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Note

G.l.c.–m.s. of mixtures of enantiomeric tetruloses and pentuloses as trifluoroacetylated *O*-(−)-menthyloxime derivatives

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Resolution of racemic carbohydrates has been achieved by g.l.c. using a chiral stationary phase[1,2], or by conversion of the enantiomers into diastereomers by a chiral reagent followed by separation on a non-chiral phase[3–5].

The g.l.c.–m.s. of diastereomeric derivatives of enantiomeric 2-tetruloses, 2-pentuloses, and 3-pentuloses is now described. These carbohydrates were separated on OV-225 as the trifluoroacetylated *O*-(−)-menthyloxime derivatives. (−)-Menthol was preferred to other chiral alcohols, *e.g.*, 2-butanol or 2-octanol, because of its optical purity and better separation of enantiomeric carbohydrates[5]. An advantage of this derivatisation method is that only *E (syn)* and *Z (anti)* oximes[6,7] can be formed, resulting in two g.l.c. peaks for each. Trifluoroacetylated sugars and methyl glycoside derivatives, separated on a chiral phase, and trimethylsilylated (−)-2-butyl glycoside derivatives, separated on a non-chiral phase, produce up to four peaks[1–4] due to the α and β furanoid and pyranoid forms. Conversion into trifluoroacetylated (−)-menthyloxime derivatives should be useful for the analysis of complex sugar mixtures.

The DL-*threo*-3-pentulose (−)-menthyloximes gave, in contrast to the tetruloses and other pentuloses, only one peak each, as they have the same configuration at C-2 and C-4. The *erythro*-3-pentulose derivatives gave two peaks, because the oxime can be *syn* to carbons with *R* or *S* configurations.

Erythruloses and mixtures of 2-pentuloses and 3-pentuloses were obtained by bromine oxidation of erythritol and pentitols, respectively. Oxidation of erythritol gave DL-erythrulose (DL-*glycero*-2-tetrulose). In g.l.c.–m.s., the c.i. mode was used with isobutane as the ionising gas and selected-ion monitoring (s.i.m.) at m/z 562 (M +1) for the trifluoroacetylated *O*-(−)-menthyloxime derivatives of DL-erythrulose. Three peaks were observed (Table I, Fig. 1). The oxime isomers of DL-erythrulose which appear first are separated, whereas the oximes having higher retention times give only one peak. The peak appearing first should be the L-erythrulose derivative, because, for all trifluoroacetylated *O*-(−)-menthyloxime derivatives of carbohydrates (DL-glyceraldehyde, DL-ribose, DL-arabinose, DL-xylose,

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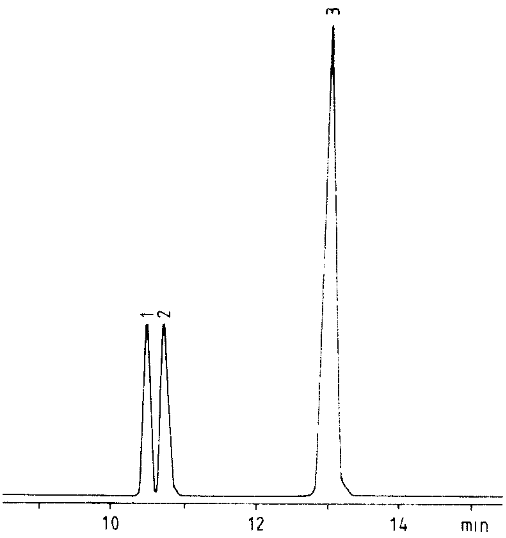

Fig. 1. Gas chromatogram of trifluoroacetylated O-(−)-menthyloxime derivatives of DL-*glycero*-2-tetrulose, using s.i.m. at m/z 562 (M +1). Peak identities: 1 and 3, L-*glycero*-2-tetrulose; 2 and 3, D-*glycero*-2-tetrulose

TABLE I

OXIDATION PRODUCTS OF ERYTHRITOL AND PENTITOLS, AND THE RETENTION TIMES (T) OF THE TRIFLUOROACETYLATED O-(−)-MENTHYLOXIME DERIVATIVES

Alditol	*Products*	T *(min)*	
Erythritol	L-*glycero*-2-Tetrulose	10.50	13.08
	D-*glycero*-2-Tetrulose	10.75	13.08
Ribitol	L-*erythro*-2-Pentulose	13.40	15.43
	D-*erythro*-2-Pentulose	13.80	15.43
	erythro-3-Pentulose	14.57	14.98
D-Arabinitol	D-*threo*-2-Pentulose	12.52	17.40
	D-*erythro*-2-Pentulose	13.79	15.47
	D-*threo*-3-Pentulose	16.84	
L-Arabinitol	L-*threo*-2-Pentulose	12.72	17.40
	L-*erythro*-2-Pentulose	13.40	15.38
	L-*threo*-3-Pentulose	17.13	
Xylitol	D-*threo*-2-Pentulose	12.55	17.40
	L-*threo*-2-Pentulose	12.72	17.40
	erythro-3-Pentulose	14.62	14.98

DL-lyxose, DL-mannose, DL-glucose, DL-galactose, DL-fucose[5], DL-*threo*- and DL-*erythro*-2-pentulose) investigated to date, derivatives having HO-2 L for aldoses, or HO-3 L for 2-uloses, appeared first.

As for other trifluoroacetylated O-alkyloximes of carbohydrates, the most-abundant fragment ions in c.i. (isobutane) mass spectra of the O-(−)-men-

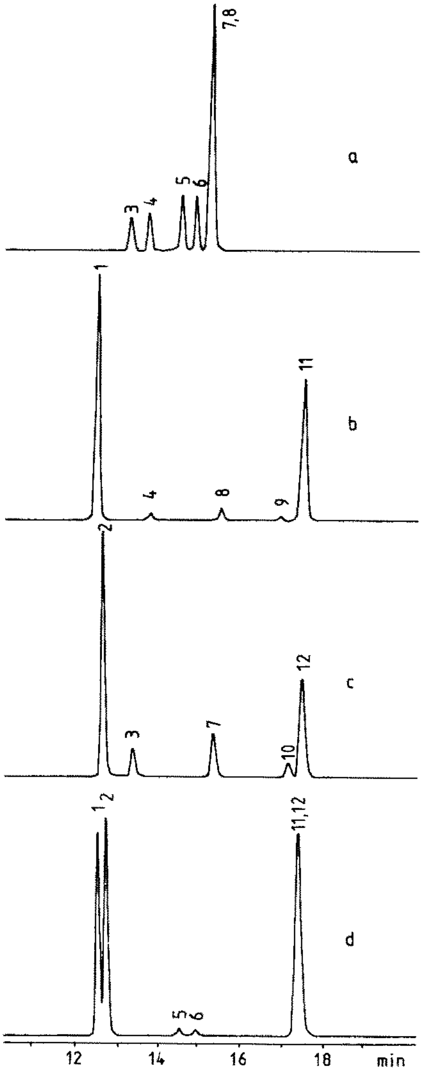

Fig. 2. Gas chromatograms of trifluoroacetylated *O*-(−)-menthyloxime derivatives of the oxidation products of (a) ribitol, (b) D-arabinitol, (c) L-arabinitol, and (d) xylitol; s.i.m. at *m/z* 688 (M +1). Peak identities: 1 and 11, D-*threo*-2-pentulose; 2 and 12, L-*threo*-2-pentulose; 3 and 7, L-*erythro*-2-pentulose; 4 and 8, D-*erythro*-2-pentulose; 5 and 6, *erythro*-3-pentulose; 9, D-*threo*-3-pentulose; and 10, L-*threo*-3-pentulose.

thyloxime derivatives resulted from addition of $C_3H_7^+$ (43 m.u.), CH_3^+ (15 m.u.), and H^+, followed by loss of F_3C-COOH (114 m.u.), F_3C-COO (113 m.u.), CHO-CO-CF_3 (126 m.u.), and CHO-CF_3 (98 m.u.)[8]. The relative intensities of fragment ions are dependent on the partial pressures of the reagent gas and the substrate[9].

The chromatograms of trifluoroacetylated *O*-(−)menthyloxime derivatives of 2- and 3-pentuloses are shown in Fig. 2 [s.i.m. at *m/z* 688 (M +1)]. As for the derivatives of DL-erythrulose, the chromatograms of the derivatives of DL-*erythro*-2-pentulose and DL-*threo*-2-pentulose show the separation of the oxime isomers appearing first, and contain one peak for the oximes having higher retention times; derivative of the carbohydrate having HO-3 L had a retention time shorter than that for the compound having HO-3 D.

The derivatives of D-*threo*-3-pentulose and L-*threo*-3-pentulose gave one peak each, but the D-*threo*-3-pentulose derivative (HO-2,4 D) had the shorter retention time. The derivative of *erythro*-3-pentulose gave two peaks, reflecting two isomeric oximes.

EXPERIMENTAL

Materials.— Erythrulose and pentuloses were obtained by oxidation of erythritol, ribitol, D- and L-arabinitol, and xylitol with bromine in the presence of calcium carbonate[10]. *O*-(−)-Menthylhydroxylammonium chloride was prepared from (−)-menthol and chloramine[11]. Other chemicals were commercial products.

Derivatisation.— The aqueous ethanolic solution (1 mL) of each mixture of oxidation products was dried in an air stream at 80°. A solution of *O*-(−)-menthylhydroxylammonium chloride (8 mg) and sodium acetate (6 mg) in water (0.2 mL) was added, and the mixture was heated at 80° for 1 h and then concentrated as described above. Methanol (0.1 mL) was evaporated from the residue, to give a crystalline precipitate. The last traces of water were removed as an azeotrope by evaporation of benzene (0.1 mL). Then the vial was closed immediately with a PTFE-coated septum, and ethyl acetate (0.015 mL) and trifluoroacetic anhydride (0.03 mL) were added by using a 50-μL syringe. After 1–2 h at room temperature or after 12 h at 0°, the samples were ready for injection

G.l.c.–m.s. — A gas chromatograph–mass spectrometer (MAT 44S) equipped with a 50-m glass-capillary column, wall-coated with OV-225, was used. G.l.c. conditions: column temperature, 180° (isothermal); helium carrier-gas, 1.5 mL/min; split ratio, 1/10; sample volume, 2 μL (scan mode) or 0.5 μL (s.i.m.); injection port, 250°; separator, 220°. M.s. conditions: pressure in c.i. source, 380 μbar, and in the forepump, 40 μbar; electron energy, 150 eV; ion source, 220°; emission current, 0.7 mA; voltage of the secondary electron multiplier 1800 V; *m/z* 300 →700, scanned in 2 s.

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