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# Capillary gas chromatographic separations of a multi-component mixture of polyalcohol compounds

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ABSTRACT

Capillary gas chromatographic separation conditions were established for a 31-component mixture of polyhydroxy compounds containing two tetritols, three pentitols, six hexitols, seven monoanhydropentitols, eight monoanhydrohexitols, three dianhydrohexitols, pentaerythritol and myoinositol. Mixtures of per-O-acetyl or per-O-trimethylsilyl derivatives of these compounds were separated on fused-silica columns using highly polar DB-23 and non-polar HP-5 stationary phases, respectively. Relative retention times for each compound with respect to pentaerythritol and myoinositol and methylene units were determined.

## INTRODUCTION

Polyhydroxy compounds are widespread in the plant kingdom [1,2] and there is great interest in their detection and identification. High-resolution gas chromatography (HRGC) offers the possibility of the rapid detection of these compounds or their derivatives in mixtures from natural sources or resulting from chemical transformations of polyols.

The recent literature covering applications of GC to these compounds can be divided into three groups. The first is concerned with improvement of GC separation methods for alditol, anhydroalditol and cyclitol derivatives [3–19]. The second involves papers dealing with the detection and determination of these compounds occurring in nature, *e.g.*, in biological fluids [20,21], human cerebrospinal fluid [22], the blood serum [23], urine of patients with uraemia [24], human urine (6-deoxyallitol and 6-deoxyglucitol) [25], eyeballs of animals and healthy humans [26], eyeballs of patients with cataract [27], animal cell plasma [28], cow milk [29], clover and peanuts [30], seeds and fodder (methylinositol) [31], raw food [32], foodstuffs [33] and plasticizers [34]. The third relates to the GC separation of enantiomers on columns with chiral stationary phases [35–39].

Our previous studies concerning the separation and identification of anhydroalditol mixtures formed in cyclization–dehydration reactions of particular pentitols [40–44] and hexitols [45,46] were performed using capillary GC (cGC) with SE-52, OV-275, Carbowax 20M and 20MTPA stationary phases and helium or hydrogen as the carrier gas. Based on these results, we were able to separate more complicated mixtures.

In this paper we present the results of the separation of per-O-acetyl and per-O-trimethylsilyl derivatives of a 31-component mixture of polyols by cGC.

## EXPERIMENTAL

### *Gas chromatographic conditions*

The 31-component mixture of polyhydroxy compounds was separated on two columns: as per-O-acetyl derivatives on a DB-23 fused-silica

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column (60 m × 0.258 mm I.D.) and as per-O-trimethylsilyl derivatives on an HP-5 fused-silica column (50 m × 0.2 mm I.D.).

Both columns were separately installed inside a Carlo Erba Vega 6180 gas chromatograph. The gas chromatograph was equipped with a cold on-column injector, a flame ionization detector and an integrator (CE Instruments DP 700). Hydrogen was used as the carrier gas at a flow-rate of 2 ml/min measured at room temperature. The temperature programme for the HP-5 column was from 115 to 180°C at 3°C/min and from 180 to 250°C at 4°C/min, and that for the DB-23 column was from 80 to 150°C at 3°C/min, from 150 to 200°C at 4°C/min and from 200 to 240°C at 5°C/min with a final hold at 240°C for 15 min.

*Reactants*

The following compounds were used: allitol, obtained by reduction of D-allose (Aldrich) with $NaBH_4$; D-altritol and galactitol, obtained by reduction of D-tagatose (Sigma) with $NaBH_4$; 1,4-anhydro-D-arabinitol [47]; 1,5-anhydro-D-arabinitol [47]; 1,4-anhydro-D,L-galactitol [47];

TABLE I

RETENTION CHARACTERISTICS OF PER-O-ACETYLATED POLYOLS ON DB-23

| GC peak | Per-O-acetyl derivative of | Retention time (min) | Relative retention time[a] | | Methylene units[b] |
|---|---|---|---|---|---|
| | | | $RRT^1$ | $RRT^2$ | |
| 1 | 1,5-Anhydroxylitol | 33.07 | 0.811 | 0.667 | 24.75 |
| 2 | 1,5-Anhydroribitol | 34.13 | 0.837 | 0.682 | 25.29 |
| 3 | 1,5-Anhydroarabinitol | 34.39 | 0.844 | 0.687 | 25.42 |
| 4 | 1,4;3,6-Dianhydroglucitol | 34.60 | 0.849 | 0.692 | 25.53 |
| 5 | Erythritol + 1,4-anhydroarabinitol | 34.87 | 0.856 | 0.697 | 25.63 |
| 6 | 1,4-Anhydroxylitol | 35.06 | 0.860 | 0.701 | 25.74 |
| 7 | 1,4;3,6-Dianhydromannitol | 35.24 | 0.864 | 0.705 | 25.85 |
| 8 | 1,4-Anhydroribitol | 36.03 | 0.884 | 0.720 | 26.26 |
| 9 | Threitol | 36.29 | 0.890 | 0.726 | 26.43 |
| 10 | 1,5;3,6-Dianhydroglucitol | 36.54 | 0.896 | 0.731 | 26.57 |
| 11 | 1,4-Anhydrolyxitol | 36.68 | 0.900 | 0.733 | 26.66 |
| 12 | Penthaerythritol | 40.77 | 1.000 | 0.815 | 29.22 |
| 13 | Ribitol | 41.67 | 1.022 | 0.833 | 29.65 |
| 14 | Arabinitol | 42.02 | 1.031 | 0.840 | 29.76 |
| 15 | 1,4-Anhydroglucitol | 42.32 | 1.038 | 0.846 | 29.86 |
| 16 | 1,5-Anhydroglucitol | 42.91 | 1.052 | 0.858 | 30.29 |
| 17 | 1,4-Anhydrogalactitol | 43.18 | 1.059 | 0.863 | 30.43 |
| 18 | 1,4-Anhydromannitol + 1,5-anhydrogalactitol | 43.34 | 1.063 | 0.866 | 30.50 |
| 19 | 1,5-Anhydromannitol | 43.49 | 1.067 | 0.869 | 30.57 |
| 20 | Xylitol + 2,5-anhydroglucitol | 43.84 | 1.076 | 0.876 | 30.74 |
| 21 | 1,6-Anhydroiditol | 45.28 | 1.111 | 0.905 | 32.26 |
| 22 | Allitol | 46.35 | 1.137 | 0.927 | 32.58 |
| 23 | Mannitol | 47.16 | 1.157 | 0.943 | 32.84 |
| 24 | Altritol | 47.35 | 1.161 | 0.947 | 32.87 |
| 25 | Galactitol | 48.03 | 1.178 | 0.960 | 34.07 |
| 26 | Glucitol | 49.05 | 1.203 | 0.981 | 34.38 |
| 27 | Myoinositol | 50.02 | 1.227 | 1.000 | 34.68 |
| 28 | Iditol | 50.89 | 1.248 | 1.017 | 34.97 |

[a] $RRT^1$ relative to pentaerythritol, $RRT^2$ relative to myoinositol.
[b] Measured relative to $C_{24}$–$C_{35}$ *n*-alkanes from 80°C at 3°C/min.

1,5-anhydro-D-galactitol [47]; 1,4-anhydro-D-glucitol [47]; 1,5-anhydro-D-glucitol [47]; 2,5-anhydro-D-glucitol [47]; 1,6-anhydro-L-iditol [47]; 1,4-anhydro-D,L-xylitol [44]; 1,5-anhydroxylitol [44]; 1,4-anhydro-D-lyxitol [44]; 1,4-anhydro-D-mannitol [47]; 1,5-anhydro-D-mannitol [47]; 1,4-anhydro-D,L-ribitol [44]; 1,5-anhydroribitol [44]; D-arabinitol (Sigma); 1,4;3,6-dianhydro-D-glucitol [47]; 1,5;3,6-dianhydro-D-glucitol [47]; 1,4;3,6-dianhydro-D-mannitol [47]; erythritol (Aldrich); galactitol (Sigma); D-glucitol (Sigma); L-iditol [48]; xylitol (Sigma); D-mannitol (Sigma); myoinositol (Sigma); pentaerythritol (Sigma); ribitol (Sigma); D,L-threitol (Aldrich); bis(trimethylsilyl)acetamide (BSTFA) (Aldrich); acetic anhydride (Polskie Odczynniki Chemiczne, Gliwice, Poland); sodium acetate (Polskie Odczynniki Chemiczne); $C_{10}$, $C_{12}$, $C_{14}$, $C_{16}$, $C_{18}$, $C_{20}$, $C_{22}$, $C_{24}$, $C_{28}$, $C_{32}$, $C_{36}$ *n*-alkanes kit (Alltech); $C_9$, $C_{11}$, $C_{13}$, $C_{15}$, $C_{17}$, $C_{19}$, $C_{21}$, $C_{23}$, $C_{25}$ *n*-alkanes kit (Alltech); *n*-hexacosane (Alltech); *n*-triacontane (Alltech); and tetratriacontane (Alltech).

*Solvents*

Chloroform, pyridine and hexane were obtained from Aldrich.

*Apparatus and columns*

A VEGA 6180 gas chromatograph was obtained from Fisons Instruments (Vienna, Austria), a DB-23 capillary column from J&W Scientific (Folsom, CA, USA) and an HP-5 capillary column from Hewlett-Packard (Geneva, Switzerland).

*Preparation of standard mixture*

About 2–5 mg of each of the 31 reactants were dissolved in 10 ml of water and 20 $\mu$l of this mixture were placed in a Reacti-vial. Water was then removed under a stream of nitrogen and 0.5

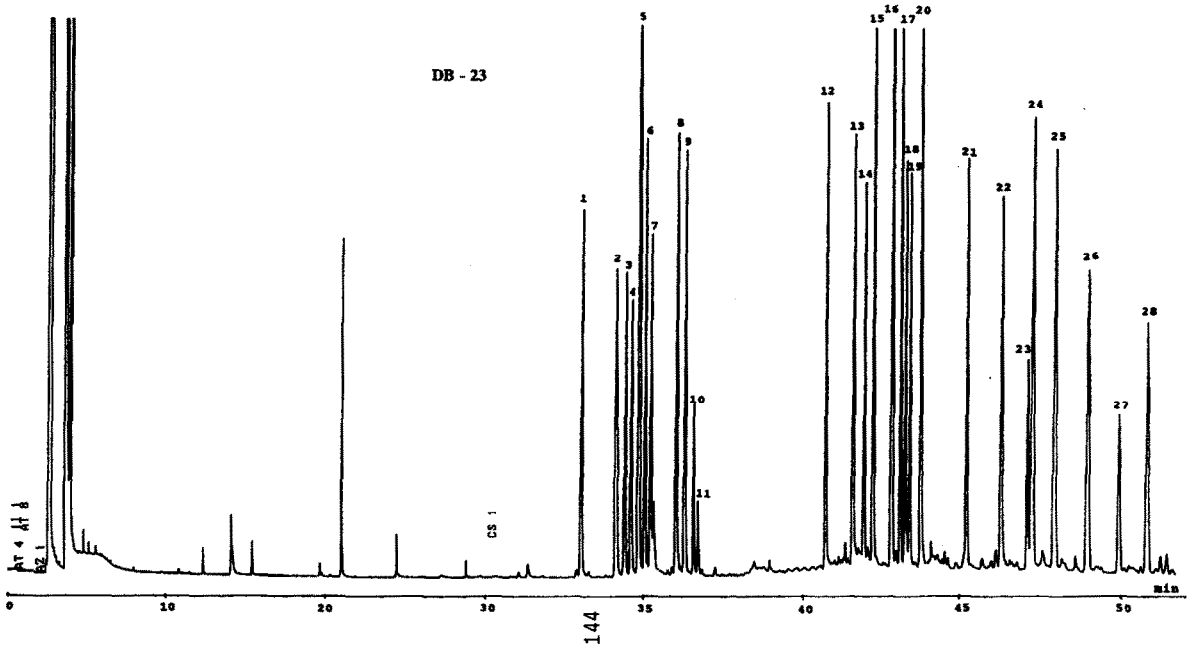


Fig. 1. Gas chromatogram of per-O-acetyl derivatives of the 31-component mixture separated on DB-23. Peaks: 1 = 1,5-anhydroxylitol; 2 = 1,5-anhydroribitol; 3 = 1,5-anhydroarabinitol; 4 = 1,4;3,6-dianhydroglucitol; 5 = erythritol + 1,4-anhydroarabinitol; 6 = 1,4-anhydroxylitol; 7 = 1,4;3,6-dianhydromannitol; 8 = 1,4-anhydroribitol; 9 = threitol; 10 = 1,5;3,6-dianhydroglucitol; 11 = 1,4-anhydrolyxitol; 12 = penthaerythritol; 13 = ribitol; 14 = arabinitol; 15 = 1,4-anhydroglucitol; 16 = 1,5-anhydroglucitol; 17 = 1,4-anhydrogalactitol; 18 = 1,4-anhydromannitol + 1,5-anhydrogalactitol; 19 = 1,5-anhydromannitol; 20 = xylitol + 2,5-anhydroglucitol; 21 = 1,6-anhydroiditol; 22 = allitol; 23 = mannitol; 24 = altritol; 25 = galactitol; 26 = glucitol; 27 = myoinositol; 28 = iditol.

ml of freshly distilled acetic anhydride and 10 mg of anhydrous sodium acetate were added. The mixture was heated at 100°C for 1 h, then the volatile components were removed under reduced pressure and the residue was dissolved in 100 μl of chloroform.

Another 20 μl portion of the same mixture, after removing water under a stream of nitrogen, was O-trimethylsilylated with 100 μl of BSTFA in 100 μl of pyridine at 100°C for 15 min.

## RESULTS AND DISCUSSION

The separation with the optimum temperature programme and with the optimum carrier gas flow-rate of the per-O-acetylated 31-component mixture of polyol compounds on a fused-silica cGC column with the stationary phase DB-23 (Table I) gave 28 well separated peaks (Fig. 1). Erythritol and 1,4-anhydroarabinitol (peak 5), 1,4-anhydromannitol and 1,5-anhydrogalactitol (peak 18) and xylitol and 2,5-anhydroglucitol (peak 20) were not separated. It is noteworthy that a separately prepared mixture of per-O-acetyl-1,4-anhydro-D-mannitol and -1,5-anhydro-D-galactitol could be separated on a glass column coated, according to Grob and Grob's procedure [49], with a mixed Carbowax 20 MTPA–SP 2340 (2:1, w/w) stationary phase. The remaining components were separated to the baseline and could be quantitatively determined.

The elution order of per-O-acetylated compounds (Fig. 1, Table I), in particular polyol groups, is as follows:

(a) alditols: erythritol (5), threitol (9), ribitol (13), arabinitol (14), xylitol (20), allitol (22), mannitol (23), altritol (24), galactitol (25), glucitol (26) and iditol (28);

(b) anhydropentitols: 1,5-anhydroxylitol (1), -ribitol (2) and -arabinitol (3), 1,4-anhydroarabinitol (5), -xylitol (6), -ribitol (8) and -lyxitol (9); the elution order of fully acetylated

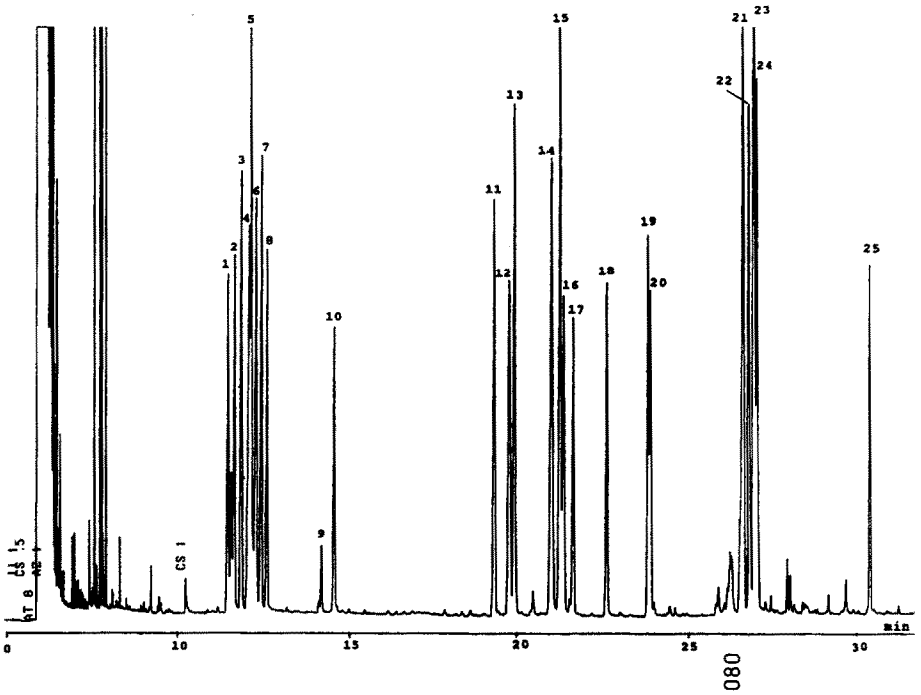


Fig. 2. Gas chromatogram of per-O-trimethylsilyl derivatives of the 31-component mixture separated on HP-5. Peaks: 1 = 1,5-anhydroarabinitol; 2 = 1,5;3,6-dianhydroglucitol + 1,4;3,6-dianhydroglucitol; 3 = 1,4-anhydroarabinitol + threitol; 4 = pentaerythritol + erythritol; 5 = 1,4;3,6-dianhydromannitol; 6 = 1,5-anhydroribitol; 7 = 1,4-anhydroribitol; 8 = 1,4-anhydroxylitol; 9 = 1,4-anhydrolyxitol; 10 = 1,5-anhydroxylitol; 11 = xylitol; 12 = arabinitol; 13 = ribitol; 14 = 2,5-anhydroglucitol + 1,4-anhydrogalactitol; 15 = 1,4-anhydroglucitol; 16 = 1,5-anhydromannitol; 17 = 1,6-anhydroiditol; 18 = 1,5-anhydrogalactitol; 19 = 1,4-anhydromannitol; 20 = 1,5-anhydroglucitol; 21 = mannitol; 22 = glucitol; 23 = allitol + galactitol + iditol; 24 = altritol; 25 = myoinositol.

1,4-anhydropentitols is in accordance with the values of their free energy differences [42];

(c) anhydroglucitols: 1,4- (peak 15), 1,5- (peak 16) and 2,5- (peak 20);

(d) anhydrogalactitols: 1,4- (peak 17) and 1,5- (peak 18);

(e) anhydromannitols: 1,4- (peak 18) and 1,5- (peak 19). Thus, among these isomeric per-O-acetyl-anhydropentitols, 1,5-anhydropentitols elute before 1,4-anhydropentitols. Further, per-O-acetyl-1,4-anhydrohexitols isomers elute before the 1,5-anhydro isomers.

The use of a fused-silica cGC column with HP-5 stationary phase for the separation of the per-O-trimethylsilylated mixture of the same polyols compounds gave only 25 peaks (Fig. 2, Table II). In this case five sets of compounds could not be separated: 1,4;3,6- and 1,5;3,6-dianhydroglucitol (peak 2), 1,4-anhydroarabinitol and threitol (peak 3), erythritol and pentaerythritol (peak 4), 2,5-anhydroglucitol and 1,4-anhydrogalactitol (peak 14) and allitol, galactitol and iditol (peak 23). Thus, only twelve peaks were separated to the base line (7–13, 18, 21, 22

TABLE II

RETENTION CHARACTERISTICS OF PER-O-TRIMETHYLSILYLATED POLYOLS ON HP-5

| GC peak | Per-O-trimethylsilyl derivative of | Retention time (min) | Relative retention time[a] | | Methylene units[b] |
|---|---|---|---|---|---|
| | | | $RRT^1$ | $RRT^2$ | |
| 1 | 1,5-Anhydroarabinitol | 11.60 | 0.380 | 0.950 | 15.17 |
| 2 | 1,5;3,6-Dianhydroglucitol + 1,4;3,6-dianhydroglucitol | 11.79 | 0.386 | 0.966 | 15.23 |
| 3 | 1,4-Anhydroarabinitol + threitol | 11.98 | 0.392 | 0.981 | 15.29 |
| 4 | Pentaerythritol + erythritol | 12.21 | 0.400 | 1.000 | 15.35 |
| 5 | 1,4;3,6-Dianhydromannitol | 12.27 | 0.402 | 1.005 | 15.37 |
| 6 | 1,5-Anhydroribitol | 12.40 | 0.406 | 1.016 | 15.42 |
| 7 | 1,4-Anhydroribitol | 12.55 | 0.411 | 1.028 | 15.46 |
| 8 | 1,4-Anhydroxylitol | 12.71 | 0.416 | 1.041 | 15.51 |
| 9 | 1,4-Anhydrolyxitol | 14.27 | 0.467 | 1.169 | 16.00 |
| 10 | 1,5-Anhydroxylitol | 14.66 | 0.480 | 1.201 | 16.11 |
| 11 | Xylitol | 19.43 | 0.636 | 1.591 | 17.48 |
| 12 | Arabinitol | 19.88 | 0.651 | 1.628 | 17.60 |
| 13 | Ribitol | 20.04 | 0.656 | 1.641 | 17.66 |
| 14 | 2,5-Anhydroglucitol + 1,4-anhydrogalactitol | 21.09 | 0.691 | 1.727 | 17.97 |
| 15 | 1,4-Anhydroglucitol | 21.36 | 0.699 | 1.749 | 18.00 |
| 16 | 1,5-Anhydromannitol | 21.45 | 0.702 | 1.757 | 18.04 |
| 17 | 1,6-Anhydroiditol | 21.76 | 0.713 | 1.782 | 18.13 |
| 18 | 1,5-Anhydrogalactitol | 22.71 | 0.744 | 1.860 | 18.42 |
| 19 | 1,4-Anhydromannitol | 23.91 | 0.783 | 1.958 | 18.78 |
| 20 | 1,5-Anhydroglucitol | 23.99 | 0.786 | 1.965 | 18.81 |
| 21 | Mannitol | 26.73 | 0.875 | 2.189 | 19.75 |
| 22 | Glucitol | 26.92 | 0.881 | 2.205 | 19.82 |
| 23 | Allitol + galactitol + iditol | 27.07 | 0.886 | 2.217 | 19.88 |
| 24 | Altritol | 27.14 | 0.889 | 2.223 | 19.93 |
| 25 | Myoinositol | 30.54 | 1.000 | 2.501 | 21.29 |

[a] $RRT^1$ relative to myoinositol, $RRT^2$ relative to pentaerythritol.

[b] Measured relative to $C_{15}$–$C_{22}$ *n*-alkanes from 115°C at 3°C/min.

and 25) and only these could be quantitatively analysed.

The elution order of per-O-trimethylsilylated compounds (Fig. 2, Table II), in particular polyol groups, is as follows:

(a) alditols: threitol (3), erythritol (4), xylitol (11), arabinitol (12), ribitol (13), mannitol (21), glucitol (22) and altritol (24);

(b) anhydropentitols: 1,5-anhydroarabinitol (1), 1,4-anhydroarabinitol (3), 1,5-anhydroribitol (6), 1,4-anhydroribitol (7), 1,4-anhydroxylitol (8), 1,4-anhydrolyxitol (9) and 1,5-anhydroxylitol (10);

(c) anhydroglucitols: 2,5- (peak 14), 1,4- (peak 15) and 1,5- (peak 20);

(d) anhydrogalactitols: 1,4- (peak 14) and 1,5- (peak 18);

(e) anhydromannitols: 1,5- (peak 16) and 1,4- (peak 19).

The identities of all peaks in both instances were determined by the standard cGC co-injection method.

The relative retention times with respect to pentaerythritol and myoinositol and the number of methylene units were determined in the usual manner for both types of derivatives and are given in Tables I and II.

On the basis of this and previous work, we can conclude that the cGC separations of the per-O-acetyl derivatives of polyols give better results than for their O-trimethylsilyl derivatives. Hence these derivatives can be used for the determination of these compounds in biological fluids [50].

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