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Chiral recognition of racemic sugars by polar and nonpolar cyclodextrin-derivative gas chromatography

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ABSTRACT

Di-*O*-pentyl-derivatized cyclodextrins and (*S*)-hydroxypropyl-per-*O*-methyl-derivatized cyclodextrins were used as chiral stationary phases in capillary gas chromatography. Di-*O*-pentyl-derivatized cyclodextrins were rather apolar, whereas the *O*-hydroxypropyl per-*O*-methyl derivatives were relatively hydrophilic and could be dissolved in water. High enantioselectivity towards thirteen trifluoroacetylated sugars was observed with both sets of chiral stationary phases. Most of the sugars studied had their enantiomeric elution-order reversed on the different stationary phases. 2,6-Di-*O*-pentyl-3-*O*-trifluoracetyl-derivatized cyclodextrins, used as a g.l.c. stationary phase, showed behavior intermediate between the other two cyclodextrin derivatives. The chromatographic separation-factors with the dipentyltrifluoroacetyl derivatives were higher than the corresponding values on the two other sets of chiral stationary phases. All columns were stable over a wide range of operating temperature.

INTRODUCTION

Natural sugars rather frequently occur in both enantiomeric configurations, and it is of importance to establish absolute stereochemistry. Most quantitative determinations have utilized polarimetric data performed on the isolated sugars[1]. Gas chromatography (g.l.c.) with chiral stationary phases is a promising modern alternative[2]. König *et al.* developed an XE-60-L valine (*S*)-phenylethylamide chiral phase for the separation of such enantiomeric pairs as aldopentoses, aldohexoses, and polyols[3–5]. Another g.l.c. stationary phase used for enantiomeric separation of sugars was L-valine-*tert*-butylamide coupled to a siloxane copolymer (Chirasil-Val)[6–8].

The idea of using carbohydrate-based chiral stationary-phases to perform sugar separations is not new. Cyclodextrin stationary phases have been used successfully in liquid chromatography (l.c.). Both anomeric and general separations of sugars may be achieved by l.c. on cyclodextrin-bonded phases[9]. The three most common cyclodextrins are: cyclohexaamylose, (α-cyclodextrin), cycloheptaamylose (β-cyclodextrin), and cyclooctaamylose (γ-cyclodextrin). Cyclodextrins are crystalline solids with high melting points, making them difficult to use as g.l.c. stationary-phase coatings[10,11]. Recently,

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König and co-workers produced a liquid, lipophilic, alkyl cyclodextrin[12], which, used as a g.l.c.-chiral stationary-phase, was suitable for separation of sugars[13].

We have recently described the synthesis of liquid, hydrophilic cyclodextrin derivatives and their use as chiral stationary phases in g.l.c.[14,15]. The separation of enantiomeric sugars by capillary g.l.c. on stationary phases composed of cyclodextrin derivatives further expands the role played by cyclodextrins in carbohydrate separations. Here, we present a comparative study of two types of new α-, β-, and γ-cyclodextrin derivatives as chiral stationary-phases. The first type consisted of non-polar derivatives (hexakis, heptakis-, and octakis-2,6-di-*O*-pentyl-cyclodextrins) and the second consisted of relatively polar derivatives [(*S*)-hydroxypropyl-per-*O*-methyl-derivatized cyclodextrins]. The chromatographic results obtained with these types of stationary phase suggested the synthesis of hexakis-, heptakis-, and octakis-(2,6-di-*O*-pentyl-3-*O*-trifluoroacetyl) cyclodextrin derivatives, which displayed intermediate retention behaviour when used as a stationary phase. The trifluoroacetylated phases demonstrated superior ability in separating monosaccharide enantiomers as compared to the dipentyl and permethylated hydroxypropyl-derivatized cyclodextrin phases.

RESULTS AND DISCUSSION

Table I presents the results for the analysis of sugar enantiomers on four different derivatized-cyclodextrin stationary-phases. Only results for the α- and β-cyclodextrin stationary-phase are listed. None of the derivatized sugars were resolved on the γ-cyclodextrin phase. Figure 1 shows the chromatogram of trifluoroacetylated DL-ribose on a 9-m hydroxypropyl-permethyl-derivatized β-cyclodextrin fused-silica solumn (*A*), on a 9-m dipentyl-derivatized β-cyclodextrin fused-silica column (*B*) and on a 9-m dipentyltrifluoroacetyl-derivatized β-cyclodextrin fused-silica column (*C*) under similar experimental conditions. Figure 2 shows the enantiomeric resolution of methyl β-DL-arabinopyranoside on a 20-m hydroxypropyl-permethyl-derivatized cyclodextrin fused-silica column.

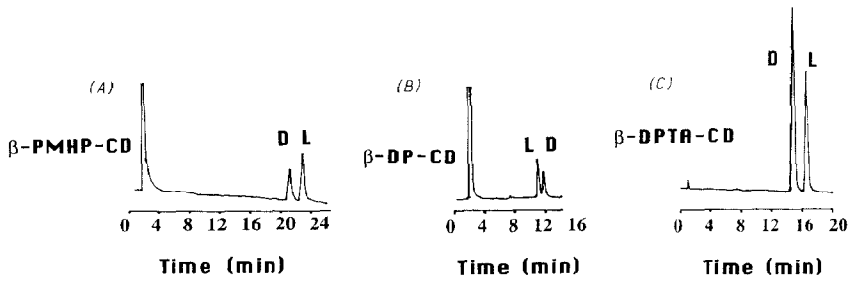

Fig. 1. Enantiomeric separation of DL-ribose after trifluoroacetylation. *A*: 9-m fused-silica column coated with hydroxypropylpermethyl-derivatized β-cyclodextrin, temperature 100°; *B*: 9-m fused-silica column coated with dipentyl-derivatized β-cyclodextrin, temperature 80°; *C*: 9-m fused silica column coated with dipentyltrifluoroacetyl-derivatized β-cyclodextrin, temperature 120°.

TABLE I

Chromatographic data on carbohydrate analysis[a]

Compound	*Parameter*[b]	*di-O-pentyl CD*		*Per-O-methyl(hydroxypropyl)CD*	
		α	*β*	*α*	*β*
β-DL-Allose	el.order	n.s.	n.s.	D, L	n.s.
	k'	9.3	-	11.3	16.5
	α	-	-	1.10	-
	T	90	-	100	90
β-DL-Arabinose	el.order	L, D	L, D	n.s.	D, L
	k'	6.1	3.2	3.0	6.6
	α	1.12	1.21	-	1.04
	T	80	70	100	90
Methyl-β-arabinopyranoside	el.order	L, D	L, D	n.s.	D, L[c]
	k'	8.6	4.5	-	7.8[c]
	α	1.06	1.11	-	1.09[c]
	T	80	90	-	90[c]
DL-Erythrose	el.order	n.s.	D, L	n.s.	L, D[c]
	k'	-	4.3	-	7.1[c]
	α	-	1.07	-	1.03[c]
	T	-	80	-	80[c]
α-DL-Galactose	el.order	D, L	D, L	n.s.	D, L
	k'	13	5.2	9.1	9.0
	α	1.13	1.04	-	1.02
	T	80	80	100	100
α-DL-glucose	el.order	D, L	L, D	n.s.	n.s.
	k'	7.2	2.4	12.5	12.0
	α	1.24	1.21	-	-
	T	90	100	100	100
DL-Glyceraldehyde	el.order	n.s.	n.s.	n.s.	D, L
	k'	28.3	-	.	17.9
	α	-	-	-	1.04
	T	100	-	-	130
α-DL-Lyxose	el.order	L, D	L, D	n.s.	D, L
	k'	13.5	6.1	7.9	5.5
	α	1.09	1.05	-	1.04
	T	80	80	100	80
α-DL-Mannose	el.order	D, L	D, L	n.s.	D, L
	k'	20	1.4	7.3	16.7
	α	1.7	1.23	-	1.02
	T	80	100	100	90
β-DL-Ribopyranose	el.order	L, D	L, D	D, L	D, L
	k'	18	4.6	10.6	7.8
	α	1.36	1.07	1.02	1.08
	T	80	80	100	100

TABLE I *continued*

Chromatographic data on carbohydrate analysis[a]

Compound	*Parameter*[b]	*di-O-pentyl CD*		*Per-O-methyl(hydroxypropyl)CD*	
		α	*β*	*α*	*β*
α-DL-Sorbose	el.order	n.s.	D, L	n.s.	L, D
	k'	9.0	3.4	-	17.9
	α	-	1.04	-	1.12
	T	90	100	-	90
α-DL-Talose	el.order	D, L	-	n.s.	n.s.
	k'	14	-	13.7	19.3
	α	1.28	-	-	-
	T	100	-	100	100
α-DL-Xylose	el.order	n.s.	D, L	n.s.	L, D
	k'	5.7	3.7	3.2	13.5
	α	-	1.05	-	1.04
	T	80	70	100	80

[a] Sugars were trifluoroacetylated before injection (see experimental section). Glyceraldehyde was acetylated. [b] el. order: elution order, k': capacity factor of the first eluting isomer, α: separation factor ($=k'1/k'2$), T: column temperature, n.s.: no enantiomer separation. [c] A 9-m column was used. [d] A 20-m column was used.

Purity and stability of the chiral stationary phase. — Oxygen can adversely affect the cyclodextrins by irreversible oxidation at elevated temperature. However, all of the chiral stationary phases used showed a great stability at high temperatures (up to 250°) as long as the nitrogen, hydrogen, or helium carrier gas was carefully freed from traces of oxygen. Excellent reproducibility was obtained as long as the columns were not overheated and the carrier-gas flow rate and split ratios were carefully regulated. The dipentyl-derivatized cyclodextrin and hydroxypropyl-permethyl-derivatized cyclodextrin columns were used for 5 months without discernible degradation of column performance. The maximum working temperature for the dipentyltrifluoroacetyl-derivatized cyclodextrin columns was set at 220° because irreproducible results were obtained at low temperature after heating above 220°, although the high-temperature separations were still satisfactory. Rapid variation between high and low column temperatures apparently causes inhomogeneities in the column coatings (*e.g.* pooling or

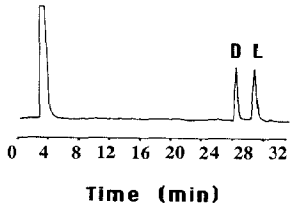

Fig. 2. Enantiomeric separation of methyl β-DL-arabinopyranoside after trifluoroacetylation on a 20-m × 0.25 mm i.d. fused-silica capillary column coated with hydroxypropylpermethyl-derivatized β-cyclodextrin. Column temperature 90°.

droplet formation), which lead to less-efficient separations. Great care must be taken not to overload the columns. Given the very light loading in a capillary column ($\sim$ 0.9 mg of derivatized cyclodextrins in a 9-m column and 2 mg in a 20-m column) the large amount of solvent passing through the column after a splitless injection may damage it irreversibly, especially at low temperature. Thus, only split injection, with a split ratio 100:1, was used.

We recently showed that it was not necessary to use an extensively purified derivatized cyclodextrin as a stationary-phase coating[14,16]. Indeed, the fully purified dipentyl-derivatized cyclodextrins were solids having m.p. $>90°$. Columns prepared with the highly purified solid material and with the original liquid-derivatized cyclodextrins gave nearly identical enantiomeric separations at temperatures $>90°$. At lower temperature, columns coated with the purified material gave poor enantiomeric separations because of the solid state of the coating[14,16].

Sugar retention. — Two important factors affect sugar retention: the cyclodextrin ring-size (α, β, or γ), and the substituents on the cyclodextrin. Table I shows that the sugar derivatives are more retained on the di-*O*-pentyl-α-cyclodextrin column than on the analogous β-cyclodextrin column. For example, the trifuoroacetylated L-arabinose k' values were 6.1 and 3.2 on the di-*O*-pentyl-α- and β-cyclodextrin column, respectively. This implies that, if an inclusion complex is formed, the sugar–α-cyclodextrin inclusion complex is more stable than the sugar–β-cyclodextrin complex. In general, for the more-polar-hydroxypropylpermethyl-derivatized cyclodextrins, the opposite occurred (namely, the trifluoroacetylated sugars were retained longer on the derivatized β-cyclodextrin relative to the α-cyclodextrin). Exceptions to this trend were lyxose and ribose (Table I). Given our experimental test-solutes, these generalizations are valid only for sugars having fewer than seven carbon atoms.

When comparing the retention of the same sugar on two different derivatized cyclodextrins (Table I) the effect of the cyclodextrin substituent is apparent. The sugar retention (k' values) increases with substituent polarity. Sugars have a greater affinity for the methylated hydroxypropyl group than for the pentyl group. For example, the k' values of L-arabinose were 3.2 and 6.6 on the di-*O*-pentyl-β-cyclodextrin and the *O*-hydroxypropyl-per-*O*-methyl-β-cyclodextrin, respectively (Table I). This shows that solute interactions with the cyclodextrin substituents may be as important in the retention process and the chiral-recognition process as the formation of an inclusion complex. It must be noted, however, that the k' values of lyxose were similar on both the polar and nonpolar chiral stationary-phases.

Sugar enantioselectivity. — Table I shows that the enantioselective elution order is often reversed on the dipentyl versus the hydroxypropylpermethyl cyclodextrin stationary-phases. Figure 1 shows the observed reversal in retention for DL-ribose. Binding reversals occasionally have been observed between α- and β-cyclodextrin[17]. For example, D-glucose eluted first on the dipentyl-derivatized α-cyclodextrin and L-glucose eluted first on the dipentyl-derivatized-β-cyclodextrin (Table I). However, the inversion of enantioselectivity observed between the dipentyl derivatives and the hydroxypropylpermethyl derivatives seems to be much more common. Inversion of elution order

occurred for 7 sugars (Table I), the only exceptions being galactose and mannose. No comparison could be made for the glucose enantiomers as they were resolved only on the di-*O*-pentylcyclodextrin phase. Once again it appears that the role played by the different substituents on the cyclodextrin is very important for chiral recognition. The ability to choose the enantiomeric elution-order is of practical importance. For example, when determining optical purities, one enantiomer is often in large excess. It is preferable to have the less-concentrated isomer eluting first. Indeed, the enantiomer in excess is likely to produce a large and tailing peak than can overlap a small, late-eluting peak. Also, enantiomeric reversals may be useful in confirming separations and in mechanistic studies.

Dipentyltrifluoroacetyl-α and β-derivatized cyclodextrin phases. — It is difficult to sort out the numerous factors and combination of factors that affect chiral recognition in g.l.c. It seems that not only the functionality but also the total shape and dimensions of the analytical substrate may affect the enantioselective interaction[2]. It was shown that the derivatization (necessary to increase the solute volatility), also had an important effect on enantioselectivity[18]. Examination of the results given in Table I and the observation that trifluoroacetyl-derivatized enantiomeric solutes were better resolved in gas chromatography and also in liquid chromatography[19] led to the synthesis of di-*O*-pentyl-*O*-trifluoroacetyl cyclodextrins. Table II lists the results obtained with these chiral stationary-phases and shows that the behavior of these phases is intermediate between the more-polar, hydrophilic phase (hydroxypropylpermethyl) and the apolar phase (dipentyl). The sugar retention and elution order on dipentyltrifluoroacetyl-derivatized cyclodextrins was closest to the retention on the dipentyl analogues, with some exceptions. For most sugars, the separation factors on the dipentyltrifluoroacetyl cyclodextrin phases were higher than the corresponding values on the other stationary phases, as illustrated by Fig. 1. For example, the α factor was as high as 2.14 for galactose enantiomers on the dipentyltrifluoroacetyl-derivatized-β-cyclodextrin phase.

Figure 3 shows the chromatograms obtained on the dipentyltrifluoroacetyl-derivatized α- and β-cyclodextrin phases with DL-gulose. Enantioselective inversion of elution order was observed on the two phases. The separation factors, α, were 1.15 and 1.88, respectively, producing resolution factors, R values, as high as 2.5 and 5.6, respectively. These results suggest that the 3-hydroxyl groups which are at the mouth of the cyclodextrin cavity, are involved in the chiral-recognition process. Clearly, better chiral recognition of trifluoroacetylated sugars was obtained when these 3-hydroxyl groups of the cyclodextrins were also trifluoroacetylated.

In conclusion, liquid derivatized cyclodextrins may be used as efficient chiral stationary-phases that are stable at high temperatures, up to 250°, when the carrier gas is carefully and completely freed from traces of oxygen. With such phases it is not only possible to separate enantiomeric forms of sugars but also to choose which enantiomer elutes first. Although the importance in chiral recognition of the 3-hydroxyl groups of the cyclodextrin was demontrated, the chiral-recognition mechanism is not yet fully understood. The classical three-point attachment concept[20] with hydrogen bonding as the major attractive forces cannot explain the observed results. In liquid chromatog-

TABLE II

Chromatographic data on carbohydrate analysis on 2,6-di-*O*-pentyl-3-*O*-trifluoroacetylcyclodextrin stationary phases[a]

Compound	*Parameter*[b]	*α-CD*	*β-CD*
	el.order	D,L	L,D
β-DL-Allopyranose	*k'*	2.6	5.5
	α	1.2	1.07
	temp.	130	110
	el. order	L, D	L, D
β-DL-Arabinopyranose	*k'*	1.8	2.0
	α	1.4	1.7
	temp.	120	120
	el. order	L, D	L, D
Methyl β-DL-arabinopyranoside	*k'*	3.0	3.0
	α	1.2	1.12
	temp.	110	110
	el. order	-	D, L
α-DL-Galactopyranose	*k'*	-	2.8
	α	-	2.14
	temp.	-	120
	el. order	-	D, L
α-DL-Glucopyranose	*k'*	-	3.4
	α	-	1.59
	temp.	-	120
	el. order	-	n.s.
DL-Glyceraldehyde	*k'*	-	17.4
	α	-	1.00
	temp.	-	120
	el. order	L, D	D, L
α-DL-Lyxopyranose	*k'*	12.6	8.0
	α	1.92	1.3
	temp.	110	100
	el. order	-	D, L
α-DL-Manopyranose	*k'*	-	6.6
	α	-	1.36
	temp.	-	120
	el. order	-	D, L
β-DL-Ribopyranose	*k'*	-	13.8
	α	-	1.13
	temp.	-	120
	el. order	-	L, D
α-DL-Sorbopyranose	*k'*	-	4.8
	α	-	1.08
	temp.	-	110

TABLE II *continued*

Chromatographic data on carbohydrate analysis on 2,6-di-*O*-pentyl-3-*O*-trifluoroacetylcyclodextrin stationary phases[a]

Compound	*Parameter*[b]	*α-CD*	*β-CD*
	el. order	-	D, L
α-DL-Talopyranose	k'	-	19.6
	α	-	1.94
	temp.	-	120
	el. order	D, L	D, L
α-DL-Xylopyranose	k'	4.2	3.6
	α	1.17	1.33
	temp.	110	100
	el. order	L, D	D, L
α-DL-Gulopyranose	k'	12.0	3.7
	α	1.15	1.88
	temp.	120	110
	el. order	-	D, L
DL-Arabinitol	k'	-	20.6
	α	-	1.06
	temp.	-	100

[a] Sugars were trifluoroacetylated before injection (see experimental section). Glyceraldehyde was acetylated.
[b] el. order: elution order, k': capacity factor of the first eluting isomer, α: separation factor ($= k'1/k'2$), n.s.: no enantiomer separation.

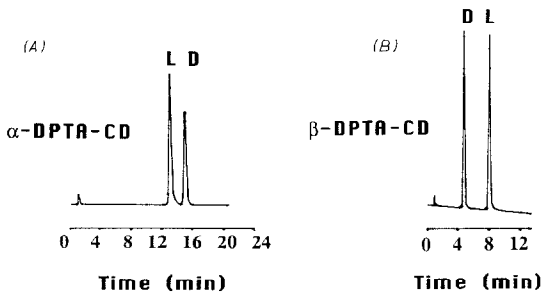

Fig. 3. Enantiomeric separation of DL-gulose after trifluoroacetylation on a 9-m fused-silica column coated with 2,6-di-*O*-pentyl-3-*O*-trifluoracetyl-derivatized α-cyclodextrin (*A*) and the analogous derivatized β-cyclodextrin (*B*), temperature 120°.

raphy, molecular inclusion was most essential for the enantioselectivity of cyclodextrins[17]. The inclusion complexes are sensitive to the cyclodextrin-cavity diameter, to the nature of the cyclodextrin derivatives, to the solute derivative, and to the solute dimension and shape. The inclusion complex is also very dependent on the nature of the solvent. The gas mobile phase, in g.l.c., should not compete in the inclusion process as does the liquid mobile phase in l.c. However, it is not clear that classic cyclodextrin inclusion-complexes are formed in g.l.c. The substituents on the cyclodextrin, pentyl,

methylated hydroxypropyl, or trifluoroacetyl, bonded at the mouth of the cyclodextrin cavity, play a significant role in the chiral-recognition process.

EXPERIMENTAL

Cyclodextrin derivatives as g.l.c. phases. — The nonpolar chiral stationary-phases were made with hexakis-, heptakis-, and octakis-(2,6-di-*O*-pentyl)-α-, β-, and γ-cyclodextrins, respectively, prepared by a Williamson reaction[21]. A solution of the appropriate cyclodextrin hydrate (1.0 g) in Me_2SO (20 mL) was treated with finely ground NaOH (2.0 g, 50.0 mmol) and 1-bromopentane (5.97 g, 39.5 mmol). The mixture was cooled slightly, stirred for 48 h, and then quenched by the addition of $CHCl_3$ (60 mL) and water (60 mL). The organic phase was separated and treated with $MgSO_4$ and Filter Cel, stirred for 20 h and filtered. The pale-yellow clear solution was concentrated under vacuum. This reaction favors etherification at O-2 and O-6 of the glucose residues, giving a viscous liquid comparising a mixture of di-*O*-pentylcyclodextrin isomers and homologues.

The hydrophilic chiral stationary-phases were prepared with (*S*)-hydroxypropyl-per-*O*-methyl-cyclodextrins in two steps. First, the desired cyclodextrin was dissolved in aq. NaOH (5% w/w) and the solution was cooled in an ice bath, and then (*S*)-propylene oxide was added slowly while stirring. After $\sim$ 6 h in the ice bath, the reaction was left to proceed for a day at room temperature. The mixture was neutralized and dialyzed briefly in order to remove contaminating salts. The retentate was filtered; the product, obtained by freeze drying, is a randomly substituted product having an average degree of substitution of 7 hydroxypropyl groups per cyclodextrin molecule. The second step was performed in an ice bath at 0°. An excess of Me I was added dropwise to a solution of the cyclodextrin derivative and NaH (50% suspension in paraffin oil) in Me_2SO. The mixture was allowed to react under gentle stirring for one h. After 24 h at room temperature, the product was extracted with $CHCl_3$, evaporation of which yielded the product[22].

Chiral stationary phases of the third type were made with 2,6-di-*O*-pentyl-3-*O*-trifluoroacetyl-cyclodextrin, prepared by trifluoroacetylation of the 2,6-di-*O*-pentyl cyclodextrins with trifluoroacetyl anhydride in tetrahydrofuran for 2 h at room temperature. The final product was extracted with $CHCl_3$, which was subsequently evaporated.

Medium (20-m) and short (9-m) fuse-silica capillary (0.25 mm i.d.) columns were coated following the static method described by Bouche and Verzele[23]. A 0.2% (w/v) ether solution of the derivatized cyclodextrin filled the capillary. After evaporation of ether at 36° under diminished pressure, the coating was estimated to be $\sim$ 0.1 μm thick, producing $\sim$ 4000 plates per column meter (solute decane) and only $\sim$ 2000 plates per meter with the carbohydrate solutes. All of the derivatized-cyclodextrin fused-silica g.l.c. capillary columns are now obtainable from Advanced Separation Technologies, Inc., Whippany, NJ.

Compounds. — Sugars (Sigma Chemicals, St Louis, MO) were derivatized with trifluoroacetic anhydride (Aldrich Chemicals, Milwaukee, WI). The racemic sugar (1 mg) was dissolved in 0.5 mL of tetrahydrofuran and 200 μL of trifluoroacetic anhydride was added. After 10 min, another aliquot of trifluoroacetic anhydride was added to ensure complete reaction. Finally, dry N_2 was bubbled through the solution to remove any excess anhydride and all tetrahydrofuran. The dry derivative was redissolved in 0.5 mL of ether to afford the injectable solution.

Gas chromatography. — Hewlett–Packard model 5710A, Varian model 3700, and Shimadzu model GC-8A gas chormatographs were used. Flame-ionization and electron-capture detectors were utilized. Split injections of 0.2–0.5 μL of sample used a split ratio 1/100. The injection port and detector temperature was 200°. Nitrogen was used as the carrier gas with a linear velocity of about 10cm·s^{-1} for the 20-m columns (gas pressure inlet: 7 p.s.i. or 0.5 kg·cm^{-2}) and 7.5 cm·s^{-1} for the 9 m columns (gas pressure inlet: 3 p.s.i. or 0.2 kg·cm^{-2}).

ACKNOWLEDGMENT

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