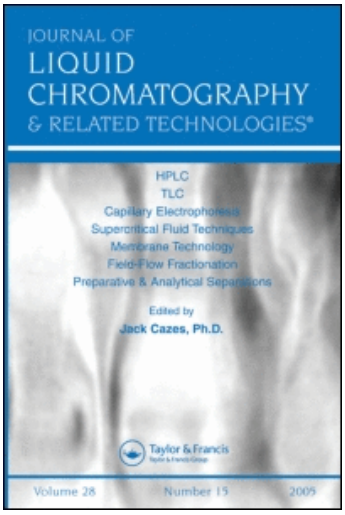

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Chiral Separation of Several Pyrethroids on Polysaccharide-Based Chiral Stationary Phases Under Normal and Reversed Phase Modes

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ABSTRACT

The enantiomers of eight pyrethroid insecticides have been separated by three polysaccharide-based chiral stationary phases (CSP), namely

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Chiralcel OD-R, Chiralpak AD, and Chiralcel OJ, both in reversed and normal phase modes. Deltamethrin, fenpropathrin, and lambda-cyhalothrin could be baseline separated on Chiralcel OD-R in reversed phase mode with R_s values of 1.39, 1.29, and 1.17, respectively. However, the best separations for deltamethrin and fenpropathrin and tau-fluvalinate were achieved when the mobile phase was 15% of ethanol in water. Lambda-cyhalothrin enantiomers were separated using a mobile phase composed of 30% of acetonitrile : water (30 : 70 v/v). In normal phase mode, Chiralcel OJ gave better chiral separation for those pyrethroids than that of Chiralpak AD. The chiral separation conditions for eight pyrethroid insecticides have been discussed.

Key Words: Polysaccharide-based chiral stationary phases; Amylose and cellulose chiral stationary phases; Chiral separation; Pyrethroid insecticides; Stereoselective high-performance liquid chromatography.

INTRODUCTION

Pyrethroid insecticides possess high pesticidal activity, low toxicity to mammalian cells, and adequate stability upon exposure to air and light.[1] The synthetic pyrethroid pesticides are more important in both agricultural and domestic applications usage. When the chemical structures of these pyretheroids contain cyclopropane (Fig. 1), they show asymmetric carbons at positions C-1, C-3, and C-α; thus, there will be eight stereoisomers available, two pairs of enantiomers, while the other two pairs of enantiomers has cis and trans-configuration with respect to the plane of the cyclopropane ring. The individual isomers of pyrethroid esters differ widely in biological activities.[2,3] High insecticide toxicity is generally associated with the (1*R*) configuration of the chiral cyclopropane ring, adjacent to the carbonyl group.[4] Enantiomers differing in configuration at C-α also differ in toxicity.[5]

The chiral separation of pyrethroids has been reported on different Pirkle type chiral stationary phases (CSP). Chapman reported the chiral separation of fenpropanate and fenvalerate by (*R*)-*N*-(3,5-dinitrobenzoyl)phenylglycine as a CSP.[6] Cayley and Simpson[7] separated the enantiomers of several pyrethroids by Pirkle type1-A CSPs.[7] Ôi et al.[8] also reported the chiral separation of pyrethroids by Pirkle type CSPs. Lisseter achieved enantiomeric separation of pyrethroids by Pirkle type stationary phases[9] Recently, the chiral separation of fenpropathrin and bifenthrin by ChiraSpher CSPs, spherical particles of silica coated with poly(*N*-acryloyl-L-phenylalanine ethyl ester), was reported [10] The chiral separation of four pyrethroids by MECC and HPLC using cyclodextrins as chiral selectors was reported by Seveik et al.[11] The cellulose derivatives CSPs were found to be the most appropriate

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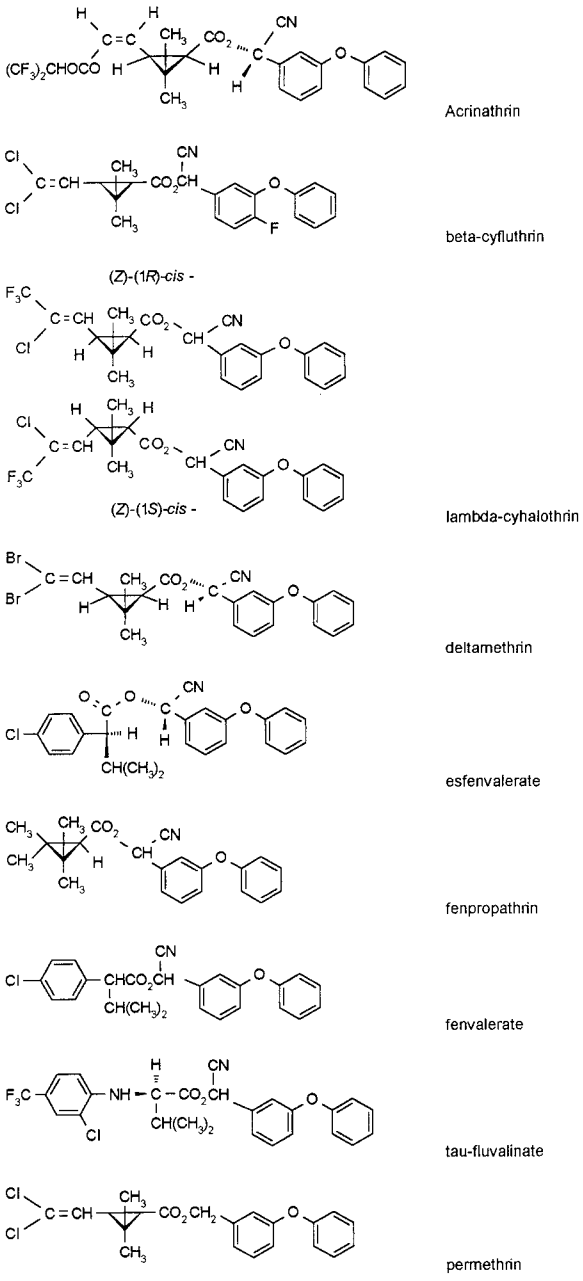

Figure 1. Chemical structures of the pyrethroids in study.

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for the separation of *cis*-biphenthrin, resmethrin, and (1R)-phenothrin, enantiomers, whereas multiple-interaction CSPs, like (*S*)-1-(α-naphthyl)-ethylamine/(*S*)-*tert*-leucine, were more selective for cyfluthrin.[12] The enantiomeric separation of cypermethrin and related pyrethroid insecticides by Chiralcel OD was reported by Edwards.[13] Chrysanthemic acid, chemically known as [2,2-dimethyl-3-(2-methylpropenyl)-cyclopropanecarboxylic acid] and its halogen-substituted analogues, was resolved on (+) (5*R*,8*S*,10*R*) 1-(3-aminopropyl)-terguride CSP.[14] The chiral separation of pyrethroic acid esters were achieved on Chiralcel OD and Chiralcel OF.[15] Polysaccharide-based CSPs are among the most widely used stationary phases for enantiomeric separation by HPLC.[17,18]

This paper describes the use of different polysaccharide-based chiral phases with different mobile phase systems, to find the optimum chiral separation conditions for eight pyrethroid insecticides. Three different polysaccharide-based CSPs have been used, namely: Chiralcel OD-R, Chiralpak AD, and Chiralcel OJ. For Chiralcel OD-R, three mobile phase systems have been studied, while for the other two polysaccharide-based CSPs, two mobile phase systems have been studied in normal phase mode. The optimum chiral separation conditions of beta-cyfluthrin, lambda-cyhalothrin, deltamethrin, esfenvalerate, fenpropathrin, fenvalerate, tau-fluvalinate, and permethrin are discussed.

EXPERIMENTAL

Chemicals and Reagents

Acrinathrin, beta-cyfluthrin, lambda-cyhalothrin, deltamethrin, esfenvalerate, fenpropathrin, fenvalerate, tau-fluvalinate, and permethrin were purchased from Riedel-de Haen (Germany). The structures of the pyrethroids are shown in Fig. 1. Under reversed phase mode, the compounds were dissolved in methanol, ethanol, and acetonitrile, respectively, while under normal phase mode, the compounds were dissolved in isopropanol and ethanol, respectively, depending on the mobile phase composition. All the pyrethroids were diluted with the mobile phase before injection. Solutions with approximate concentration of 20 $\mu g\,mL^{-1}$ were used for injection. All solvents were filtered by a 0.5 μm filter and degassed with helium.

Apparatus

The chromatography was performed on a Waters liquid chromatograph (Milford, MA) equipped with a Millennium^{32} Chromatography working

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station, Waters 2996 Photodiode Array detector, Waters 600E system controller and 600E solvent delivery system.

Chromatographic Conditions

Reversed Phase Mode

Cellulose *tris*(3,5-dimethylphenyl carbamate) CSP known as Chiralcel OD-R (250 × 4.6 mm I.D.) was purchased from Daicel Chemical Industries, Ltd (Tokyo, Japan). Acetonitrile, methanol, and ethanol were used as organic modifiers in mobile phase. The mobile phase compositions are shown in Table 1. Due to the limitation of column pressure, the flow-rate was set at 0.3 and 0.5 mL min^{-1} with the different mobile phases used.

Table 1. Capacity factors (k_1, k_2), separation factors (α), and resolution (R_s) of pyrethroids under reversed phase mode on Chiralcel OD-R.

Compound	Mobile phase (v/v)	k_1	k_2	α	R_s
Lambda-cyhalothrin	Methanol : water (90 : 10)	3.60	4.42	1.18	1.17
	Ethanol : water (85 : 15)	2.69	5.08	1.15	0.98
	Acetonitrile : water (70 : 30)	5.31	5.91	1.11	1.17
	Acetonitrile : water (75 : 25)	3.18	3.52	1.11	1.13
	Acetonitrile : water (80 : 20)	1.99	2.20	1.10	0.84
	Acetonitrile : water (85 : 15)	1.27	1.40	1.10	0.72
Deltamethrin	Methanol : water (90 : 10)	6.56	6.91	1.05	0.57
	Ethanol : water (80 : 20)	7.83	8.87	1.13	1.36
	Ethanol : water (85 : 15)	4.23	4.78	1.13	1.39
	Ethanol : water (90 : 10)	2.42	2.69	1.11	1.12
	Ethanol : water (95 : 5)	1.46	1.60	1.09	0.85
Fenpropathrin	Methanol : water (90 : 10)	3.99	4.29	1.08	0.82
	Ethanol : water (80 : 20)	4.61	5.17	1.12	1.27
	Ethanol : water (85 : 15)	2.63	2.97	1.13	1.29
	Ethanol : water (90 : 10)	1.63	1.82	1.12	1.15
	Ethanol : water (95 : 5)	1.03	1.16	1.12	0.88
Tau-fluvalinate	Methanol : water (90 : 10)	5.61	6.06	1.08	0.47
	Ethanol : water (85 : 15)	4.73	5.68	1.20	0.91
Permethrin	Methanol : water (90 : 10)	7.15	7.56	1.06	0.55
	Ethanol : water (85 : 15)	4.24	4.40	1.04	0.30

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Normal Phase Mode

Amylose *tris*(3,5-dimethylphenyl carbamate) CSP known as Chiralpak AD (250 × 2 mm I.D.) and cellulose *tris*(4-methylbenzoate) CSP known as Chiralcel OJ (250 × 2 mm I.D.) were obtained from GROM (Herrenberg-Kayh, Germany). The mobile phase compositions were 5% and 10% of ethanol or isopropanol in *n*-hexane. The flow-rate was maintained at 0.3 mL min^{-1}. The experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Chiral Separation of Pyrethroids Under Reversed Phase Mode

Table 1 shows the results of the chiral separation of pyrethroids with Chiralcel OD-R. Only five pyrethroids, namely lambda-cyhalothrin, deltamethrin, fenpropathrin, tau-fluvalinate, and permethrin were separated using a mixture of methanol or ethanol and water as mobile phase. The enantiomers of deltamethrin, fenpropathrin, and tau-fluvalinate were best separated using ethanol and water, then methanol and water as a mobile phase. However, when acetonitrile and water were used as mobile phase, only the enantiomers of lambda-cyhalothrin could be separated. Figure 2 shows the chromatograms of lambda-cyhalothrin with the mobile phase of acetonitrile : water 70 : 30 (v/v), fenpropathrin and deltamethrin with ethanol : water 85 : 15 (v/v).

In order to optimize the chiral separation, different compositions of acetonitrile and water as mobile phases have been investigated. Table 1 shows the capacity factors (k_1, k_2), the separation factors (α), and resolution factors (R_s) of five pyretheroids using different percentages of organic modifiers (acetonitrile, ethanol, and methanol) in water. The data indicate that the capacity factors *k* values increased with increasing the concentration of water in mobile phase for all compounds. The maximum separation factor (α) and resolution factors (R_s) values were obtained when the mobile phase consisted of ethanol : water (85 : 15 v/v).

Chiral Separation of Pyrethroids Under Normal Phase Mode

Two polysaccharide-based CSPs have been used, namely amylose *tris*-(3,5-dimethylphenyl carbamate) CSP known as Chiralpak AD and cellulose *tris*(4-methylbenzoate) CSP known as Chiralcel OJ. The enantiomers of acrinathrin, beta-cyfluthrin, fenpropathrin, and fenvalerate could be separated on Chiralpak AD. The enantiomers of acrinathrin, beta-cyfluthrin, lambda-cyhalothrin,

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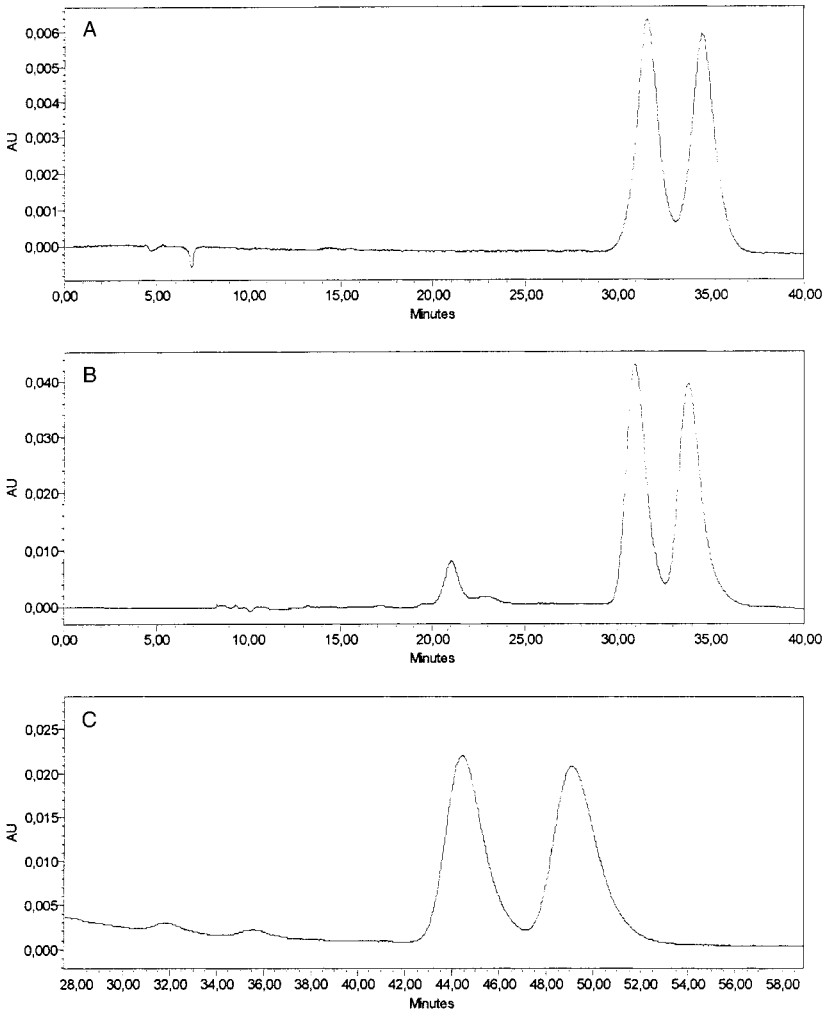

Figure 2. Chromatograms of chiral separation under reverse phase. (A) Lambda-cyhalothrin with the mobile phase of acetonitrile : water = 70 : 30 (V/V), flow rate 0.5 mL min^{-1}, Chiralcel OD-R. (B) Fenpropathrin with the mobile phase of ethanol : water = 85 : 15 (v/v), flow rate 0.3 mL min^{-1}, Chiralcel OD-R. (C) Deltamethrin with the mobile phase of ethanol : water = 85 : 15 (v/v), flow rate 0.3 mL min^{-1}, Chiralcel DR-R.

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Table 2. Capacity factors (k_1, k_2, k_3, k_4), separation factors (α), and resolution (R_s) of pyrethroids under normal phase mode on Chiralpak AD and Chiralcel OJ.

Compound	Column	Mobile phase[a]	k_1	k_2	k_3	k_4	R_{s1}	R_{s2}	R_{s3}
Acrinathrin	AD	A	1.02	1.17			0.46		
		B	1.53	1.79			0.41		
	OJ	C	1.44	1.62			0.29		
		D	1.56	1.78			0.35		
Beta-cyfluthrin	AD	A	1.27	1.77	2.04		1.19	0.77	
		B	1.76	2.65	3.09		1.02	0.79	
	OJ	A	4.95	7.55			1.29		
		B	7.34	11.67			1.74		
		C	4.17	5.34	6.14	6.53	1.41	0.80	0.24
		D	4.95	6.50	7.70	7.81	1.63	0.83	0.10
Lambda-cyhalothrin	OJ	A	1.84	2.13			0.39		
		B	2.63	3.18			0.42		
		C		1.87					
		D	1.97	2.24			0.33		
Esfenvalerate	OJ	A	4.08	7.88			2.76		
		B	5.93	12.10			2.74		

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		C	3.00	6.20		3.35		
		D	4.26	8.81		3.43		
Fenpropathrin	AD	A	1.61	1.86		0.71		
		B	2.35	2.69		0.49		
Fenvalerate	AD	A	2.01	2.23	2.83	0.49	1.44	
		B	2.96	3.27	4.31	0.46	1.47	
	OJ	A	4.14	6.43	8.09	1.62	0.96	
		B	5.98	9.62	12.12	1.84	0.98	
		C	3.50	4.51	7.18	1.09	2.31	
		D	4.25	5.43	8.91	0.98	2.39	
Tau-fluvalinate	OJ	A	4.17	6.77		1.59		
		B	6.32	10.64		1.78		
		C	3.26	5.73		2.39		
		D	4.11	7.33		2.58		
Permethrin	OJ	A	2.46	3.43		1.65		
		B	3.01	4.75		1.94		
		C	1.34	1.85	2.34	1.75	1.11	
		D	1.28	2.00	2.90	1.47	1.44	

[a]The mobile phase were: A, *n*-hexane : iso-propanol = 90 : 10 (v/v); B, *n*-hexane : iso-propanol = 95 : 5 (v/v); C, *n*-hexane : ethanol = 90 : 10 (v/v); D, *n*-hexane : ethanol = 95 : 5 (v/v).

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esfenvalerate, fenvalerate, tau-fluvalinate, and permethrin were separated on Chiralcel OJ. The capacity factors (k_1, k_2), resolution factors (R_s), and the mobile phase composition under normal phase with Chiralpak AD and Chiralcel OJ, are shown in Table 2. Because of the good solubility of pyrethroids in *n*-hexane, methanol, or ethanol, the *k* values of most pyrethroids did not change much with the change of mobile phase composition.

When Chiralpak AD is used, the enantiomers of the pyrethroids could be separated only with isopropanol and *n*-hexane as mobile phase. It is shown that the *k* values are decreased with increasing the concentration of isopropanol in the mobile phase. It is of interest that beta-cyfluthrin and fenvalerate gave three peaks, while acrinathrin and fenpropathrin gave only two peaks on Chiralpak AD.

Using Chiralcel OJ, the enantiomers of the eight pyrethroids used in this study could be separated with isopropanol and/or ethanol and *n*-hexane as mobile phase. The *k* and the resolution factors (R_s) decreased with increasing the concentration of isopropanol in the mobile phase, except for esfenvalerate and permethrin. When ethanol and *n*-hexane were used as mobile, *k* and the resolution factors (R_s) increased with increasing the concentration of ethanol in the mobile phase, it could be due to the good solubility of permethrin in *n*-hexane.

Optimum Separation for Each Pyrethroid Pesticide

Pyrethroid pesticides are synthesized and sold in the form of a single, most active isomer, or in mixtures containing two, four, or eight different stereoisomers. Acrinathrin, lambda-cyhalothrin, deltamethrin, esfenvalerate, fenvalerate, and tau-fluvalinate have one pair of enantiomers. Beta-cyfluthrin, fenvalerate, and permethrin have two pair of enantiomers, while acrinathrin should have eight enantiomers. In this study, the enantiomers of acrinathrin could be separated only under normal phase with Chiralpak AD and Chiralcel OJ. The resolutions of the enantiomers were not good. The *k* values did not change too much with different compositions of the mobile phase.

Beta-cyfluthrin is a mixture of two enantiomeric pairs, which were partially separated only under normal phase mode on Chiralcel OJ, and isopropanol and *n*-hexane as the mobile phase, however, only two peaks were obtained. Using Chiralcel OJ and ethanol and *n*-hexane as a mobile phase, gave four peaks, although not base-line separated, corresponding to the two pairs of enantiomers [Fig. 3(A)].

The enantiomers of lambda-cyhalothrin could be separated, both under reversed phase and normal phase modes. Using methanol or ethanol and water as the mobile phase, the shape of the peaks was broad. However,

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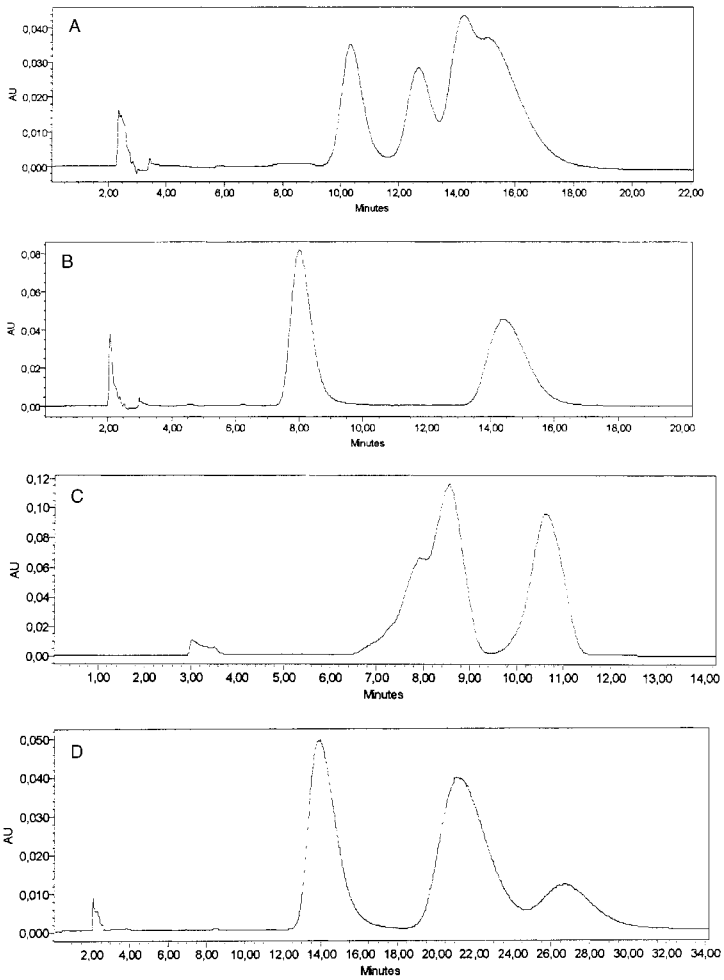

Figure 3. Chromatograms of chiral separation under reverse phase. (A) The separation of beta-cyfluthrin with the mobile phase of ethanl : *n*-hexane = 10 : 90 (v/v), flow rate 0.3 mL min Chiralcel OJ. (B) The separation of estenvalerate with the mobile phase of ethanol : *n*-hexane = 20 : 90 (v/v), flow rate 0.3 mL min^{-1}, Chiralcel OJ. (C) The separation of fenvalerate with the mobile phase of isopropanol : *n*-hexane = 5 : 95 (v/v), flow rate 0.3 mL min^{-1}, Chiralpak AD. (D) The separation of fenvalerate with mobile phase of isopropanol : *n*-hexane = 5 : 95 (v/v), flow rate 0.3 mL min^{-1}, Chiralcel OJ. (F) The separation of tau-fluvalinate with mobile phase of ethanol : *n*-hexane = 10 : 90 (v/v), flow rate 0.3 mL min^{-1}, Chiralcel OJ. (G) The separation of permethrin with the mobile phase of ethanol : *n*-hexane = 10 : 90 (v/v), flow rate 0.3 mL min^{-1}, Chiralcel OJ.

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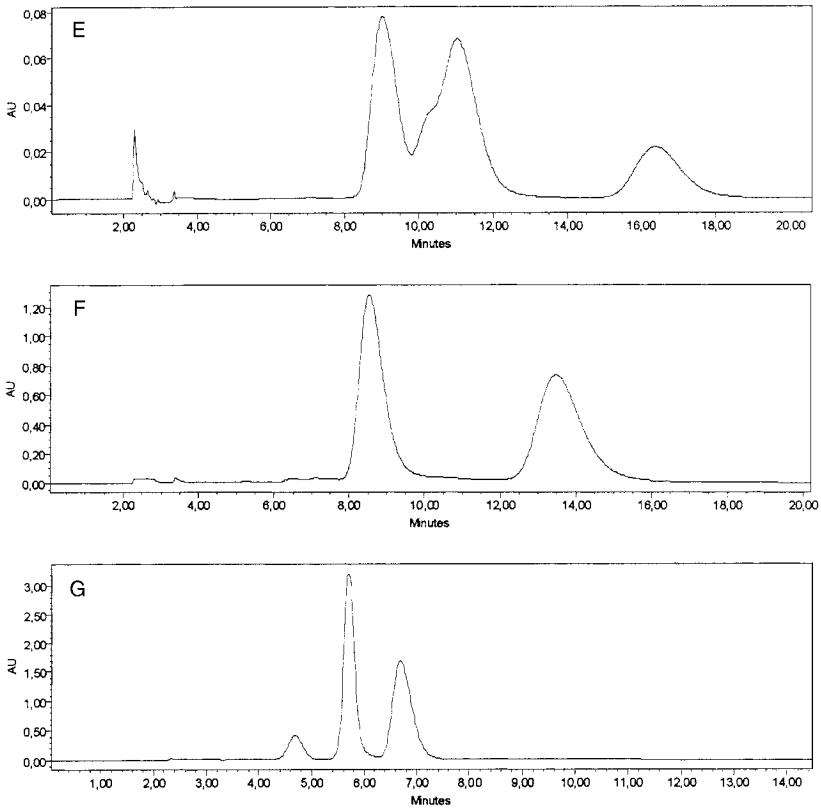

Figure 3. Continued.

under normal phase mode, the enantiomers could be separated on Chiralcel OJ but the resolution of enantiomers was still poor. The best chiral separation of lambda-cyhalothrin was achieved on CHIRALCEL OD-R with acetonitrile and water as the mobile phase [Fig. 2(A)].

Esfenvalerate consists of a pair of enantiomers, which could be separated under normal phase on Chiralcel OJ using ethanol and *n*-hexane as a mobile phase.

Fenpropathrin contains one pair of enantiomers, which separated under both reversed phase and normal phase modes. In normal phase, the separation was achieved only on Chiralpak AD using ethanol and *n*-hexane as a mobile phase. However, the resolutions of enantiomers in normal phase were not as good as in reversed phase mode using ethanol and water as a mobile phase.

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The best chiral separation of fenpropathrin was obtained on Chiralcel OD-R with ethanol and water as the mobile phase [Fig. 2(B)].

Deltamethrin enantiomers were separated on Chiralpak AD under reversed phase mode using ethanol : water (85 : 15 v/v) as a mobile phase [Fig. 2(C)].

There are two chiral centers in fenvalerate, thus, it has four enantiomers, which could be separated only under normal phase on Chiralpak AD [Fig. 3(B)] and Chiralcel OJ [Fig. 3(C) and (D)].

Tau-fluvalinate is chemically known as (*RS*)-α-cyano-3-phenoxybenzyl *N*-(2-chloro-α,α,α-trifluoro-*p*-tolyl)-D-valinate. The material is a 1 : 1 mixture of (*R*)-α-cyano-, 2-(*R*)- and (*S*)-α-cyano-, 2-(*R*)-diastereoisomers, which could be separated on both reversed phase and normal phase mode. In reversed phase mode, methanol or ethanol with water was used as a mobile phase. The shape of the peaks was poor. However, on Chiralcel OJ, the resolutions of tau-fluvalinate improved using different compositions of isopropanol or ethanol and *n*-hexane.

Permethrin with two asymmetric carbons should have four enantiomers. In reversed phase mode, only two peaks could be obtained in all of the mobile phase systems used. The shape of the peaks in reversed phase mode was poor. In normal phase mode, partial separation could be achieved on Chiralcel OJ using isopropanol and *n*-hexane as mobile phase, but only two peaks could be obtained. Using ethanol and *n*-hexane as a mobile phase, three peaks could be separated [Fig. 3(F)]. The area of the second peak equals the area of the first peak, plus the third one. The four enantiomers of permethrin could not be fully resolved under the chromatographic conditions described.

CONCLUSIONS

The enantiomers of eight pyrethroid insecticides have been separated by three polysaccharide-based CSPs, both in reversed phase and normal phase modes. In normal phase, Chiralcel OJ gave better chiral separation for the pyrethroid insecticides. The composition of mobile phase plays an important role in the resolution of pyrethroid enantiomers, both in reversed phase and normal phase modes. Deltamethrin, fenpropathrin, and tau-fluvalinate were separated on Chiralcel OD-R using ethanol : water (15 : 85 v/v) as a mobile phase, while lambda-cyhalothrin was separated using acetonitrile : water (30 : 70 v/v) as a mobile phase. Most of the pyretheroids used in this study were separated by using ethanol : *n*-hexane (5 : 95 v/v) as a mobile phase. While in normal phase mode, the mobile phase consisting of 5% or 10% of isopropanol in hexane proved efficient when using Chiralpak AD.

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