conditions: temperature programme, 150° for 2 min, →180° at 5°/min, 180° for 20 min; helium carrier gas at 1.5 mL/min; split ratio, 1/10; sample volume, 1 μL;

injection port, 250°; separator, 220°. M.s. conditions: pressure in c.i. source, 390 μbar, and in the forepump, 37 μbar; electron energy, 150 eV; ion source, 220°; emission current, 0.7 mA; voltage of the secondary electron multiplier, 1800 V; *m/z* 200→800, scanned in 2 s.

RESULTS AND DISCUSSION

C.i. mass spectrometry was preferred over the e.i. mode, because fewer fragment ions were formed and the spectra were more readily interpreted. The c.i. mode has the disadvantage that the relative intensities of fragment ions are dependent on the partial pressures of the reagent gas and the substrate[14].

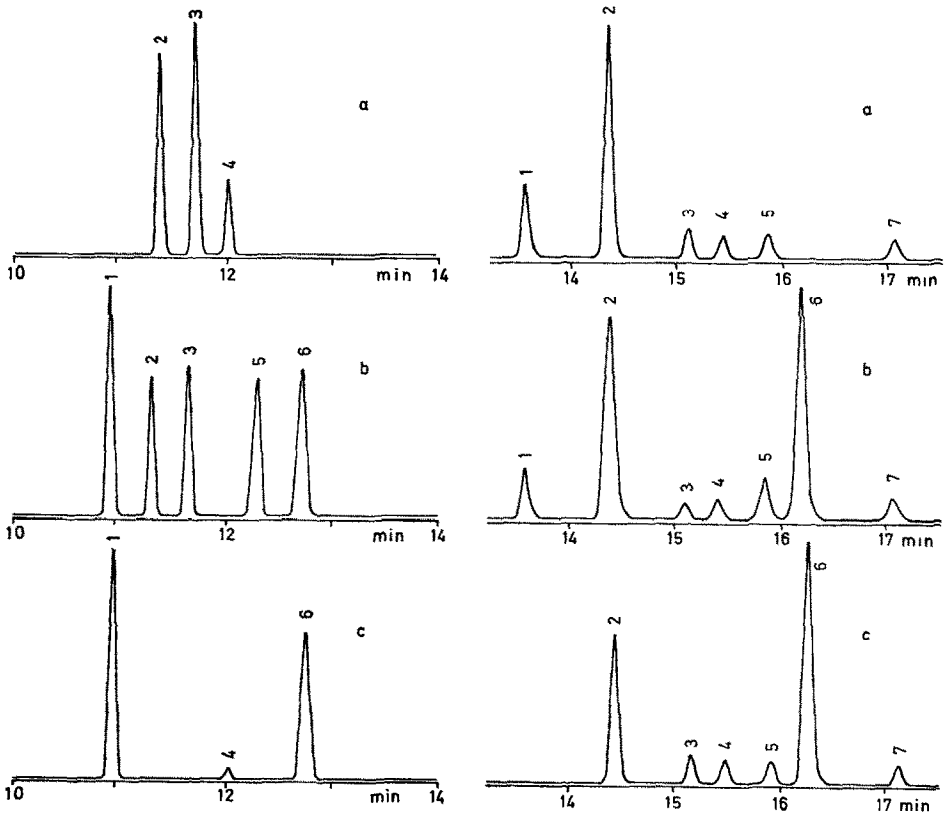


Fig. 1. Chromatograms of trifluoroacetylated *O*-butyloxime derivatives of the oxidation products of (*a*) ribitol, (*b*) D-arabinitol, and (*c*) xylitol, using s.i.m. at *m/z* 606 (M + 1). Peak identities: 1 and 6, DL-*threo*-2-pentulose; 2 and 3, DL-*erythro*-2-pentulose; 4, *erythro*-3-pentulose; 5, D-*threo*-3-pentulose.

Fig. 2. Chromatograms of trifluoroacetylated *O*-butyloxime derivatives of 2-pentosuloses and 2,3- and 2,4-pentodiuloses that are oxidation products of (*a*) ribitol, (*b*) D-arabinitol, and (*c*) xylitol; s.i.m. at *m/z* 579 (M + 1). Peak identities: 1 and 2, DL-*erythro*-2-pentosulose; 2 and 6, DL-*threo*-2-pentosulose; 3,4,5, and 7, DL-*glycero*-2,3- and -2,4-pentodiulose.

TABLE I

MASS-SPECTRAL DATA OF TRIFLUOROACETYLATED *O*-BUTYLOXIME DERIVATIVES OF PENTULOSES[a]

m/z	*Assignment*	*Relative intensity (%)*					
		DL-erythro-*2-Pentulose*		DL-threo *2-Pentulose*		erythro-*3-Pentulose*	D-threo-*3-Pentulose*
		1	2	1	2		
648	M + 43	1	4	2	4	1	1
607	M + 1 (^{13}C)	20	20	20	20	20	20
606	M + 1	100	100	100	100	100	100
605	M	46	20	35	21	46	16
575	M + 43 − 73	1	2	1	4		
492	M + 1 − 114	8	28	12	79	27	19
436	M + 1 − 56 − 114	4	1	2	1	14	8
420	M + 1 − 73 − 113		1		6		
380	M + 1 − 2 × 113	13	8	8	5	56	21

[a]Pressure of methylpropane in the ion source, 390 μbar; concentrations of pentuloses in derivative solutions (μg/μL): DL-*erythro*-2-pentulose, 0.73; DL-*threo*-2-pentulose, 1.30; *erythro*-3-pentulose, 0.41; D-*threo*-3-pentulose, 0.54.

Fig. 1 shows the chromatograms of trifluoroacetylated *O*-butyloxime derivatives of pentuloses [selected ion monitoring (s.i.m.) at *m/z* 606 (M + 1)]. The advantage of s.i.m. is that interference by derivatives of other oxidation products or unchanged pentitols is avoided. Oxidation of the pentitols gave the expected pentuloses.

The most intense peak in the mass spectra of the pentulose derivatives had *m/z* 606 (M + 1) (Table I). The addition of $C_4H_9^+$ (57 m.u.)[2,4], the predominant ion of isobutane[15], could not be observed; however, the addition of $C_3H_7^+$ (43 m.u.) occurred. The $(M + C_4H_9)^+$ ion lost O-C_4H_9· (73 m.u.). In some spectra, the peak at *m/z* 492 was the second most intense and resulted from the loss of F_3C-COOH (114 m.u.) from $(M + 1)^+$. Moreover, mass differences of 56 (C_4H_8) and 113 (F_3C-COO·) occurred, resulting in peaks with *m/z* 436 (M + 1 − 56 − 114), 420 M + 1 − 73 − 113), and 380 (M + 1 − 2 × 113).

Peaks for the molecular ion M^+ were found in all spectra and were not formed by e.i. ionisation. M^+ can arise by charge transfer from fluorine substituents to the reagent gas or the helium–isobutane mixture.

The amounts (1–5%) of 2-pentosuloses and 2,3- and 2,4-pentodiuloses also formed were too small to allow useful mass spectra to be obtained. Fig. 2 shows the chromatograms of the 2-pentosuloses and 2,3- and 2,4-pentodiulose derivatives [s.i.m. at *m/z* 579 (M + 1)]. Comparison with the retention times of 2-pentosuloses, obtained by oxidation of D-ribose and D-xylose with Cu(II) acetate, allowed peaks 1, 2, and 6 to be assigned to 2-pentosuloses. The other peaks, which occur in all chromatograms, could be due to DL-*glycero*-2,3- and -2,4-pentodiulose derivatives.

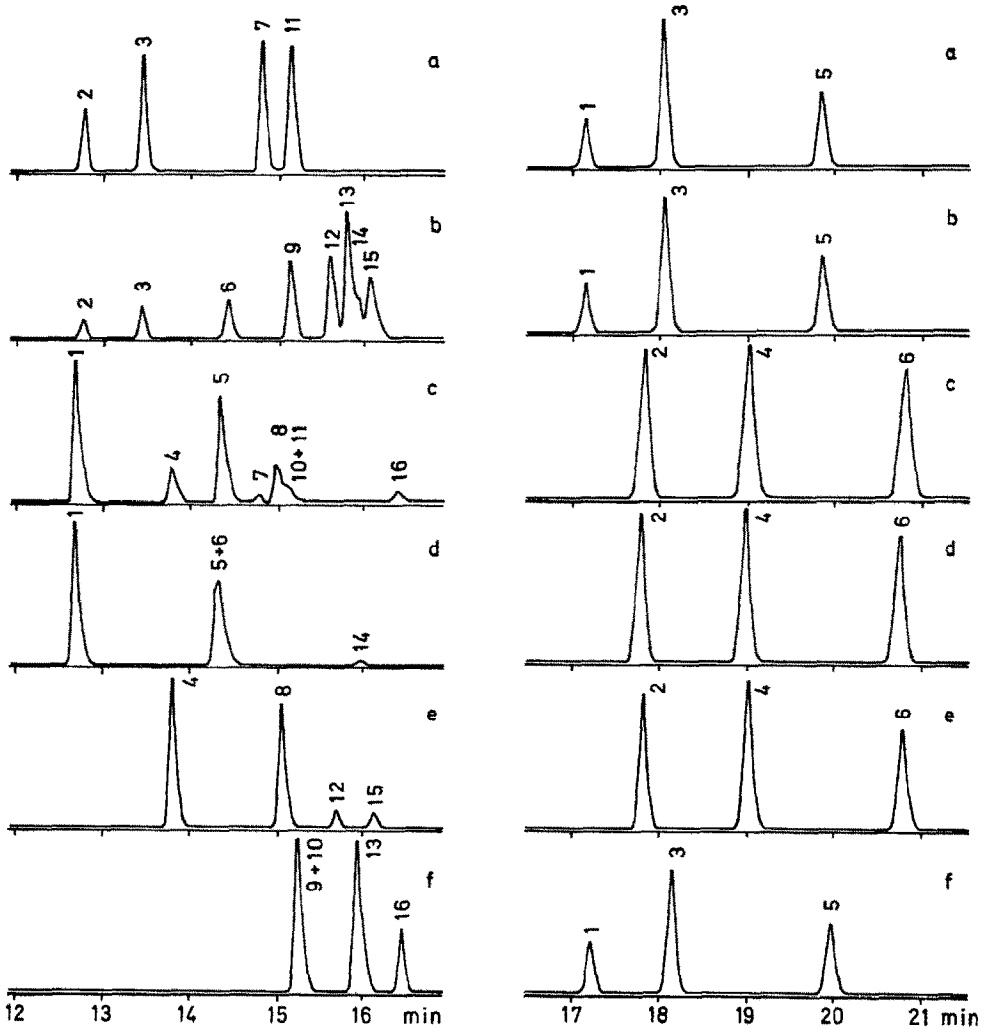


Fig. 3. Chromatograms of trifluoroacetylated *O*-butyloxime derivatives of the oxidation products of (*a*) allitol, (*b*) D-altritol, (*c*) D-glucitol, (*d*) D-mannitol, (*e*) D-iditol, and (*f*) galactitol; s.i.m. at *m/z* 732 (M + 1). Peak identities: 1 and 5, D-fructose; 2 and 3, DL-psicose; 4 and 5, DL-sorbose;, 6 and 14, D-*arabino*-3-hexulose; 7 and 11, DL-*ribo*-3-hexulose; 9 and 13, DL-tagatose; 10 and 16 DL-*xylo*-3-hexulose; 12 and 15, D-*lyxo*-3-hexulose.

Fig. 4. Chromatograms of trifluoroacetylated *O*-butyloxime derivatives of 2,5-hexodiuloses that are oxidation products of (*a*) allitol, (*b*) D-altritol, (*c*) D-glucitol, (*d*) D-mannitol, (*e*) D-iditol, and (*f*) galactitol; s.i.m. at *m/z* 705 (M + 1). Peak identities: 1, 3, and 5, *erythro*-2,5-hexodiulose; 2, 4, and 6, DL-*threo*-2,5-hexodiulose.

Theoretically, diulose *O*-alkyloximes can give four peaks, but, because of steric hindrance, probably not all *O*-alkyloxime derivatives were formed.

Of the hexulose derivatives, only the mass spectrum of the first peak of trifluoroacetylated DL-*xylo*-3-hexulose *O*-butyloxime could not be recorded, because it overlapped those of the corresponding derivatives of DL-tagatose (first peak) and

TABLE II

MASS-SPECTRAL DATA OF TRIFLUOROACETYLATED *O*-BUTYLOXIME DERIVATIVES OF HEXULOSES[a]

m/z	*Assignment*	DL-*Psicose*		D-*Fructose*		DL-*Sorbose*		DL-*Tagatose*		DL-ribo-*3-Hexulose*		D-arabino-*3-Hexulose*		D-lyxo-*3-Hexulose*		DL-xylo *3-Hexulose*	
		1	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*
774	M + 43			2	3	2	2		3	1			1		1		
733	M + 1 (^{13}C)	14	5	24	24	24	24	24	25	4	4	6	19	6	11		25
732	M + 1	58	21	100	100	100	100	100	100	19	17	23	77	26	45		100
731	M	33	12	75	27	74	35	40	25	10	10	6	58	7	11		39
620	M + 15 − 126	19	18	6	7	21	20	15	13	3	2	3	3	3	4		4
619	M + 1 − 113	17	12	5	14	14	24	9	12	3	2	4	7	6	9		18
618	M + 1 − 114	10	7	17	56	26	77	28	41	13	10	16	27	21	38		77
617	M − 114	7		11	35	14	44	7	12	4	4	4	18	7	12		40
562	M + 1 − 57 − 113	5	3	3	2	8	1	9	2	3	3	5	7	5	7		9
522	M + 15 − 98 − 126	4	3	1			1					20	3	3	10		
507	M + 1 − 2 × 113 (^{13}C)	20	19	3	4	16	18	17	8	19	18	19	20	18	19		13
506	M + 1 − 2 × 113	100	100	15	22	80	95	87	44	100	100	100	100	100	100		66
505	M − 2 × 113	25	25	6	11	21	25	20	12	24	22	23	22	24	25		30
448	M + 1 − 57 − 113 − 114	4	1	1	1	7	6	8	3	3	3	5	5	6	7		8
394	M + 15 − 2 × 113 − 126	26	25	1	1	12	17	7	5	9	8	6	5	9	4		
392	M + 1 − 2 × 113 − 114	25	30	3	4	32	42	31	16	23	17	25	12	28	25		10
280	M + 1 − 4 × 113	19	23			7	14	4	3	8	12	5	5	11	4		

[a]Pressure of methylpropane in the ion source, 390 μbar; concentration of hexuloses in derivative solutions (μg/μL): DL-psicose, 0.74; D-fructose, 11.4; DL-sorbose, 1.78; DL-tagatose, 4.78; DL-*ribo*-3-hexulose, 1.39; D-*arabino*-3-hexulose, 1.43; D-*lyxo*-3-hexulose, 1.91; DL-*xylo*-3-hexulose, 3.09.

TABLE III

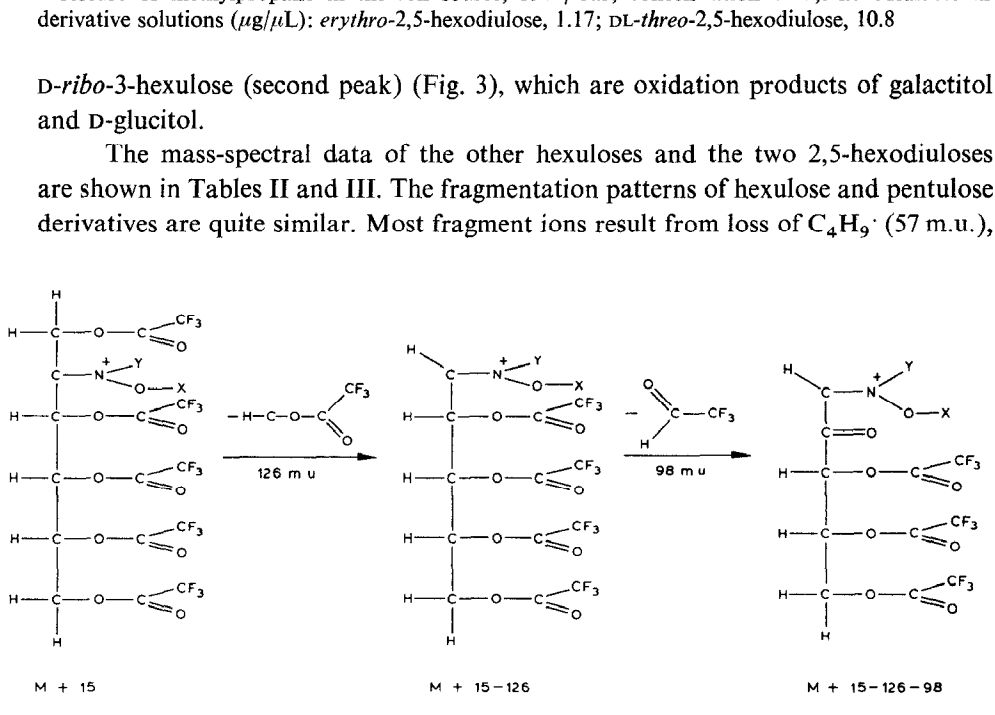
MASS-SPECTRAL DATA OF TRIFLUOROACETYLATED *O*-BUTYLOXIME DERIVATIVES OF 2,5-HEXODIULOSES[a]

m/z	*Assignment*	*Relative intensity (%)*					
		erythro-*2,5-Hexodiulose*			DL-threo-*2,5-Hexodiulose*		
		1	*2*	*3*	*1*	*2*	*3*
706	M + 1 (^{13}C)	27	27	27	26	26	26
705	M + 1	100	100	100	100	100	100
704	M	52	57	53	61	56	57
593	M + 15 − 126	31	24	24	19	14	14
592	M + 1 − 113	23	17	19	16	14	16
591	M + 1 − 114	10	14	16	15	27	39
519	M + 1 − 73 − 113	3	4	5	1	3	3
480	M + 1 − 2 × 113 (^{13}C)	21	15	20	6	6	8
479	M + 1 − 2 × 113	95	70	90	27	28	39
478	M − 2 × 113	24	19	25	8	8	11
407	M + 15 − 73 − 113 − 126	7	6	9	2	2	3
367	M + 15 − 2 × 113 − 126	19	11	16	2	2	2

[a]Pressure of methylpropane in the ion source, 390 μbar; concentration of 2,5-hexodiuloses in derivative solutions (μg/μL): *erythro*-2,5-hexodiulose, 1.17; DL-*threo*-2,5-hexodiulose, 10.8

D-*ribo*-3-hexulose (second peak) (Fig. 3), which are oxidation products of galactitol and D-glucitol.

The mass-spectral data of the other hexuloses and the two 2,5-hexodiuloses are shown in Tables II and III. The fragmentation patterns of hexulose and pentulose derivatives are quite similar. Most fragment ions result from loss of $C_4H_9^{\cdot}$ (57 m.u.),



Scheme 1 Possible fragmentation pattern of trifluoroacetylated O-butyloxime derivatives of hexuloses

$F_3C\text{-}COO^{\cdot}$ (113 m.u.), and $F_3C\text{-}COOH$ (114 m.u.). The peaks with *m/z* 620, 522, and 394 cannot be explained by this fragmentation, and a possible origin is shown in Scheme 1. The CH_3^+ ion may be derived from isobutane, possibly by the addition of $C_4H_9^+$ followed by the loss of C_3H_6.

Fig. 4 shows the chromatograms of trifluoroacetylated *O*-butyloxime derivatives of 2,5-hexodiuloses [s.i.m. at *m/z* 705 (M + 1)]. In the mass spectra, the peak at (M + 1) always predominated. Most fragment ions result from the loss of $O\text{-}C_4H_9^{\cdot}$ (73 m.u.), $F_3C\text{-}COO^{\cdot}$ (113 m.u.), and $F_3C\text{-}COOH$ (114 m.u.). The peaks at *m/z* 593, 407, and 367 can be explained by analogy with the hexuloses, by addition of CH_3^+ (15 m.u.) and subsequent loss of $CHO\text{-}COCF_3$ (126 m.u.), $O\text{-}C_4H_9^{\cdot}$, and $F_3C\text{-}COO^{\cdot}$.

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