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Systematic modification of the separation selectivity of cyclodextrin-based gas chromatographic stationary phases by varying the size of the 6-O-substituents

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Abstract

Several heptakis(2,3-di-O-methyl)-β-cyclodextrin derivatives were synthesized in which the size of the primary 6-O-substituent was varied systematically from deoxy-fluoro, through methyl, *n*-pentyl, *n*-propyldimethylsilyl, *tert.*-butyldimethylsilyl, to triisopropylsilyl. The resulting solid cyclodextrin derivatives were dissolved at identical molal concentrations in OV-1701-vi to form useful gas chromatographic stationary phases for enantiomer separations. It was found that while all phases could be operated at temperatures as high as 250°C, the lower operating temperatures decreased greatly as the size of the substituent increased. Chiral selectivity also varied significantly with the size of the substituent: for almost all of the test compounds chiral selectivity had a local maximum when the substituent was the *tert.*-butyldimethylsilyl group.

Keywords: Chiral stationary phases, GC; Enantioselectivity; Enantiomer separation; Cyclodextrins; Pinene; Isoflurane; Phenylethylamine

1. Introduction

Since the first use of cyclodextrins (CDs) as gas chromatographic (GC) stationary phases by Casu et al. in 1979 [1], a large number of CD derivatives have been prepared and used as chiral GC stationary phases [2–6]. These CD derivatives differ in their physical, chemical, and chromatographic properties depending on the size of the CD ring and the type of its substituents. Generally, the C-6 nonchiral carbon atoms on the primary face of CDs are substituted with nonpolar groups, such as alkyl or silyl groups, to reduce the polarity and/or liquify the CD. Substituents on the secondary side (at the C-2 and C-3 chiral carbon atoms), such as alkyl or acyl, are introduced to alter the chiral selectivity of the resulting material [4]. Thus, it was unexpected, when replacement of the 6-O-methyl group with the 6-O-*tert.*-butyldimethylsilyl group resulted in stationary phases that offered better chiral selectivities for a large number of analytes [7,8]. Using molecular modeling, Kobor et al. [9] found that the shapes of the heptakis(2,3-di-O-methyl-6-O-methyl)-β-cyclodextrin and the heptakis(2,3-di-O-methyl-6-O-*tert.*-butyldimethylsilyl)-β-cyclodextrin were different. They argued that the differences in the enantioselectivities were caused by the shape differences.

These observations prompted us to systematically explore the relationship between the size of the substituent on the nonchiral face of the CD and the

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chiral selectivity of the resulting stationary phase. We were also interested to find out if the minimum operating temperatures of the CD-based stationary phases varied with the size of the substituents on the nonchiral face of the CD. The latter is of great importance when one has to analyze very volatile substances, such as fluoroether anesthetics [10,11], or when one wants to carry out preparative-scale separations and needs higher separations selectivity values without concomitant drastic reductions in separation efficiency [12–16]. Therefore, six different single-isomer β-CD derivatives were designed and synthesized. They all carry identical methoxy groups on the C-2 and C-3 chiral carbon atoms, but different hydrophobic functional groups, varying in size, on the C-6 nonchiral carbon atoms. Since all these derivatives were solid, they were dissolved at identical molalities in OV-1701-vi to serve as stationary phases. The retention factors, enantioselectivities, and column efficiencies were then determined for a large variety of chiral test compounds at different temperatures.

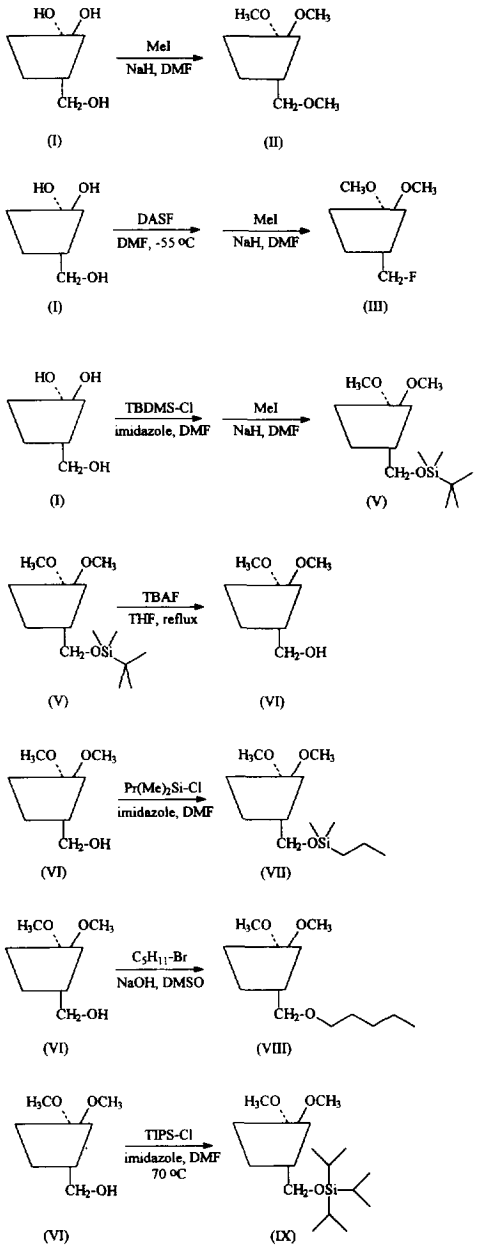


Fig. 1. Reaction scheme for the synthesis of heptakis(2,3-di-O-methyl)-β-cyclodextrin derivatives. For abbreviations see text

2. Experimental

2.1. Synthesis of the single-isomer CD derivatives

β-Cyclodextrin was obtained from American Maize-Products Company (Hammond, IN, USA). All other reagents used in the synthesis were from Aldrich (Milwaukee, WI, USA) and Hüls America (Piscataway, NJ, USA). The synthetic schemes used, shown in Fig. 1, were adapted from the literature. The purity of the final products was monitored by thin-layer chromatography, HPLC, and their structure was confirmed by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy [17].

2.1.1. Heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin (II, BMe)

According to [18], a 20-ml solution of 1.0 g dried β-cyclodextrin (I) in dry dimethylformamide (DMF) was added dropwise to sodium hydride at 0°C. The cold solution was stirred for 1 h and 4.0 ml of methyl iodide was added dropwise. The reaction mixture was stirred for another 3 h and poured into an ice–water mixture. The product was extracted with diethyl ether, washed with cold water, dried, concentrated, and purified by column chromatography using silica as stationary phase and toluene–ethanol (4:1) as mobile phase, to yield a white, crystalline solid product, II.

2.1.2. Heptakis(6-deoxy-6-fluoro-2,3-di-O-methyl)-β-cyclodextrin (III, BFMe)

β-Cyclodextrin (I) was selectively fluorinated using the modified method of Sharma and Korytnyk [19]. Dried I (2.5 g) was dissolved in 30 ml of dry DMF under anhydrous conditions. The solution was cooled to −55°C and diethylaminosulfur trifluoride (DAST: 10.2 ml) was added by a syringe. The reaction mixture was then allowed to warm to room temperature and stirred for 20 h. The mixture was carefully poured into an ice–water mixture, the cloudy solution was centrifuged, the precipitate was rinsed with methanol and dried. Methylation of the off-white product, followed by column chromatography, as described above, yielded a white solid material, III.

2.1.3. Heptakis(2,3-di-O-methyl-6-O-tert.-butyldimethylsilyl)-β-cyclodextrin (V, BSiMe)

Derivative V was prepared as described by Takeo et al. [18]. A solution of dried I (5.81 g) in dry DMF was reacted with *tert.*-butyldimethylsilyl chloride (TBDMS-Cl: 6.65 g), in the presence of imidazole (8.78 g), to yield 6-O-*tert.*-butyldimethylsilyl-β-cyclodextrin (IV). Methylation of IV and subsequent purification by column chromatography, as described above, afforded a white solid product, V.

2.1.4. Heptakis(2,3-di-O-methyl)-β-cyclodextrin (VI)

Compound V was desilylated by refluxing a solution of V [2.5 g in 15 ml tetrahydrofuran (THF)] with 1 *M* tetrabutylammonium fluoride in dry tetrahydrofuran (25 ml) for 5 h [18]. Then the reaction mixture was concentrated, dissolved in dichloromethane, and washed with brine. The organic phase was dried and concentrated. Column chromatography yielded a white solid product, VI. This material was then used to prepare CD derivatives VII, VIII, and IX.

2.1.5. Heptakis(2,3-di-O-methyl-6-O-propyldimethylsilyl)-β-cyclodextrin (VII, BSiPMe)

Compound VI (0.35 g) was reacted with propyldimethylsilyl chloride [$Pr(Me)_2Si$-Cl: 0.4 ml] in the presence of imidazole (0.46 g) in dry DMF, as described for the preparation of IV [18]. Column chromatography as above yielded a white solid product, VII.

2.1.6. Heptakis(2,3-di-O-methyl-6-O-pentyl)-β-cyclodextrin (VIII, BPMe)

Compound VI (0.3 g) was dissolved in dimethylsulfoxide (DMSO) and mixed with powdered sodium hydroxide (0.19 g). The mixture was stirred for 30 min, followed by the addition of 1-bromopentane (0.6 ml). The stirring was continued for 7 days at room temperature [4]. The reaction mixture was then poured into an ice–water mixture and extracted with dichloromethane. The organic solution was washed with brine, dried, and concentrated. Column chromatography as above yielded a light yellow product, VIII.

2.1.7. Heptakis(2,3-di-O-methyl-6-O-triisopropylsilyl)-β-cyclodextrin (IX, BTIPSMe)

Compound VI (0.30 g) was reacted with triisopropylsilyl chloride (TIPS-Cl: 0.5 ml) in the presence of imidazole (0.38 g) in dry DMF at 70°C, similarly to the preparation of IV [18]. Column chromatography, as above, yielded a white thick paste as product, IX.

2.2. Preparation of the capillary columns

All CD derivatives were mixed with OV-1701-vi polysiloxane (Supelco, Bellefonte, PA, USA) when used as stationary phases. Untreated and deactivated 30 m×0.25 mm I.D. fused-silica capillary columns (Polymicro Technologies, Phoenix, AZ, USA and J&W Scientific, Folsom, CA, USA, respectively) were coated, using the static method [20], with the dichloromethane solutions of the stationary phases. All capillary columns had identical film thickness (0.25 μm) and identical molal CD concentration (0.14 molal CD derivative in OV-1701-vi). Each capillary column was conditioned at 160°C for ca. 10 h or until a stable baseline was observed. Efficiency for all columns was determined at 160°C with heptadecane ($C_{15}H_{32}$) which gave k' of 2.4 and N of 2500–3120 plates/m for BMe and BFMe columns and k' of 1.6–2.9 and N of 4290–4810 plates/m for the other columns.

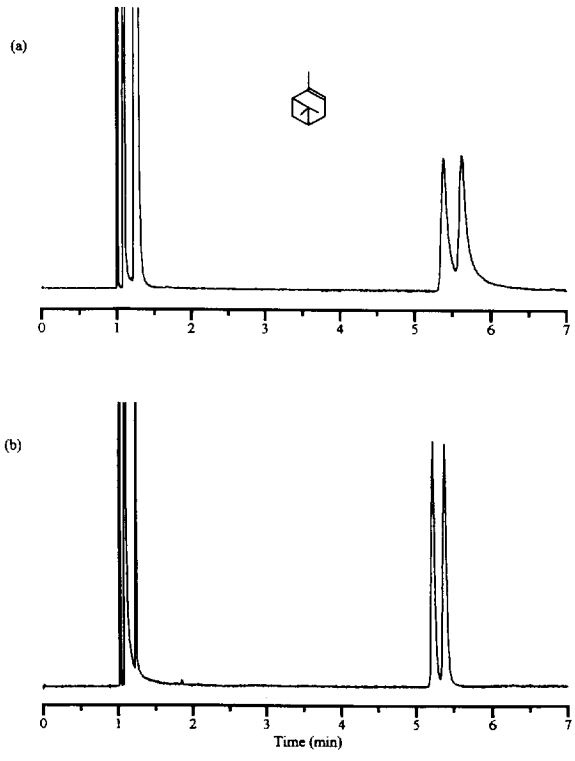


Fig. 2. Enantiomeric separation of α-pinene at 80°C on (a) BMe- and (b) BSiMe-coated columns.

2.3. Gas chromatographic measurements

All chromatographic separations were performed with an HP 5890 Series II gas chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with a septumless split/splitless injector, a flame ionization detector, and a ChemStation data collection/analysis system. Hydrogen was used as carrier gas at an average linear velocity of 50 cm/s, measured by injecting methane as unretained compound. The injector and detector temperatures were maintained at 250°C. All separations were performed isothermally with a split ratio of 1:300. Column efficiencies were calculated using the peak width at half height, unless otherwise specified.

Table 1
Operating temperature ranges for derivatized cyclodextrin (CD) stationary phases

CD	CD concentration in OV-1701-vi		Operating temperature (°C)
	% (w/w)	mol/kg	
BFMe	20	0.149	160–250
BMe	20	0.140	160–250
BPMe	26	0.141	120–250
BSiPMe	28	0.140	80–250
BSiMe	30	0.141	20–250
BTIPSMe	34	0.141	20–250

3. Results and discussion

3.1. Solubility of the CD derivatives in OV-1701-vi

Since the CD derivatives prepared in this study are solid materials, they have to be mixed with a liquid matrix, such as the medium polarity OV-1701-vi polysiloxane, to serve as liquid stationary phases over a wide operating temperature range. The CD derivatives described here have been used routinely at temperatures as high as 250°C (the maximum operating temperature recommended for OV-1701-vi), yielding column efficiencies (for both chiral and nonchiral solutes) as high as 4200 plates/m. However, for some of the CD derivatives, column efficiency drops below 1500 plates/m and the peaks tail when the column temperature is decreased below a particular value (defined as the minimum operating temperature in this study) indicating that the CD derivative reached its solubility limit in OV-1701-vi and begins to solidify. For example, the chromatograms of the enantiomers of the nonpolar α-pinene, obtained at 80°C on the BMe- and the BSiMe-coated columns, are shown in Fig. 2. Though the apparent selectivity is slightly higher on the solidified BMe phase ($\alpha=1.055$, compared to $\alpha=1.037$ on the BSiMe phase), peak resolution is much better on the still liquid BSiMe stationary phase.

Table 1 lists the operating temperature ranges for the CD derivatives studied here. When the 6-O-substituents on the primary side of heptakis(2,3-di-O-methyl)-β-cyclodextrin are small, such as methyl or deoxy-fluoro, the solubility in OV-1701-vi is low and the minimum operating temperature is high. These CD derivatives are useful as chiral stationary phases only at high temperatures, in the 160–250°C range. However, heptakis(2,3,6-tri-O-methyl)-β-cyclodextrin behaves as a supercooled liquid and can be used at lower temperatures, as reported by Venema and Tolsma [21] and Bicchi et al. [22,23],

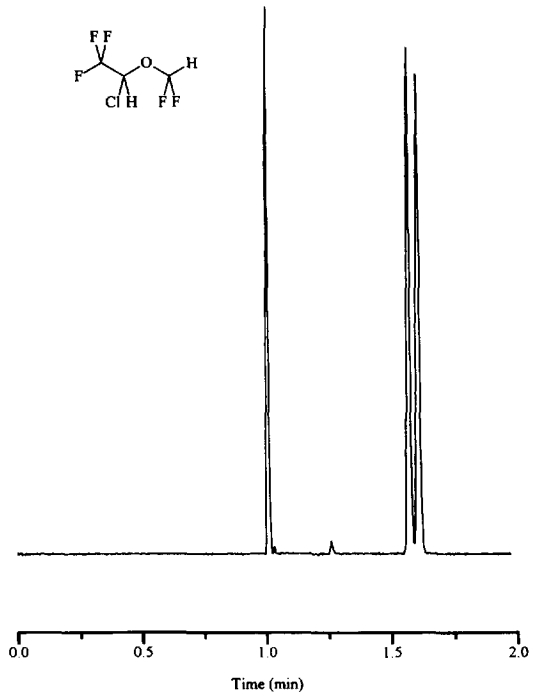


Fig. 3. Enantiomeric separation of isoflurane at 40°C on the BTIPSMe-coated column.

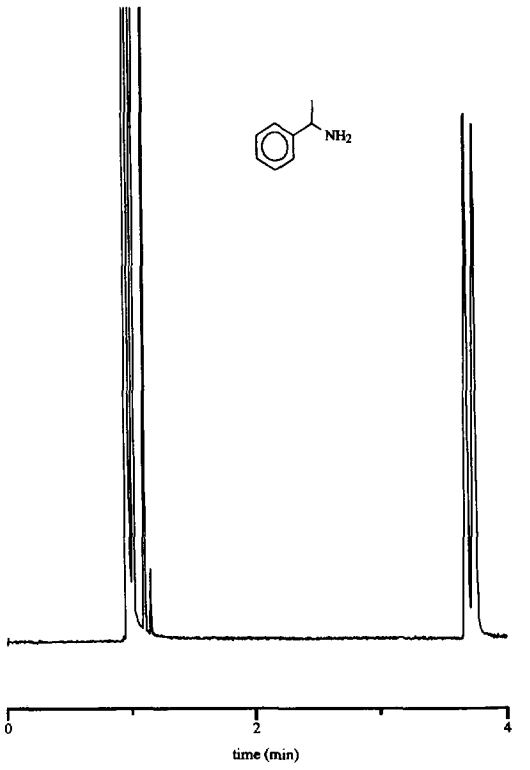


Fig. 4. Enantiomeric separation of underivatized 1-phenylethylamine at 120°C on the deactivated BSiMe-coated column.

assuming that prior to the separation it is conditioned at or above 200°C.

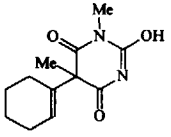
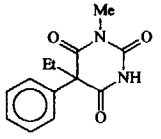
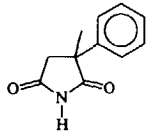
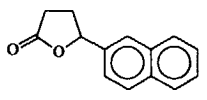
As the size of the substituent on the primary face becomes larger, the solubility of the CD derivative in OV-1701-vi increases and the minimum operating temperature of the stationary phase decreases. For example, the *tert.*-butyldimethylsilyl- and triisopropylsilyl-substituted BSiMe and BTIPSMe can be used at temperatures as low as 40°C without significant loss in column efficiency (i.e. column efficiencies are better than 1500 plates/m). Interestingly, the silyl ether substituted CD derivatives can be used at lower temperatures than the alkyl ether derivatives of identical carbon number (the minimum operating temperatures of BSiPMe and BPMe are 80 and 120°C, respectively). Fig. 3 shows the separation of the enantiomers of the volatile anesthetic, isoflurane, at 40°C on the BTIPSMe-coated column.

3.2. Chromatographic properties of the derivatized CD stationary phases

Since it was argued [9] that derivatization on the primary side can alter both the size and the shape of the CD molecule, the interactions between the CD and the different analytes must also change and manifest in different retention factors as well as enantioselectivities. The chromatographic properties (under identical conditions and identical column pretreatment) of all the CD derivatives studied here are listed in Tables 2–5. Though the relationships between the chromatographic properties and the structure of the CD substituent are complex, one can draw a few general conclusions.

Independently from the operating temperature, the selectivities of the BMe and the BFMe phases, which carry the small methyl and deoxy-fluoro substituents, respectively, are very similar suggesting that both substituents influence the size and shape of the CD molecule similarly. Their minimum operating temperatures are similarly high. When the size of the primary substituent increases (as in BPMe and BSiPMe), the CD derivative becomes more nonpolar and more soluble in OV-1701-vi. Consequently, these phases have a lower minimum operating

Table 2
Retention factors, separation selectivities, and column efficiencies for derivatized cyclodextrin-coated columns at 200–220°C

Compound	Temp. (°C)	BFMe			BMe			BPMe			BSiPMe			BSiMe			BTIPSMe		
		k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m
	200	11.265 11.956	1.061	4063 4183	11.439 12.063	1.055	3410 3434	8.667 8.717	1.006	NA[a]				8.409 8.940	1.063	3819 3888	6.670 6.694	1.004	NA[a]
	200	13.934 15.276	1.096	3949 3979	14.296 15.314	1.071	3354 3556	11.047 11.214	1.015	3851 3876				10.107 10.644	1.053	3724 3817	8.288	1	2375[b]
	220	4.278 4.372	1.022	4077 4041	4.349 4.448	1.023	3968 3760	3.391	1	3611	3.219 3.265	1.014	3570 3601	3.088 3.176	1.028	3719 3676	2.330	1	3825
	220	12.646 12.705	1.005	NA[a]	12.070 12.119	1.004	NA[a]	9.710	1	3964	9.925 10.062	1.014	4131 4058	9.932 10.184	1.025	4258 3853	8.027	1	2253[b]

[a] Column efficiency could not be calculated.
[b] Indicates incipient separation.

Table 3
Retention factors, separation selectivities, and column efficiencies for the derivatized cyclodextrin-coated columns at 160–180°C

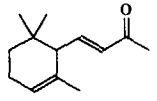
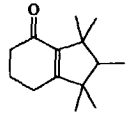
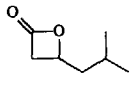
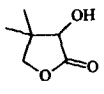
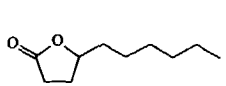
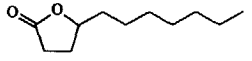
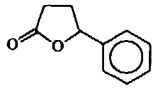
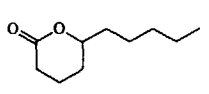
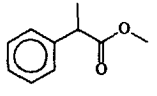
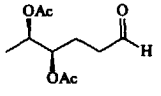
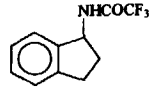
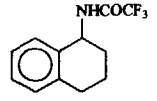
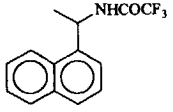
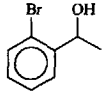
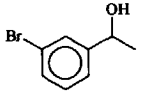
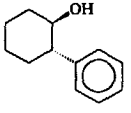
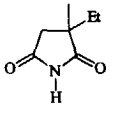
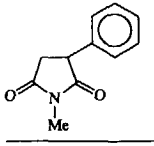
Compound	Temp. (°C)	BFMe			BMe			BPMe			BSiPMe			BSiMe			BTIPSMe		
		k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m
	160	3.175 3.235	1.019	1461[a] 1289[a]	3.190 3.273	1.026	1882 1774	2.433	1	2486	2.878 2.904	1.009	2545[a] 2312[a]	2.942 3.019	1.026	4144 3779	2.432	1	3490
	160	5.044 5.246	1.040	951 907	5.009 5.227	1.044	1814 1781	3.523	1	1175[c]	4.172 4.242	1.017	4109 4034	4.237 4.431	1.046	3874 3804	3.536	1	3836
	160	0.972 0.990	1.018	1304[a] 987[a]	0.978 0.999	1.022	2332 2383							0.922 0.946	1.027	3877 3541			
	160	1.548 1.568	1.013	NA[b]	1.495 1.531	1.024	2287 2103	1.044	1	2590	1.108 1.127	1.018	3378 3546	1.185 1.244	1.050	3559 3445			
	160	1.921 1.947	1.014	NA[b]	1.826	1	1418	1.183	1	2702	1.307	1	1332[c]	1.558 1.604	1.029	3647 3231			
	160	2.058 2.115	1.028	725[a] 745[a]	2.092 2.189	1.046	1603 1626	1.190	1	1677	1.311 1.338	1.021	3301 2640	1.757 1.829	1.041	3281 3233			
	160	7.645 7.694	1.006	NA[b]	6.979 7.024	1.006	NA[b]	4.734	1	3083	5.565 5.645	1.014	4469 3810	6.649 6.837	1.028	4021 3804	4.313	1	2049[c]

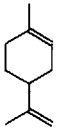
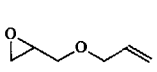
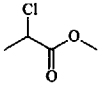
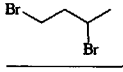
Table 3 (Continued)

Compound	Temp. (°C)	BFMe			BMe			BPMe			BSiPMe			BSiMe			BTIPSMe		
		k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m
	160	12.291 12.358	1.005	NA[b]	11.082 11.144	1.006	NA[b]	7.464	1	3141	8.852 8.978	1.014	4335 3824	10.642 10.938	1.028	3996 3723			
	160	14.161 14.832	1.047	3070 2988	12.939 13.498	1.043	3177 3124	8.615 8.746	1.015	3745 3848	9.392 9.913	1.055	3876 3818	11.002 12.313	1.119	3781 3723	7.009 7.173	1.023	4090 4136
	160	8.676 8.754	1.009	NA[b]	8.009	1	2404	5.520	1	3460	6.337	1	2236[c]	7.252 7.318	1.009	NA[b]	4.935	1	3963
	160	1.104 1.148	1.040	2062 1987	1.055 1.090	1.033	2350 2430							0.999 1.029	1.031	3771 3435	0.797	1	3381
	160	4.686 4.839	1.033	1724 1580	4.412 4.517	1.024	2340 2269							3.539 3.625	1.024	3904 3481			
	160	5.182	1	1600	5.245	1	987[c]	3.735 3.765	1.008	NA[b]	4.158	1	4280	4.590 4.677	1.019	3868 3830	3.434	1	3487
	160	7.814 8.051	1.030	2435 2292	7.939 8.337	1.050	2840 2753	5.608 5.690	1.015	3536 3625	6.318 6.455	1.022	4163 4100	7.174 7.490	1.044	3931 3997	5.227 5.284	1.011	3910[a] 3983[a]

	160	22.214 22.370	1.007	NA[b]	22.320 22.523	1.009	NA[b]	16.620 16.702	1.005	NA[b]	17.745 17.892	1.008	3390[a] 3409[a]	18.420	1	2108[c]	15.096	1	1782[c]
	160	4.827 5.836	1.209	1422 1205	5.027 5.882	1.170	1992 1796	2.711 2.849	1.051	3052 2875	3.391 3.906	1.152	3631 3719	4.499 5.984	1.330	3594 3576	2.427 2.527	1.041	3757 4012
	160	5.740 5.828	1.015	2157 1928	5.819 6.059	1.041	2533 2440	3.421	1	2124	4.206 4.243	1.009	2733[a] 2545[a]	5.387 5.471	1.016	3679 2987	3.032	1	2575
	160	6.944 7.324	1.055	1870 1788	7.121 7.470	1.049	2090 2043	4.471 4.554	1.019	3284 3289	5.402 5.605	1.038	3965 3764	6.474 6.974	1.077	3101 2911	4.037 4.132	1.014	3935 3603
	160	6.363 6.628	1.042	941 902	6.446 6.764	1.049	1619 1600	3.645	1	1243[c]	3.868 3.978	1.028	3858 3198	4.986 5.271	1.057	3757 3677	2.291	1	3492
	180	10.194 10.299	1.010	3294[a] 3901[a]	9.829 9.955	1.013	3642 3661				7.601 7.674	1.010	3303[a] 3384[a]	8.070 8.268	1.025	3980 3914	5.911	1	3038

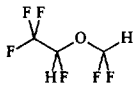
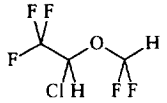
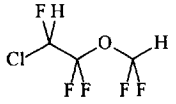
[a] Column efficiency calculated from the peak width at 88.2% peak height.
[b] Column efficiency could not be calculated.
[c] Indicates incipient separation.

Table 4
Retention factors, separation selectivities, and column efficiencies for the derivatized cyclodextrin-coated columns at 80°C

Compound	Temp. (°C)	BFMe			BMe			BPMe			BSiPMe			BSiMe			BTIPSMe		
		k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m	k'	α	N/m
	80				4.361 4.599	1.055	673[b] 577[b]				2.440 2.500	1.024	3096 3088	4.114 4.265	1.037	2047 1988	1.835	1	3227
	80										5.069 5.284	1.042	3586 3564	7.761 8.502	1.096	3016 2997	4.266 4.459	1.045	3694 3806
	80													4.348 4.652	1.070	2027 1950	2.468 2.518	1.021	4149 3960
	80													1.380 1.422	1.030	3132 2566	0.722 0.729	1.010	NA[a]
	80										1.383 1.468	1.062	3510 3162	2.125 2.460	1.158	2948 2820	1.152 1.214	1.054	3112 3333
	80													2.845 2.886	1.014	3750 2321	1.728 1.759	1.018	3484 3142
	80													12.366 12.437	1.006	NA[a]	5.573 5.704	1.023	3770 3726

[a] Column efficiency could not be calculated.
[b] Indicates stationary phase solidification.

Table 5
Retention factors, separation selectivities, and column efficiencies for the derivatized cyclodextrin-coated columns at 40°C

Compound	Temp. °C	BSiMe			BTIPSMe		
		k'	α	N/m	k'	α	N/m
	40	0.185 0.218	1.181	2647 2399	0.135	1	3553
	40	0.887 1.130	1.274	1074 902	0.559 0.597	1.068	2273 2352
	40	1.153 1.327	1.150	1154 1014	0.661 0.726	1.099	2579 2218
	40	1.416 1.444	1.019	712[a] NA[b]	0.908	1	1687[c]

[a] Column efficiency calculated from the peak width at 88.2% peak height.
[b] Column efficiency could not be calculated.
[c] Indicates incipient separation.

temperature than BMe or BFMe (Table 1). However, both BPMe and BSiPMe show lower retention factors and chiral selectivity values than BMe and BFMe (except for a few lactone solutes). When the primary substituent is the larger *tert.*-butyldimethysilyl group (BSiMe), the minimum operating temperature becomes as low as ambient, and the scope of applicability as well as the enantioselectivity of the phase improves tremendously, in agreement with previous reports [7,8,24,25]. The phase can be used effectively even at temperatures as low as 40°C (Table 5). When the primary substituent becomes even bulkier, as in the triisopropylsilyl-substituted BTIPSMe, the retention factors and the enantioselectivity values decrease dramatically, and become the lowest among the six CD derivatives studied. Nevertheless, due to the very nonpolar nature of the substituent, the BTIPSMe stationary phase affords capillary columns with excellent efficiencies, even at very low temperatures.

Thus, in conclusion, it can be stated that the substituents on the primary face of CD also influence the enantioselectivity and must be carefully considered in the design of new chiral stationary phases. Of the six heptakis(2,3-di-O-methyl)-β-cyclodextrin derivatives investigated here BSiMe, with a *tert.*-butyldimethylsilyl group as the primary substituent, is the most broadly applicable, both in terms of the chiral compound classes that can be separated on it and its operating temperature range. Some of the enantiomers that could be successfully separated on this stationary phase include hydrocarbons, alkyl halides, ethers, epoxides, ketones, lactones, esters, aldehydes, underivatized alcohols and diols, hydroxy acid esters, amides, succinimides, and underivatized amines (Fig. 4).

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