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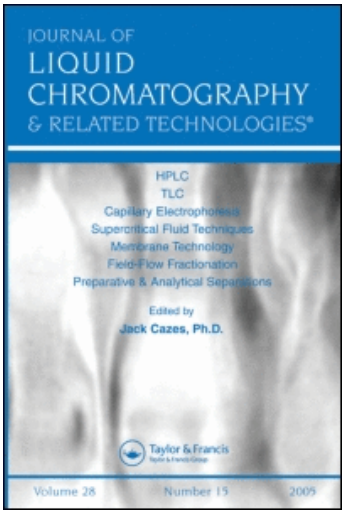

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Arabinose, Fucose, Ribodesose, Lyxose, and Ribose Used as Chiral Stationary Phases in HPLC

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Abstract: In this paper, we present the first enantioseparations using arabinose, ribose, ribodesose, lyxose, and fucose as chiral selector bonded to silica gel via 3-(triethoxysilyl)propyl isocyanate in HPLC. These chiral stationary phases possess good enantioseparation selectivity in the normal-phase mode, and there is a big chiral discriminating complementary. This work indicates that monosaccharides could soon become very attractive as a new kind of chiral stationary phase for HPLC.

Keywords: Arabinose, Chiral stationary phase, Fucose, Lyxose, Ribodesose, Ribose

INTRODUCTION

As continuously lucubrate of the stereochemistry, people more and more realize that chiral compounds play a very important role in many domains. Chromatographic separation based on chiral stationary phases (CSPs) represents one of the most direct and facile approaches for the determination of enantiomeric purity.[1] In order to develop new stationary phases of enantioselective chromatography, a number of investigations have been performed.[2–4]

Polysaccharide derivatives have been extensively used as chromatographic chiral selectors in chiral stationary phases for the separation of

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enantiomers by HPLC. When coated or bonded onto a silica matrix, they represent one of the most popular types of CSPs.[5,6] Cyclodextrin bonded phases have been used for the reversed-phase separation of a variety of diastereoisomers, structural isomers, enzymes, and routine compounds, especially used as chromatographic chiral stationary phases to separate enantiomers; they are cyclic, toroidal-shaped oligosaccharides.[7–9] This class of compounds has great potential for host–guest interactions.[10]

Since polysaccharides and cyclodextrins are composed of glucopyranose units, the 3,5-dimethylphenylcarbamates of cellooligosaccharide ($n = 2, 4$) were synthesized and their chiral recognition abilities were evaluated as chiral stationary phases for HPLC.[11]

Some mono-, di- and oligosaccharides also have been used as chiral selectors in capillary electrophoresis.[12–14] More recently, Schurig et al. presented the first enantiomeric separations using modified linear dextrins as new selectors in gas chromatography.[15]

To the best of our knowledge, there is no example described of enantiomer separations by arabinose, ribose, ribodesose, lyxose, and fucose as chiral selector bonded to silica gel via an arm of 3-(triethoxysilyl)propylisocyanate in HPLC. Surprisingly, they also possess high enantioseparation selectivity in normal-phase mode, and there is a big chiral discriminating complementary. This is a report, for the first time, that arabinose, ribose, ribodesose, lyxose, and fucose were bonded onto silica gel and used as chiral stationary phases in HPLC.

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EXPERIMENTAL

Reagents

D-(-)-Arabinose, D-(-)-ribose, 2-deoxy-D-ribose (ribodesose), D-lyxose, and L-(-)-fucose were purchased from Alfa Aesar. Silica gel (YWG-80, pore size 7 nm, particle size 5 μm) was supplied by Qingdao Ocean Chemical Factory (China). Racemates were obtained from Sigma and Fluka. 3-(Triethoxysilyl)propylisocyanate was from TCI (Japan). Solvents used in chromatographic experiments were of HPLC grade. All other organic solvents and chemical reagents were of at least analytical-reagent grade (Beijing Chemical Factory, China).

Apparatus

Stainless steel empty columns (250 mm × 2.0 mm i.d.) and 1/3 HP liquid pump were purchased from Alltech (USA). The HPLC system was equipped with a LabTech LC600 liquid delivery pump and UV–vis

detector (USA). A personal computer equipped with a LabTech HPLC Workstation for the LC system was used to process the chromatographic data. Detection was performed at 254 nm.

Synthesis

Arabinose, ribose, ribodesose, lyxose, and fucose chiral stationary phases were prepared as follows: Equal amounts (4 mmol) of 3-(triethoxysilyl)-propyl-isocyanate was trickled into the flask slowly which stirred with monosaccharide in anhydrous pyridine (10 mL) for 0.5 h in an ice-bath. The admixture was stirred at room temperature for 2 h, 3 g of silica gel was added and then the temperature was increased to 80°C for 0.5 h. After the reaction was continued for 24 h at 100°C, the mixture was filtered and washed with water, methanol, THF, and hexane, successively. Finally, the product was dried in vacuo at 60°C for 12 h. Figure 1 shows the scheme of the synthesis of the chiral stationary phases.

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Experimental Methods

The CSP was packed into the stainless steel empty column (250 mm × 2.0 mm i. d.) by a conventional high-pressure slurry packing procedure with hexane/isopropanol (9:1, *v*/*v*) as the slurry solvent using a 1/3 HP liquid pump. The column was rinsed with ethanol and then equilibrated with hexane/isopropanol (9:1, *v*/*v*) as the eluent at a flow rate of 0.1 mL/min until the baseline stabilized. For comparative reasons, the ratio of hexane/isopropanol always was 9:1 (*v*/*v*) in the eluent for most experiments.

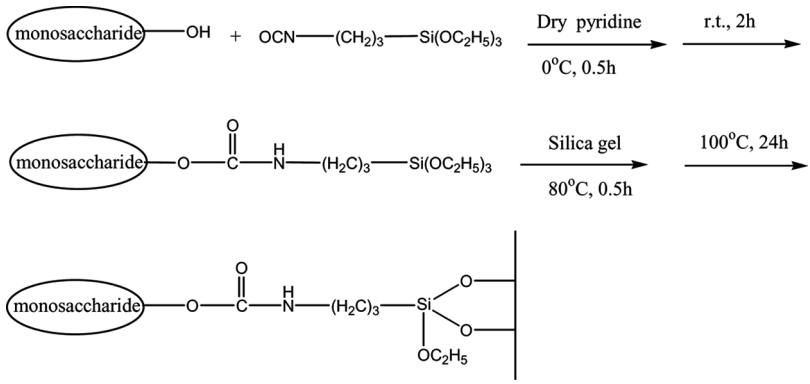

Figure 1. Scheme of the synthesis of chiral stationary phases.

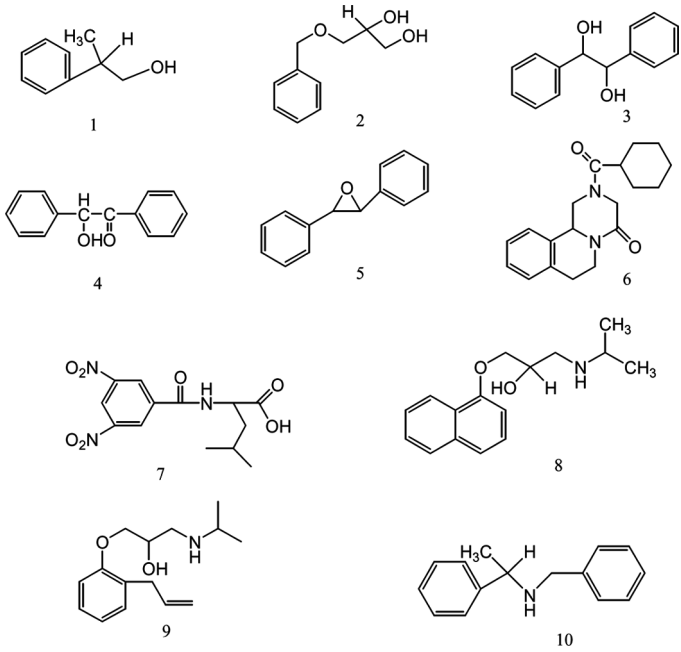

Figure 2. Molecular structures of chiral compounds.

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Table 1. The retention factors (k_1) and separation factors (α) on five chiral columns

	Arabinose		Ribose		Ribodesose		Lyxose		Fucose	
	k_1	α	k_1	α	k_1	α	k_1	α	k_1	α
1			0.58	1.54	0.77	1.41	1.00	1.41		
2	0.97	3.58	0.63	1.48					0.80	1.39
3	1.03	2.98								
4	0.96	3.64								
5	0.45	2.84	0.28	3.45			0.54	2.62	0.38	2.93
6	0.36	3.50	0.79	1.71			1.42	4.26		
7			0.57	3.20	0.41	3.34			0.23	4.94
8							1.41	2.03	1.12	4.71
9	1.22	2.73			0.93	1.48				
10	0.97	3.65	0.90	3.52	0.51	3.99	0.96	5.46	0.33	4.25

HPLC condition: silica gel, 5 μm; column size: 250 mm × 2.0 mm; eluent: hexane/isopropanol = 90:10; flow rate: 0.1mL/min; temperature: 30°C; detection, 254 nm.

RESULTS AND DISCUSSION

We investigated the chiral recognition ability of five chiral columns using ten racemates, which are 2-phenyl-1-propanol (1), 3-benzyloxy-1,2-propanediol (2), hydrobenzoin (3), benzoin (4), trans-stilbene oxide (5), praziquantel (6), DNB-(R,S)-leucine (7), DL-propranolol(s) (8), alprenolol(s) (9), and N-benzyl-1-phenylethylamine (10) (Figure 2). Table 1 summarizes their retention factors (k_1) for the first eluted enantiomer and separation factors (α). The retention factor k_1 is $(t_1\text{-}t_0)/t_0$ and separation factor α is k_2/k_1 for enantiomers 1–10.

As can be seen from the Table 1, seven enantiomers were separated with the arabinose column, six enantiomers with ribose, four enantiomers with ribodesose, five enantiomers with lyxose and for fucose, respectively. Most chiral compounds could be recognized by at least one column.

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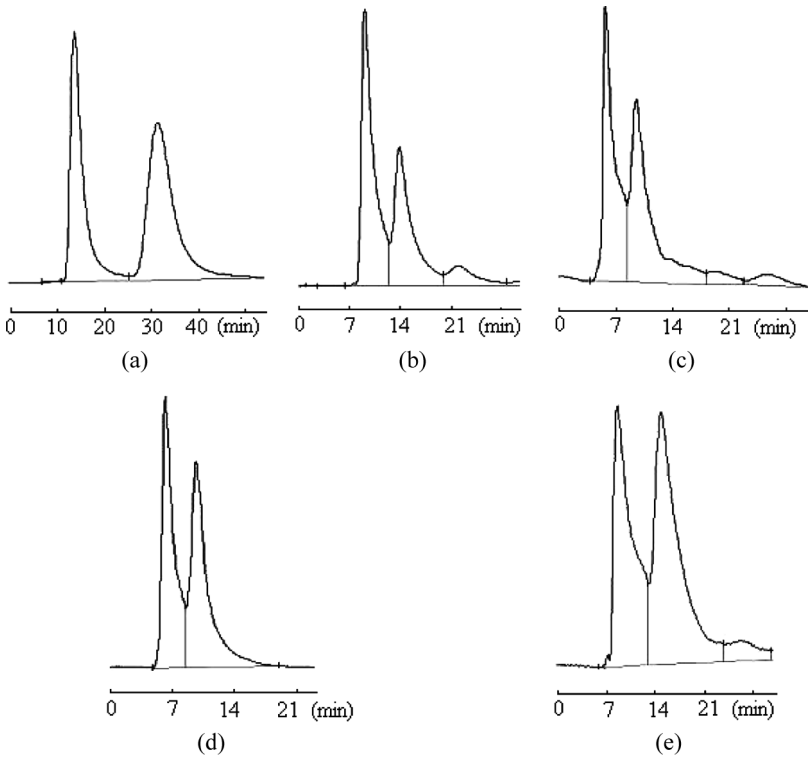

Figure 3. Enantioseparation chromatograms of racemates. (a) benzoin on arabinose column; (b) trans-stilbene oxide on ribose column; (c) DNB-(R,S)-Leucine on ribodesose column; (d) trans-stilbene oxide on lyxose column; (e) DNB-(R,S)-Leucine on fucose column.

Among these columns, there is a big chiral discriminating complementary. Their separation ability toward 10 chiral compounds was arabinose > ribose > lyxose, fucose > ribodesose.

Figure 3 exhibits the enantioseparation chromatograms of racemates. They are benzoin on arabinose column (A), trans-stilbene oxide on ribose column (B), DNB-(R,S)-Leucine on ribodesose column (C), trans-stilbene oxide on lyxose column (D), DNB-(R,S)-Leucine on fucose column (E), respectively. All chromatograms showed good peaks and resolution for these racemates.

The chiral recognition mechanism of chiral stationary phases is that besides the dispersion, dipole-dipole, and hydrogen-bond forces, the steric fit between the chiral saccharide and conformation of the solute molecule may be main interaction.[2,5,7] This interaction would be affected by the kind of monosaccharide.[11–15] However, it's very difficult for the mechanism of chiral recognition to be understood completely. The influence of the chiral microenvironment on the chiral properties of chromatographic systems is far from being completely understood.

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CONCLUSION

From the above comprehensive studies, we know that optically active arabinose, ribose, ribodesose, lyxose, and fucose bonded to silica gel can be used as chiral stationary phases in normal-phase mode for HPLC. They not only possess good enantioseparation selectivity, but also there is a big chiral discriminating complementary. This work indicates that the monosaccharides could soon become very attractive as a new kind of chiral selector in HPLC.

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