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Note

Gas chromatographic separation of enantiomeric sugars as diastereomeric trifluoroacetylated (−)-bornyloximes

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Most gas chromatographic (GC) methods do not allow the separation of enantiomeric sugars. The resolution of racemic carbohydrate mixtures has been achieved by using a chiral stationary phase[1,2]. In the chromatograms four peaks for each carbohydrate enantiomer are observed, due to the cyclic α- and β-furanosides and -pyranosides, complicating the resolution of complex sugar mixtures. Reaction with optically active alcohols[3,4] produces diastereomeric glycosides, and the chromatograms also contain up to four peaks for each sugar enantiomer.The oxidation of aldoses to aldonic acids and conversion of enantiomeric compounds with optically active alcohols into the diastereomeric esters[5,6] has the advantage of giving only one peak for each enantiomeric carbohydrate, but this method is not applicable to ketoses and derivatization is very difficult. More practicable is the derivatization of sugars with (+)-1-phenylethanethiol to the dithioacetals[7] and with (−)-menthylhydroxylammonium chloride to the menthyloximes[8], also giving acyclic derivatives.

In this paper the separation of enantiomeric sugars as diastereomeric trifluoroacetylated (−)-bornyloximes is described. As the comparable (−)-menthyloximes, each enantiomer derivative produces two peaks in the chromatogram, the *Z*- and *E*-oxime isomers.

EXPERIMENTAL

Apparatus

A Hewlett-Packard 5830A gas chromatograph equipped with a 50-m capillary column wall-coated with OV-225 (WGA, Griesheim, G.F.R.) was used. The split liner was filled to about 2 cm with 3% OV-225 on Chromosorb W HP (80–100 mesh), held on both sides by quartz-wool.

Materials

The carbohydrates and trifluoroacetic anhydride were obtained from Sigma (Munich, G.F.R.), and (−)-borneol from EGA (Steinheim, G.F.R.). O-(−)-Bornylhydroxylammonium chloride was synthesized from the sodium alcoholate and chloramine[9].

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Derivatization

About 0.5 mg of a sugar or a carbohydrate mixture was added to a solution of 4 mg of O-(−)-bornylhydroxylammonium chloride and 3 mg of sodium acetate in 0.1 ml of water. This mixture was held at 80°C for 1 h. Further preparation was carried out as described previously[10].

RESULTS AND DISCUSSION

The separation of enantiomeric carbohydrates was good. In most instances both pairs of oxime isomers of enantiomeric sugars were separated; only the second peaks of D- and L-glyceraldehyde and D- and L-arabinose overlapped (Fig. 1). As expected, the glyceraldehyde derivatives had the shortest retention times of the sugar derivatives investigated, but as for the trifluoroacetylated (−)-menthyloximes[8], the fucose (6-deoxygalactose) and rhamnose (6-deoxymannose) derivatives were eluted before the pentose derivatives (Table I and Figs. 1 and 2).

The derivatives of the carbohydrate enantiomers with the hydroxy function at C-2 on the left-hand side in Fischer's projection (*S* configuration at C-2 in the parent sugar) had the shorter retention times (Table I and Figs. 1 and 2), but when both the C-2 and C-3 in the parent sugars have the same configuration, the second peaks appeared in inverted sequence (ribose, lyxose and mannose).

To illustrate the applicability of this method to the determination of the absolute configuration of carbohydrates, it was applied to the hydrolysates of gum

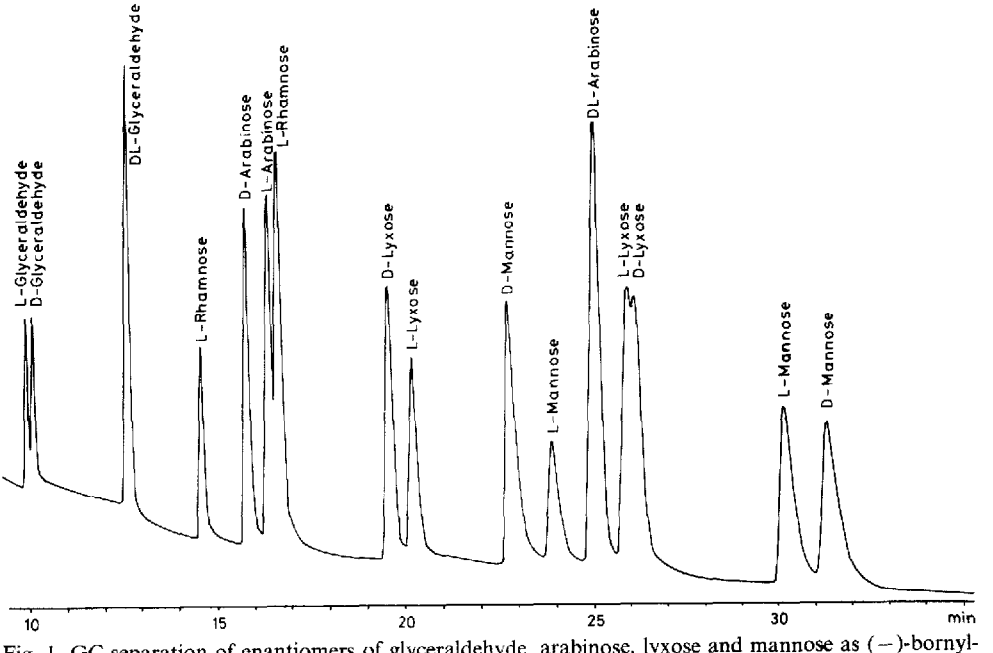

Fig. 1. GC separation of enantiomers of glyceraldehyde, arabinose, lyxose and mannose as (−)-bornyloxime pertrifluoroacetates. Temperatures: column, 180°C (isothermal); injector and detector, 250°C. Gas flow-rates: nitrogen carrier gas, 2.5 ml/min; hydrogen, 20 ml/min; air 200 ml/min. Sample volume: 1 μl. Splitting ratio: 1:10.

TABLE I

RETENTION TIMES OF THE (−)-BORNYLOXIME PERTRIFLUOROACETYL DERIVATIVES OF SOME CARBOHYDRATES

Each carbohydrate enantiomer give two peaks, the *E*- and *Z*-isomers; 50-m capillary column; conditions as in Fig. 1.

Carbohydrate	*Retention time (min)*			
	D-Enantiomer		*L-Enantiomer*	
	I	*II*	*I*	*II*
Glyceraldehyde	10.06	12.60	9.89	12.60
Ribose	16.42	20.82	15.53	21.26
Arabinose	15.78	24.94	16.36	25.08
Xylose	20.11	27.18	19.93	26.37
Lyxose	19.55	26.12	20.17	25.91
Glucose	23.83	33.48	23.44	32.14
Mannose	23.27	31.57	24.46	30.47
Galactose	24.34	38.67	23.60	37.97
Fucose	12.99	19.49	12.57	19.39
Rhamnose*			14.56	16.61

* D-Rhamnose was not available.

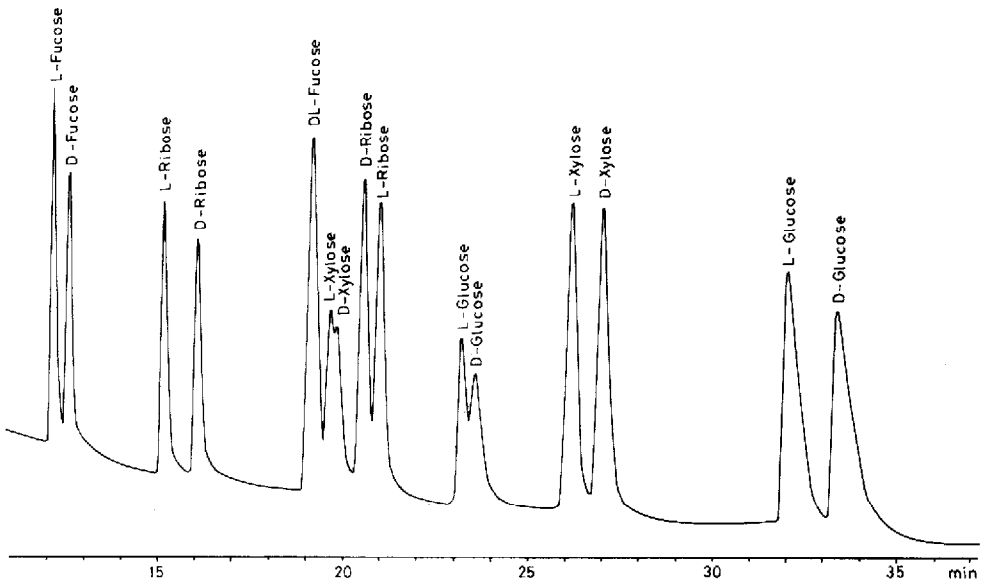

Fig. 2. GC separation of enantiomers of fucose, ribose, xylose and glucose as (−)-bornyloxime pertrifluoroacetates. Conditions as in Fig. 1.

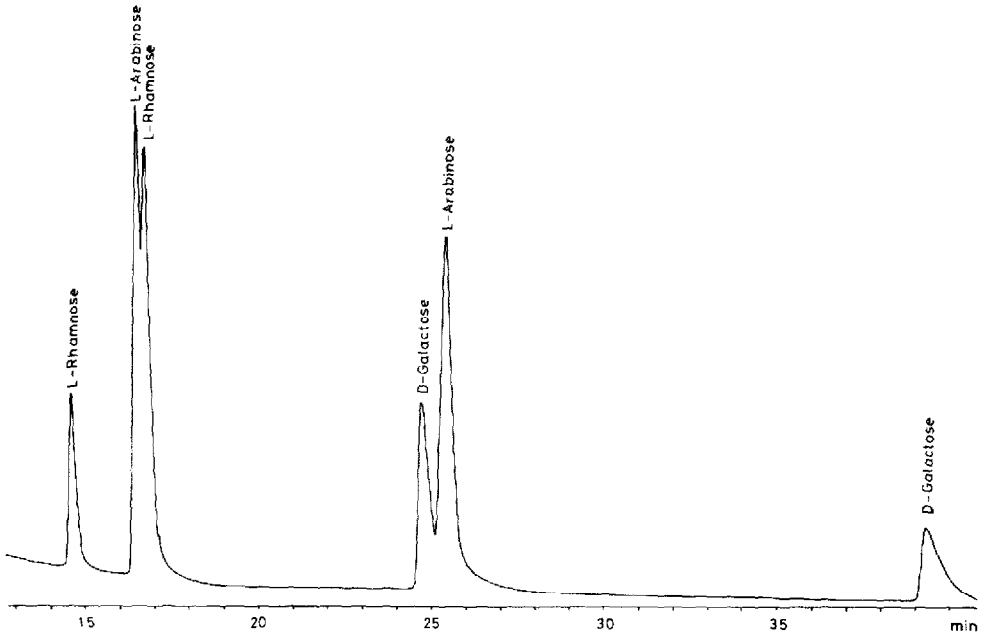

Fig. 3. Gas chromatogram of carbohydrates in the hydrolysate of gum arabic, as trifluoroacetylated (−)-bornyloximes. Conditions as in Fig. 1.

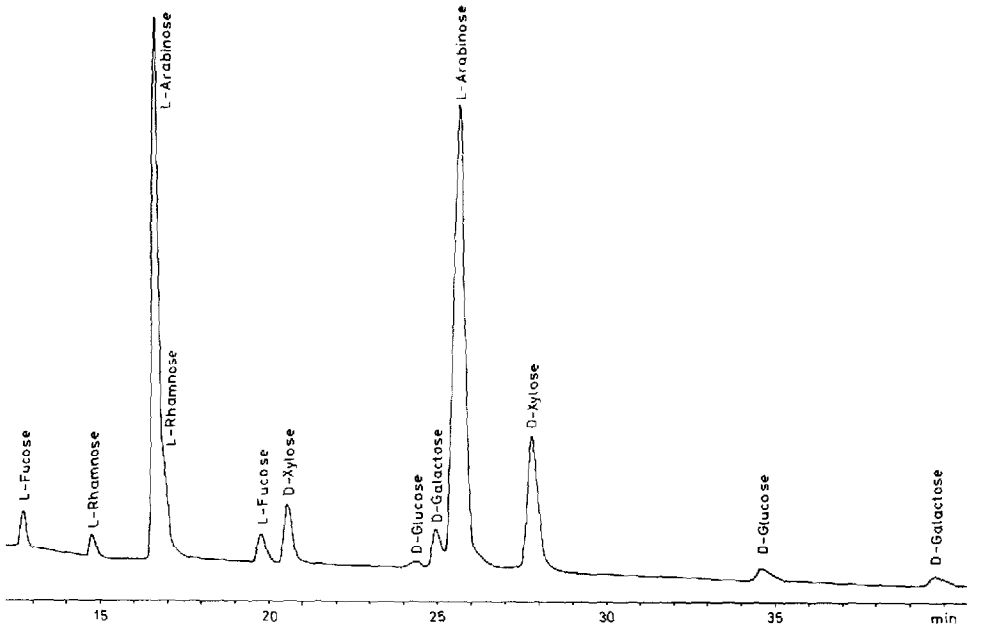

Fig. 4. GC separation of sugars contained in the hydrolysate of gum tragacanth as the (−)-bornyloxime pertrifluoroacetates. Conditions as in Fig. 1.

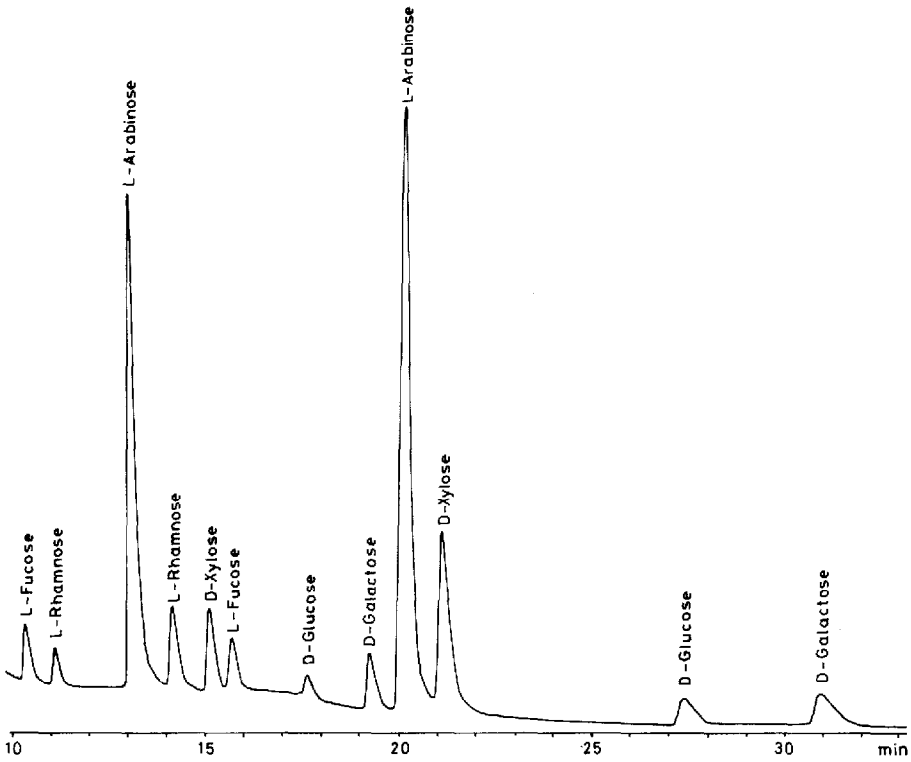

Fig. 5. Gas chromatogram of carbohydrates in the hydrolysate of gum tragacanth as trifluoroacetylated (−)-menthyloximes. Conditions as in Fig. 1.

arabic (Fig. 3) and gum tragacanth (Fig. 4), two naturally occurring polysaccharides. Both hydrolysates contain L-rhamnose, L-arabinose and D-galactose, and the hydrolysate of gum tragacanth also contains L-fucose, D-xylose and D-glucose.

As the peaks of the derivatives of L-arabinose (first peak) and L-rhamnose (second peak) partially overlap, the sugars contained in the hydrolysate of gum tragacanth were also derivatized to the trifluoroacetylated (−)-menthyloximes (Fig. 5). The separation of these carbohydrate derivatives is better, but the absolute configuration of xylose and glucose cannot be determined as the derivatives of D- and L-xylose and D- and L-glucose nearly have the same retention times[8].

REFERENCES

1 W. A. König, I. Benecke and H. Bretting, *Angew. Chem.*, 93 (1981) 688–690.
2 W. A. König, I. Benecke and S. Sievers, *J. Chromatogr.*, 217 (1981) 71–79.
3 G. J. Gerwig, J. P. Kamerling and J. F. G. Vliegenthart, *Carbohydr. Res.*, 62 (1978) 349–357.
4 J. Briggs, P. Finch, E. Percival and H. Weigel, *Carbohydr. Res.*, 103 (1982) 186 189.
5 G. E. Pollock and D. A. Jermany, *J. Gas Chromatogr.*, 6 (1968) 412–415.
6 G. E. Pollock and D. A. Jermany, *J. Chromatogr. Sci.*, 8 (1970) 296.
7 M. R. Little, *Carbohydr. Res.*, 105 (1982) 1–8.
8 H. Schweer, *J. Chromatogr.*, 243 (1982) 149–152.
9 W. Theilacker and K. Ebke, *Angew. Chem.*, 68 (1956) 303.
10 P. Decker and H. Schweer, *J. Chromatogr.*, 236 (1982) 369–373.