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The Enantiomer Separations of Allethrone and Propargyllone Using Two Long Chain Acylated β-Cyclodextrin Derivatives as CGC Capillary Stationary Phases

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Abstract: Using two β-cyclodextrin derivatives (CDs) with long chain of acyl groups as chiral stationary phases (CSPs) of capillary gas chromatography (CGC), the enantiomers of racemic allethrone and propargyllone were well resolved after derived with acetyl chloride. The enantiomer excess values (e.e.%) of 1S-allethrone and 1S-propargyllone were also determined successfully using these CDs.

Keywords: Enantiomer separation, allethrone, propargyllone, capillary gas chromatography (CGC), β-cyclodextrin derivatives.

For high bioactivity of chiral pesticides, more and more chiral isomers are prepared by enantiomer resolution or asymmetric synthesis, and the sales of chiral pesticides continuously increase in recent years[1]. 1S-Allethrone **I** and 1S-propargyllone **II** are indispensable intermediates for synthesizing 1S-bioallethrin and prallethrin respectively, which are representatives of chiral pesticides. Usually, 1S enantiomers of allethrone and propargyllone are more active than their 1R enantiomers when they are esterified with appropriate chrysanthemic acid, so it is significant to resolve two enantiomers of racemic allethrone and propargyllone and determine the enantiomer excess values (e.e.%) of 1S-allethrone and 1S-propargyllone.

The enantiomer separation of allethrone by GC and HPLC and the enantiomer separation of propargyllone by HPLC using tripeptide as chiral stationary phases have been reported, but using β-cyclodextrin derivatives (CDs) as CGC chiral stationary phases (CSPs) for the resolution of them has not been done. In this paper, we synthesized two CDs substituted with different long chain of acyl groups and used them as CSPs of CGC. The enantiomers of racemic allethrone and propargyllone were well resolved after derived as their acetate (**III** and **IV**) using acetyl chloride (**Figure 1**), and the e.e.% of 1S-allethrone and 1S-propargyllone were also determined successfully.

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Experimental

Synthesis and characterization of two new acylated cyclodextrin derivatives.

The two chiral stationary phases were synthesized by the procedures described in reference[2,3], and the characterization data are as follows:
2,6-di-O-pentyl-3-O-heptanoyl-β-cyclodextrin (CSP1):
$\delta_H(CDCl_3)$, 0.88(m, 9H，$C\underline{H}_3$)，1.30(m, 14H，$CH_3C\underline{H}_2$)，1.59(m, 5H，$OCH_2C\underline{H}_2$)，3.21～3.83(m, 8H，CD($\underline{H}$)，$OC\underline{H}_2$)，4.92(s, 1H，CD($\underline{H}$)). IR(film, cm^{-1}): 3400, 2980, 2850, 1740, 1460, 1380, 1160-1050.
2,6-di-O-pentyl-3-O-octanoyl-β-cyclodextrin (CSP2):
$\delta_H(CDCl_3)$, 0.85(m, 9H，$C\underline{H}_3$)，1.25(m, 18H，$CH_3C\underline{H}_2C\underline{H}_2$)，1.48(m, 6H，$OCH_2C\underline{H}_2$), 3.21～3.81(m, CD($\underline{H}$))，4.93(s, 1H, CD($\underline{H}$)). IR(film, cm^{-1}): 3400, 2960, 2850, 1740, 1460, 1380, 1250, 1160-1050.

Column preparation

Fused-silica capillary tubes (0.25 mm I.D., Yong Nian Optical Fibre factory, Hebei province, China) were treated by depositing sodium chloride onto column inner wall. The columns were then statically coated at 35°C with a 0.5% (w/v) solution of stationary phase in dichloromethane. Following coating, the columns were conditioned under a slow nitrogen flow at 40°C, 80°C, 120°C, 160°C for 1 h each and finally at 180°C for 4 h.

Two columns were prepared by the method, and their properties are listed in **Table 1**.

Table 1 Column properties of the two columns

CSPs	Col. dimension m×mm I.D.	Film thickness μm*	Retention factor k	Col. temp. ℃	Col. efficiency plates/m	Solute
CSP1	20×0.25	0.31	2.72	120	2151	n-dodecane
CSP2	20×0.25	0.31	2.30	120	2944	n-dodecane

*Film thickness is calculated assuming that the density of the stationary phases is equal to 1.000

A Model SP-6800 Gas Chromatograph (Lunan Analytical Instrument Factory, Shandong, China) equipped with a capillary split injection system and flame-ionization detector (FID) was used. N-2000 Chromatography Data Station (Zhejiang University) was used to obtain the data. Carrier gas was high purity nitrogen(99.99%). The injection split ratio was 30:1. Both the injector and detector temperatures were 250°C.

Results and Discussion

Allethrone and propargyllone were derived as their acetate using acetyl chloride before test (**Figure 1**). The acetate of allethrone and propargyllone can be well resolved at 120°C, and the separation results are listed in **Table 2**, **Figure 2** and **Figure 3**.

Figure 1

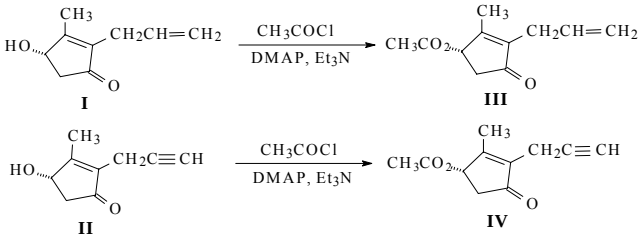


Figure 2 The chromatogram of racemic **III** on CSP1. Chromatographic conditions as **Table 2**

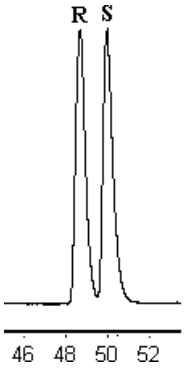


Figure 3 The chromatogram of racemic **IV** on CSP2. Chromatographic conditions as **Table 2**

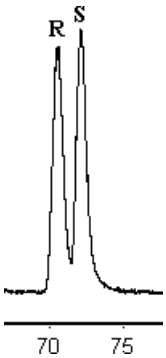


Table 2 The results of enantiomer separation of **III** and **IV**.*

Solute	CSPs	Temp. °C	Retention factor *k*		Relative retention value α
III	CSP1	120	33.56	34.51	1.03
	CSP2	120	26.49	27.21	1.03
IV	CSP1	120	53.73	54.87	1.02
	CSP2	120	42.22	43,20	1.02

*Carrier gas: N_2; Column inlet pressure: 75kPa; *SP-6800 Gas Chromatograph with FID (China).

The e.e.% of 1S-allethrone and 1S-propargyllone was determined on CSP1. The results are listed in **Table 3, Figure 4** and **Figure 5**.

Table 3 The determination of e.e.% of 1S-allethrone and 1S-propargyllone on CSP1*

Solute	Temp.°C	Retention factor k		Relative retention value α	e.e.%
1S-III	120	39.06	40.22	1.03	98.03%
1S-IV	120	60.44	62.17	1.03	97.28%

* Carrier gas: He; Column inlet pressure: 150kPa; Shimazdu GC-14A with FID (Japan)

Figure 4 the chromatogram of 1S-**III** on CSP1. Chromatographic conditions as **Table 3.**

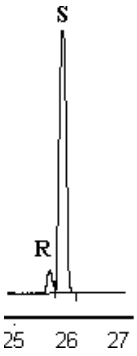
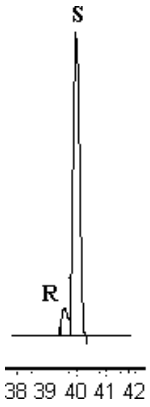


Figure 5 the chromatogram of 1S-**IV** on CSP1. Chromatographic conditions as **Table 3**



Conclusion

Using two CDs with long chain of acyl groups as chiral stationary phases of CGC, the enantiomers of racemic allethrone and propargyllone were well resolved after deriving with acetyl chloride. The e.e.% of 1S-allethrone and 1S-propargyllone were also determined successfully using these CDs.

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