Chinese Chemical Letters Vol. 15, No. 12, pp 1457-1460, 2004 1457
http://www.imm.ac.cn/journal/ccl.html

The Direct Resolution of the Enantiomers of Four Chiral Pesticides

Peng WANG, Shu Ren JIANG, Zhi Qiang ZHOU*

Department of Applied Chemistry, China Agricultural University, Beijing 100094

Abstract: Cellulose-tris(3,5-dimethylphenylcarbamate)(CDMPC) were synthesized as high-performance liquid chromatography (HPLC) chiral stationary phase(CSP). The successful resolution of four chiral pesticides on the CSP was realized and the influence of the temperature on the separation was studied.

Keywords: HPLC, CSP, pesticide, resolution.

Chromatographic enantioseparations, particularly direct separation of enantiomers by high-performance liquid chromatography, have advanced markedly and this resolution procedure has become one of the most useful methods in many fields dealing with drugs, natural products, agrochemicals, *etc.*, not only for determining their optical purity, but also for obtaining optical isomers. The design and development of a chiral stationary phase(CSP) capable of effective chiral recognition of a wide range of enantiomers is the key point of the HPLC technique. A number of CSPs for HPLC have been prepared and more than 100 CSPs have been commercialized[1]. Among the many types of CSPs for HPLC, polysaccharide mainly including cellulose and amylase based CSPs showed good chiral recognition ability towards a wide number of different racemic compounds[2].

Cellulose-tris(3,5-dimethylphenylcarbamate) CSP was prepared. Four chiral pesticides including five enantiomers were selected to investigate the stereoselectivity of the CSP, which were provided by Institute for the Controling Agrichemicals, Ministry of Agriculture. The chiral separation of diniconazole[3], alpha- and theta-cypermethrin[4,5] has been reported, but the direct separation of the five samples on the CDMPC CSP has not been reported before. Each sample was resolved on the CSP by applying *n*-hexane: *iso*-propanol mobile phase. All the racemates of the five samples obtained good resolution on the CSP under different conditions.

Experimental

The synthesis of CDMPC and the preparation of the CSP

Microcrystalline cellulose（1.0 g）was dissolved in pyridine[2,6], and refluxed for 12 h,

* E-mail: zqzhou@cau.edu.cn

3,5-dimethylphenylisocyanate(3.5 g) was added, then the mixture was refluxed for another 48 h. After cooling methanol (30 mL) was added. The precipitate was filtered, washed with methanol twice, and dried under vacuum for 24 h. IR spectra showed that the adsorption of hydroxyl groups(3340 cm^{-1}) disappeared.

Spherical silica reacted with 3-aminopropyltriethoxysilane in toluene at 110 ℃ for 24 h, the product, aminopropylsilica(APS) was filtered and washed with toluene and dried at 80 ℃ under vacuum. CDMPC (0.45 g) was dissolved in 30 mL THF, APS(2.55 g) was added. The mixture was stirred for 15 min, after evaporating solvent, dried at 60 ℃ for 8 h under vacuum. The slurry of CSPs in hexane-isopropanol (90:10 v/v) solution was packed into stainless steel column (250 mm×4.6 mm i.d.) under 3.7×10^7 Pa to prepare chiral HPLC column.

Chromatographic conditions

Hewlett Packard 1100 Series HPLC (Agilent) was used. The mobile phase was the mixture of appropriate percentage of *iso*-propanol in *n*-hexane. Flow rate: 1.0 mL/min, injection volume: 10 μL, detection wavelength: 230 nm.

Results and Discussion

The chemical structures of the samples were listed in **Figure 1**. Five enantiomers were all well resolved on the CSP at room temperature. The results were listed in **Table 1, Figure 2,** the influence of the temperature on the separation was listed in **Table 2**.

Figure 1 Chemical structures of the enantiomers under investigation

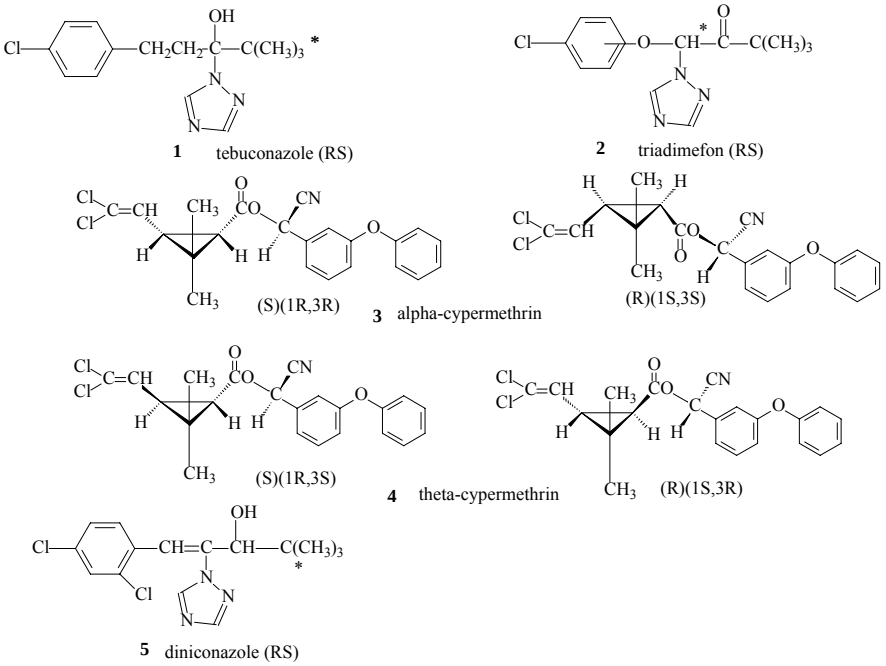
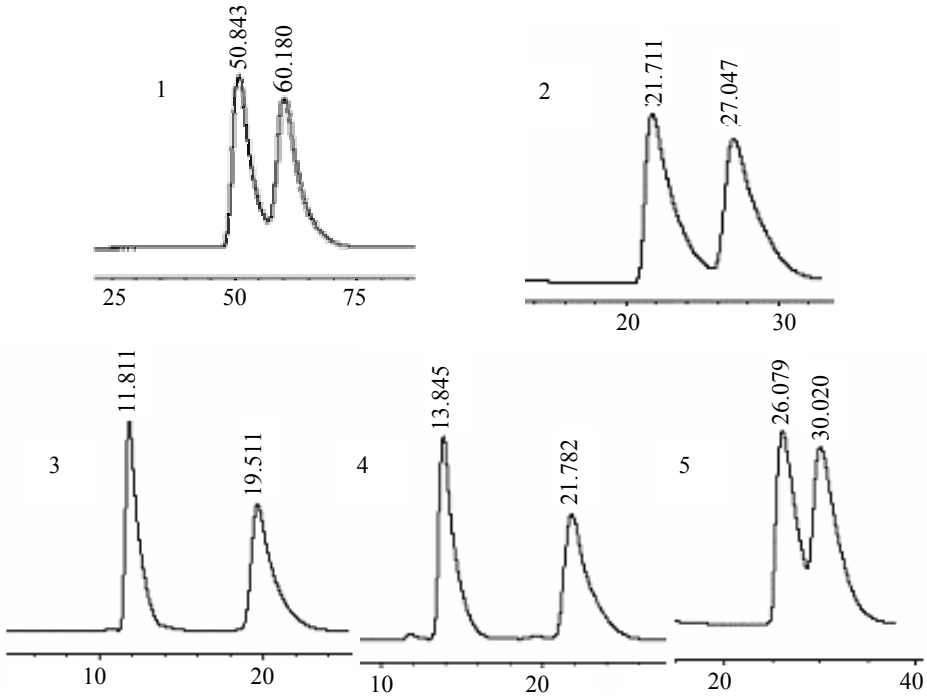


Table 1 The results of the enantiomer separation of the five enantiomers at room temperature

No	sample	*n*-hexane:*iso*-propanol	α	Rs
1	tebuconazole	95:5	1.19	1.22
2	triadimefon	99:1	1.26	1.47
3	alpha-cypermethrin	99:1	1.73	2.82
4	theta-cypermethrin	99:1	1.62	2.55
5	diniconazole	98:2	1.16	1.09

Figure 2 The chromatograms of the resolution of the enantiomers at room temperature



1 tebuconazole, 2 triadimefon, 3 alpha-cypermethrin, 4 theta-cypermethrin, 5 diniconazole

Table 2 The effect of temperature on the resolution of the five enantiomers (the percentage of *iso*-propanol in *n*-hexane mobile phase was as **Table 1**)

Temperature (℃)	1		2		3		4		5	
	α	Rs	α	Rs	α	Rs	α	Rs	α	Rs
0	1.28	0.97	1.20	1.21	1.58	2.11	1.48	2.20	1.14	0.77
5	1.25	0.98	1.20	1.19	1.52	1.93	1.44	2.04	1.12	0.69
10	1.21	0.92	1.19	1.14	1.44	1.87	1.37	1.95	1.12	0.71
15	1.19	0.86	1.18	1.17	1.38	1.74	1.33	1.70	1.12	0.71
20	1.17	0.82	1.16	1.11	1.35	1.63	1.30	1.65	1.12	0.73
25	1.16	0.81	1.16	1.15	1.31	1.53	1.27	1.48	1.12	0.76

The results showed that the CDMPC CSP was appropriate for the resolution of the four chiral pesticides, and alpha-cypermethrin and theta-cypermethrin obtained excellent resolution. When the temperature decreased, the resolution factors all increased for sample 1 to 4, while there was no effect of temperature on the separation of sample 5. We have established ideal methods for the separation of the four chiral pesticides.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (No. 20377052).

References

1. K. Tachibana, A. Ohnishi, *J. Chromatogr. A*, **2001**, *906*, 127.
2. Y. Okamoto, Y. kaida, *J.Chromatgr. A*, **1994**, *666*, 403.
3. O. Nsobumi, K. Hajimu, A.Fumiko, *J. Chromatogr. A*, **1995**, *694*,129.
4. J. P. kutter, *J. Chromatogr.*, **1992**, *33*, 103.
5. D. P. Ewards, M. G. Ford, *J. Chromatogr. A*, **1997**, *777*, 363.
6. Z. Q. Zhou, E. R. Ding, J. G. Hou, *J. Liq. Chrom. & Rel. Technol.*, **1998**, *21*, 3021.

Received 31 March, 2003