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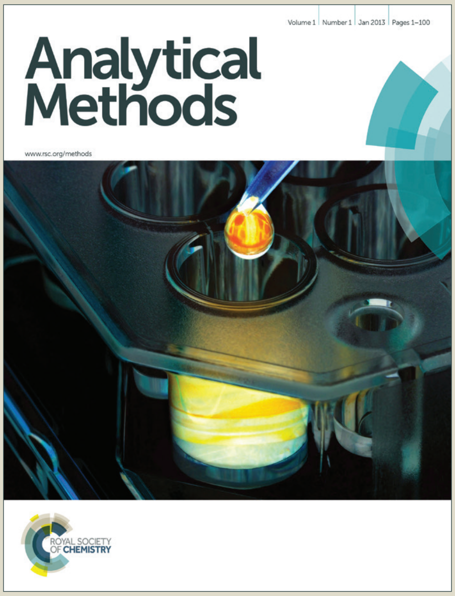

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Chiral Separation of Ten Arylphenoxypropionate Herbicides on Four Chiral Columns by Supercritical Fluid Chromatography

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Abstract

Many chemical products used in the agrochemical industries contain chiral centers and consist of one or two pairs of enantiomers, which can lead to important consequences regarding bioactivity. The resolution of racemates on the analytical level for herbicides development is vital. Investigative chiral arylphenoxypropionates are widely used herbicides. The chromatographic chiral resolution of ten racemic arylphenoxypropionate herbicides, using supercritical fluid chromatography, was studied on Sino-Chiral OJ, Chiralcel OD-H, Chiralpak IB, and Chiralpak AD-H columns. A comparison was made between the chiral herbicides separations on Sino-Chiral OJ column using a pure carbon dioxide (CO_2) mobile phase and using a CO_2 mobile phase with an added 1% modifier (methanol, ethanol,

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2-propanol). The retention factors for enantiomers of substances decreased upon adding organic modifier. The enantiomeric separation ability of four chiral selectors with respect to compounds was examined under various experimental conditions. The results indicated that Sino-Chiral OJ column showed the best chiral recognition by yielding six analytical herbicides in baseline separation. Only one analyte was completely separated by bonded-Chiralpak IB column, which had a lower chiral recognition ability than coated chiral stationary phase columns. Clodinafop-propargyl and haloxyfop-methyl did not obtain separation under the investigated conditions. Additionally, the chiral recognition mechanisms between the chiral stationary phase and the analyte enantiomers were clarified.

Keywords: arylphenoxypropionate herbicides; enantioseparation; chiral stationary phase; supercritical fluid chromatography

1. Introduction

Chiral arylphenoxypropionate herbicides are widely used in agro-forestry production. The relevant studies of such herbicides' selectivity, conductivity, and herbicidal activity have become the foundations of herbicides development. It is well known that the enantiomers in chiral herbicides usually exhibit different bioactivity and toxicity. [1–5] For example, the R-form of the organophosphorus pesticide EPN has high activity while the S-form performs contrary and has a strong neural delay effect. [6–7] The enantiomers activities of haloxyfop against annual grass weeds are mainly performed by the R-form, which has 1000-times higher herbicidal activity than the S-form.[8–9] According to research, the R-isomers of arylphenoxypropionate herbicides are more biologically active than the S-isomers, which fail to prevent agricultural crop pests and have toxicity and side effects.[10–12] Practice has shown that the degradation and the fate of racemates in the environment exhibit great enantiomeric differences. Furthermore, the herbicides' quality is reduced by inefficient or toxic enantiomers that can pollute the environment. For limits of manufacturing techniques and cost, the majority of chiral pesticides are produced and marketed as racemates.[6] The studies that focus on enantio-separations of chiral herbicides are significant for avoiding or reducing the adverse effects on the ecological environment and leading the production of single-enantiomer herbicides.

Owing to its selectivity, sensitivity, and accuracy, chromatographic technology has been successfully integrated into the tool for the separation of enantiomers or stereoisomers.[13] Among all commercial chiral stationary phases (CSPs), polysaccharide-based stationary phases are the most successful and have taken a dominant position in the development of chromatography technology because of their dealing with drugs, herbicides, and natural products for determining optical purity and obtaining optical isomers on a large scale.[14–18] Zhou[19] separated quizalofop-ethyl with R_s values of 1.21 by HPLC using coated amylose tris 3,5-dimethylphenylcarbamate stationary phase and 100% n-hexane as a mobile phase. The capacity factor of two enantiomers was 23.98 and 28.94 respectively. Chen[20] analyzed the direct separation of diclofop-methyl enantiomers by HPLC using CSP packed with cellulose tris 4-methylbenzoate coated on aminopropyl silica gel. Diclofop-methyl obtained highest resolution (R_s=3.63) using n-hexane—2-propanol (80:20, V/V).

Supercritical fluid chromatography (SFC), a chromatographic separation technology using supercritical fluid as the mobile phase, has a 40-year history. Carbon dioxide (CO_2), pure or with a percentage of polar solvents, is used almost exclusively as the eluent. Compared with general HPLC, the use of SFC can result in higher efficiency, higher resolutions in shorter analysis time, and simpler sample pretreatment.[21,22] Enantioseparations in SFC have been reported for several commercially available CSPs, including native and derivatized cyclodextrin,[23,24] brush-type,[25,26] polysaccharide,[27,28] and poly-methacrylate phases.[29] These studies have demonstrated that the advantages of SFC, including separations of a wide variety of analytes, durability of the chiral columns, and a selection of detection options,[30–34] partly compensate for the lack of chiral separation in HPLC.

Arylphenoxypropionate herbicides belong to an important class of contact herbicides that have been used for grassy weeds. The two enantiomers of these compounds exhibit different herbicide activity (the R-enantiomer being the biologically active one). Additionally, enantiomeric separations are mostly carried out using HPLC, and it is therefore of great interest to investigate the enantioseparation of these herbicides on SFC with various CSPs. The aim of the present work was to examine the different chiral columns affecting the resolution, by SFC, of ten arylphenoxypropionate herbicides (clodinafop-propargyl, cyhalofop-butyl, diclofop-methyl, fluazifop-butyl, haloxyfop-methyl, propaquizafop, quizalofop-ethyl, dichlorprop-methyl, fenoprop-methyl and mecoprop-methyl). The four CSPs used for this work were Sino-Chiral OJ, Chiralcel OD-H, Chiralpak IB, and Chiralpak AD-H. The mechanism of chiral recognition was also analyzed.

2. Materials and methods

2.1 Chemicals

Four compounds (clodinafop-propargyl, cyhalofop-butyl, fenoprop-methyl, and mecoprop-methyl) of the ten chiral arylphenoxypropionate herbicides (Table **1**, Fig. **1**) were purchased from Er. Enrenstorfer (Augsburg, Germany). The other six compounds were purchased from AccuStandard, Inc (New Haven, CT, USA).

Table 1 Ten chiral arylphenoxypropionate herbicides

Symbol	Compound	Purity(%)	CAS NO.
a	Clodinafop-propargyl	99.0	105512-06-9
b	Cyhalofop-butyl	99.0	122008-85-9
c	Diclofop-methyl	100	51338-27-3
d	Fluazifop-butyl	99.5	69806-50-4

e	Haloxyfop-methyl	100	69806-40-2
f	Propaquizafop	99.6	111479-05-1
g	Quizalofop-ethyl	100	76578-14-8
h	Dichlorprop-methyl	98.3	57153-17-0
i	Fenoprop-methyl	98.0	4841-20-7
j	Mecoprop-methyl	99.0	2786-19-7

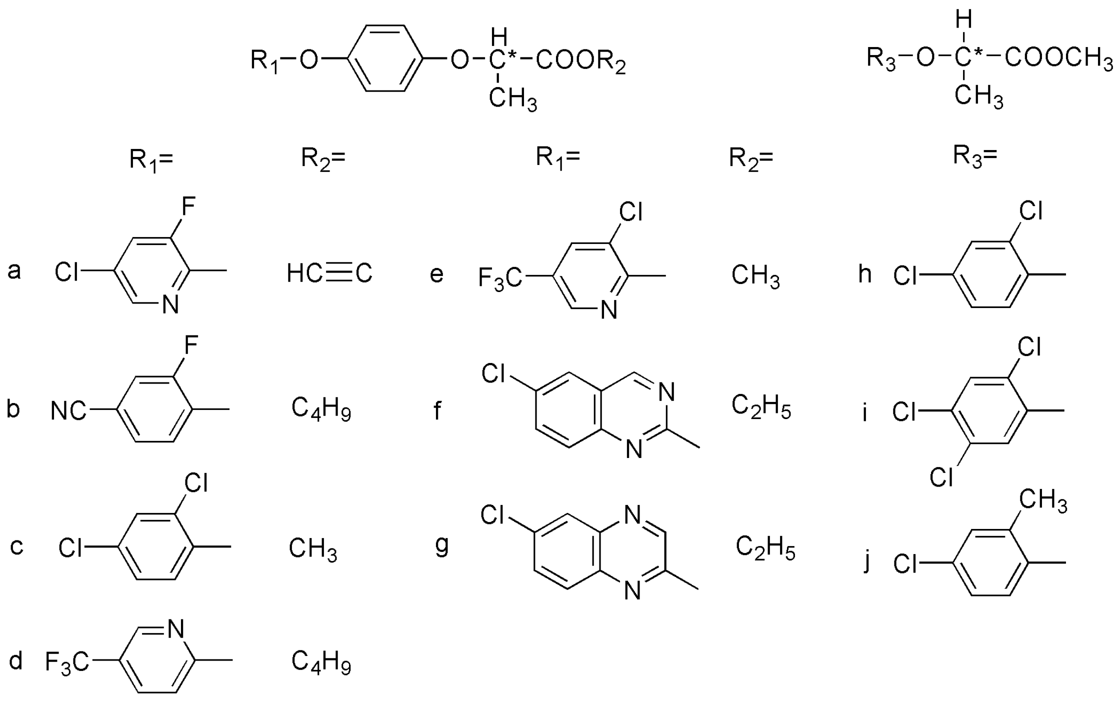

Fig. 1 Molecule structure of ten chiral arylphenoxypropionate herbicides

The HPLC-grade organic solvents (methanol, ethanol, and 2-propanol) were purchased from Tianjin Shield Specialty Chemical Co. Ltd (Tianjin, China). The CO_2 was of dry-ice grade and purchased from Jingong Specialty Gas Co. Ltd (Hangzhou, China).

2.2 Instrumentation

Chromatographic studies were performed on a Thar SD-ASFC-2 SFC system from Thar Technologies (Pittsburgh, PA, USA) equipped with a Gilson UV/VIS-151 detector (Middleton, WI, USA) and a Rheodyne 7410 injector with a 20μL loop volume (Cotati, CA, USA). The system was controlled by the software of Thar Instruments Superchrom.

2.3 Chromatographic measurements

Sino-Chiral OJ column (250 mm × 4.6 mm, 5µm) (Funsea Technology Co. Ltd, Beijing, China), whose basic properties are similar to those of Chiralcel OJ, was packed with cellulose tris 4-methylbenzoate coated on a silica gel (CTMB). Chiralcel OD-H column (250 mm × 4.6 mm, 5µm) consisted of cellulose tris 3,5-dimethylphenylcarbamate coated on a silica gel. Chiralpak IB column (250 mm × 4.6 mm, 5µm) was packed with cellulose tris 3,5-dimethylphenylcarbamate bonded to a silica gel (CDMPC). Chiralpak AD-H column (250 mm × 4.6 mm, 5µm) consisted of amylose tris 3,5-dimethylphenylcarbamate coated on a silica gel (ADMPC). The Chiralcel and the two Chiralpak columns were manufactured by Daicel Chemical Industries, Ltd, Japan.

The column oven was set at 30 °C, the UV-detector was set to monitor 230 nm, the backpressure was 150 bar, and the flow rate was 2 ml/min. Supercritical CO_2 modified with methanol, ethanol, or 2-propanol was used as the mobile phase.

When the organic modifier was changed, the equilibration time was more than 20 min and the baseline was monitored to confirm the shift.

3. Results and discussion

The CSP is a crucial factor for enantiomeric separation which was investigated in our work. The enantioseparation of chiral substances under pure CO_2 mobile phase was compared with that under CO_2 mobile phase with added organic modifiers. The optimum conditions were determined and the mechanism of chiral recognition was discussed.

3.1 Separation under pure supercritical CO_2 mobile phase condition

The separation of ten arylphenoxypropionate herbicides under supercritical CO_2 mobile phase conditions is shown in Table **2**. On Sino-Chiral OJ column, three herbicides were partially separated and another three were in the baseline separation. On Chiralcel OD-H column, five analytes were partially resolved and only diclofop-methyl was completely separated. On both Chiralpak AD-H and Chiralpak IB columns, two compounds were partially separated and baseline separation of one compound was achieved. Clodinafop-propargyl, cyhalofop-butyl, and haloxyfop-methyl could not be separated from the peak co-elution on any chiral column under supercritical CO_2 mobile phase conditions. Sino-Chiral OJ and Chiralcel OD-H columns were most successful for separating chiral compounds. The enantiomeric separation of six compounds on Sino-Chiral OJ column showed better efficiency with high resolutions (1.34 – 6.79), thus Sino-Chiral OJ column is more suitable for separating these ten arylphenoxypropionate herbicides.

Table 2 The enantiomeric separation results of ten chiral herbicides on four chiral columns with pure CO_2 mobile phase, flow rate 2 ml/min, 35°C and backpressure 150 bar

Compounds	Sino-Chiral OJ				Chiralcel OD-H				Chiralpak IB				Chiralpak AD-H			
	k_1	k_2	α	R_S	k_1	k_2	α	R_S	k_1	k_2	α	R_S	k_1	k_2	α	R_S
Clodinafop-propargyl	25.72	/	/	/	22.27	/	/	/	10.86	/	/	/	27.52	/	/	/
Cyhalofop-butyl	17.18	/	/	/	51.16	/	/	/	18.75	/	/	/	21.01	/	/	/
Diclofop-methyl	19.44	20.90	1.08	1.44	26.85	38.13	1.42	9.02	11.73	14.11	1.20	4.12	19.50	/	/	/
Fluazifop-butyl	4.96	5.85	1.18	1.34	12.21	12.92	1.06	0.66	5.30	/	/	/	8.72	/	/	/
Haloxyfop-methyl	5.27	/	/	/	6.85		/	/	3.76	/	/	/	6.13	/	/	/
Propaquizafop	/	/	/	/	149.47	152.21	1.02	0.43	69.79	71.29	1.02	0.44	/	/	/	/
Quizalofop-ethyl	54.81	71.50	1.30	6.79	54.19	57.91	1.07	1.47	28.26	29.19	1.03	0.58	85.51	98.41	1.15	1.71
Dichlorprop-methyl	2.87	3.21	1.12	1.42	3.40	/	/	/	2.41	/	/	/	2.31	2.79	1.21	0.85
Fenoprop-methyl	2.54	3.14	1.24	2.65	3.51	3.99	1.14	1.27	2.33	/	/	/	3.13	/	/	/
Mecoprop-methyl	2.57	3.30	1.29	3.10	2.34	2.87	1.23	1.09	1.48	/	/	/	1.69	1.93	1.15	0.51

3.2 Effect of organic modifier

When separating polar compounds by SFC with a nonpolar mobile phase such as CO_2, a little organic solvent can be added to enhance its eluting power, selectivity, and speed of separation. Enantioseparation of the group of investigated herbicides under CO_2-based mobile phase with methanol, ethanol, or 2-propanol, were studied. The percentage of modifier ranged from 1% to 5% (v/v). The chiral separations on Sino-Chiral OJ column were discussed based on the comparisons between pure CO_2 mobile phase and CO_2 with 1% modifier added.

Table 3 The enantiomeric separation results of 10 compounds on Sino-Chiral OJ with pure CO_2 and 1% modifier added, flow rate 2 ml/min, 35°C and backpressure 150 bar

Compounds	Modifiers	k_1	k_2	α	R_s
Diclofop-methyl	1% methanol	13.69	14.70	1.07	1.46
	1% ethanol	15.18	16.30	1.07	1.59
	1% 2-propanol	16.58	17.90	1.08	1.82
	0	19.44	20.90	1.08	1.44
Fluazifop-butyl	1% methanol	3.20	3.89	1.21	1.73
	1% ethanol	3.64	4.28	1.17	1.54
	1% 2-propanol	4.14	4.88	1.18	1.20
	0	4.96	5.85	1.18	1.34
Quizalofop-ethyl	1% methanol	40.71	55.87	1.37	7.36
	1% ethanol	41.74	56.61	1.36	7.32
	1% 2-propanol	48.14	63.07	1.31	6.85
	0	54.81	71.50	1.30	6.79
Dichlorprop-methyl	1% methanol	2.17	2.43	1.12	1.51
	1% ethanol	2.33	2.67	1.15	1.75
	1% 2-propanol	2.59	2.92	1.12	1.52
	0	2.87	3.21	1.12	1.42
Fenoprop-methyl	1% methanol	1.96	2.39	1.22	2.24
	1% ethanol	2.06	2.57	1.25	2.67
	1% 2-propanol	2.34	2.85	1.22	2.55
	0	2.54	3.14	1.24	2.65
Mecoprop-methyl	1% methanol	2.00	2.46	1.23	3.00
	1% ethanol	2.10	2.70	1.29	2.83
	1%2-propanol	2.35	3.00	1.28	3.16
	0	2.57	3.30	1.29	3.10

As shown in Table **3**, adding organic modifiers to the mobile phase shortened retention times, especially for diclofop-methyl and quizalofop-ethyl. The capacity factor data of each solute using 1% modifiers indicated that the retention of the eluting enantiomers using different modifiers in mobile phase was in the order of methanol < ethanol < 2-propanol.

Figure **2** shows that there was no distinct regularity for the resolutions of ten herbicides, but we could see that the resolution of each substance using mobile phase with methanol, ethanol, or 2-propanol was higher than using pure CO_2. For example, diclofop-methyl obtained baseline separation using 1% methanol, 1% ethanol, and 1% 2-propanol with R_s values of 1.46, 1.59, and 1.82, respectively. The resolution under pure CO_2 was 1.46. The resolution of fluazifop-butyl using 1% methanol and 1% ethanol was 1.73 and 1.54, respectively, which were both higher than using pure CO_2 (R_s=1.34). The resolution of mecoprop-methyl using 1% 2- propanol (R_s=3.16) was higher than using pure CO_2 (R_s=3.10). The remaining substances had similar features. From these results, we concluded that adding organic alcohol can modulate the chiral recognition and that different modifiers have different influences on separation.

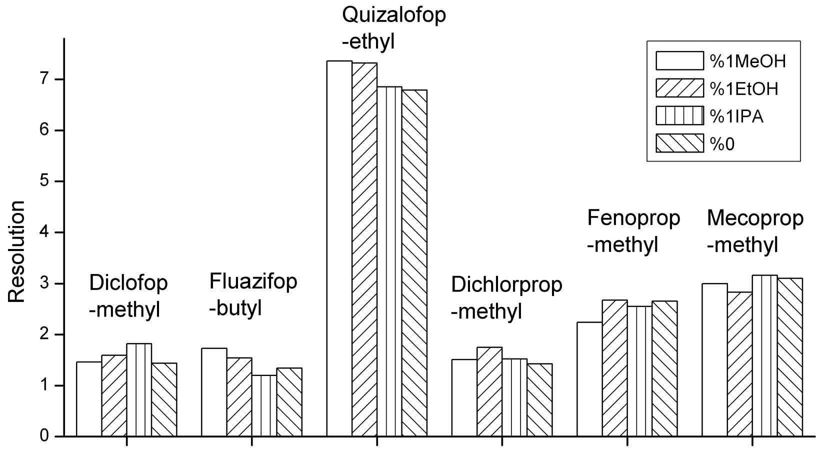

Fig. 2 The resolutions of ten compounds with pure CO_2 and 1% modifier added

3.3 Effect of four chiral columns

The enantioseparation of ten arylphenoxypropionate herbicides using Sino-Chiral OJ, Chiralcel OD-H, Chiralpak IB, and Chiralpak AD-H as chiral columns was comparatively examined and analyzed.

As shown in Table **4**, six compounds were separated completely by using Sino-Chiral OJ column, while the other four compounds were not separated. On Chiralcel OD-H column, one compound was in baseline separation and five compounds were partially separated. Three compounds were separated on Chiralpak IB column. Seven compounds were separated with low resolution by using Chiralpak AD-H column. The results are summarized as follows: clodinafop-propargyl and haloxyfop-methyl could not be separated under any condition, cyhalofop-butyl and propaquizafop were partially separated, and the other six substances were in baseline separation.

Table 4 Separation of 10 arylphenoxypropionate herbicides on 4 chiral columns with flow rate 2 ml/min, 35°C and backpressure 150 bar

CSP	R_S=0	R_S<1	1<R_S<1.5	R_S>1.5
Sino-Chiral OJ	Clodinafop-propargyl, Cyhalofop-buty, Fluazifop-buty, Propaquizafop			Diclofop-methyl, Fluazifop-butyl, Quizalofop-ethyl, Dichlorprop-methyl, Fenoprop-methyl, Mecoprop-methyl
Chiralcel OD-H	Clodinafop-propargyl, Cyhalofop-butyl, Fluazifop-butyl, Dichlorprop-methyl	Propaquizafop	Fluazifop-butyl Quizalofop-ethyl, Fenoprop-methyl, Mecoprop-methyl	Diclofop-methyl

Chiralpak IB	Clodinafop-propargyl, Cyhalofop-butyl, Fluazifop-butyl, Dichlorprop-methyl, Fenoprop-methyl, Mecoprop-methyl	Propaquizafop, Quizalofop-ethyl		Diclofop-methyl
Chiralpak AD-H	Clodinafop-propargyl, Haloxyfop-methyl, Propaquizafop	Cyhalofop-butyl, Fluazifop-butyl	Fenoprop-methyl, Mecoprop-methyl	Diclofop-methyl, Quizalofop-ethyl, Dichlorprop-methyl

By comprehensive comparison of separations under all conditions, the optimal separation conditions were confirmed with shorter retention times and higher resolution, which was a top priority. The optimal separation conditions of the ten compounds are shown in Table **5**.

Table 5 The optimal separation conditions of 10 arylphenoxypropionate herbicides with flow rate 2 ml/min, 35°C and backpressure 150 bar

Compounds	CSP	Modifiers	k_1	k_2	α	R_s
Clodinafop-propargyl	/	/	/	/	/	/
Cyhalofop-butyl	Chiralpak AD-H	2% ethanol	9.34	9.91	1.06	0.83
Diclofop-methyl	Chiralcel OD-H	5% methanol	3.98	4.50	1.13	2.84
Fluazifop-butyl	Sino-Chiral OJ	1% methanol	3.20	3.89	1.21	1.73
Haloxyfop-methyl	/	/	/	/	/	/
Propaquizafop	Chiralpak IB	no modifier	69.79	71.29	1.02	0.44
Quizalofop-ethyl	Sino-Chiral OJ	5% methanol	10.80	14.94	1.38	7.18
Dichlorprop-methyl	Sino-Chiral OJ	1% ethanol	2.33	2.67	1.15	1.75
Fenoprop-methyl	Sino-Chiral OJ	1% ethanol	2.06	2.57	1.25	2.67
Mecoprop-methyl	Sino-Chiral OJ	1%2-propanol	2.35	3.00	1.28	3.16

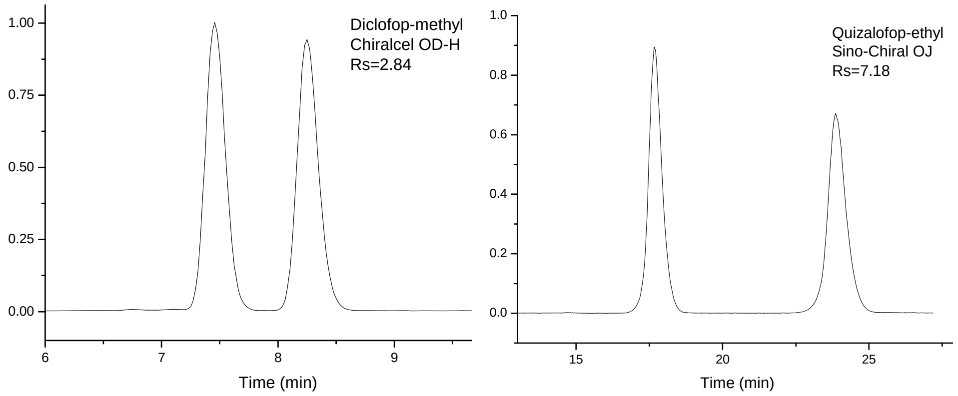

Fig.3 SFC chromatograms of diclofop-methyl and quizalofop-ethyl under the optimal separation

conditions: 5% methanol in CO_2; flow rate 2.0 ml/min; backpressure 150bar; column temperature, 35°C.

3.4 Mechanism of chiral recognition

Enantio-selectivity on the CSPs arises from a three-point interaction between the analyte and the chiral selector. This interaction forms a labile diastereomeric complex with one enantiomer while the other enantiomer forms a diastereomeric complex through a two-point interaction. This difference in interaction results in different complex stabilities, different retentions, and hence enantioseparation.[35]

The chiral recognition mechanisms between the CSP and the analyte enantiomers are rather complex and often not fully clarified. C=O and benzyl groups exist in CTMB-CSP. Both CDMPC-CSP and ADMPC-CSP contain C=O, −NH, and benzyl. An extra −NH group exists in CDMPC and ADMPC compared with CTMB. The structures of the ten herbicides all have an electronegative atom (F, Cl), C=O group, or benzene ring that directly links to the chiral center, which may interact with the CSP through hydrogen bonding, dipole-dipole interaction, or π-π interaction. Both halogen atoms (F, Cl) and C=O groups can interact with the −NH group and hydrogen atom contained in the CSP by hydrogen bonding. Taylor[14] interpreted the "three point" theory that two of the three interactions between the CSP and the enantiomers should be different. It may be disadvantageous, resulting in the reduction or elimination of the chiral recognition ability if there were two points of function with interaction of the same kind. Sino-Chiral OJ column with CTMB offered the best chiral discrimination, permitting six analytes to be baseline resolved.

The Chiralpak IB prepared with a covalently bonded chiral selector had the lowest chiral recognition ability. The molecular structure of the polysaccharide-derivatives was destroyed[36] by the added spacers during preparation of the coated CSPs and their multiple binding sites. The matching degree between the selected compounds and the chiral cavity of Chiralpak IB was decreased.

The high separation efficiency of diclofop-methyl may be a result of the high matching between the molecule structure and the chiral groove of four stationary phases. It should be noted that propaquizafop, which had the same dinitrogen heterocyclic ring as quizalofop-ethyl, could be separated on CDMPC-CSP, thus CDMPC was suitable for separating the chiral compounds with dinitrogen heterocyclic ring structure.

The nitrogen naphthalene nucleus in propaquizafop assists in the insertion of the cellulose chiral cavity by extending the molecular structure, which probably results in the separation of propaquizafop on CDMPC-CSP only. Cyhalofop-butyl could only be separated by ADMPC-CSP, which has a left-handed quadruple helix.[37] In addition, the benzene ring and −CN in cyhalofop-butyl could interact with the benzene ring and cymene of the column through π-π interaction.

Separation of clodinafop-propargyl and haloxyfop-methyl were not obtained. Both compounds consist of atoms of F and Cl that can interact with CSP through hydrogen bonding, which may interrupt the chiral discrimination. For these two compounds, the alternate position of −N in the heterocycle was substituted by the halogen groups (Cl, F), so the interaction would be reduced or hindered by structure.

4. Conclusions

The enantiomeric separations of ten chiral arylphenoxypropionate herbicides, on Sino-Chiral OJ, Chiralcel OD-H, Chiralpak IB, and Chiralpak AD-H chiral columns by SFC, are presented. Supercritical CO_2, modified with methanol, ethanol, or 2-propanol, was used as mobile phase. The chiral recognition mechanism of the herbicides was discussed. Baseline separations of three compounds were obtained and another three were separated with Sino-Chiral OJ column under pure CO_2 mobile phase. On Chiralcel OD-H column, one compound was in baseline separation and five compounds were partially separated. By using Chiralpak IB and Chiralpak AD-H as columns, 3 compounds were separated and baseline separation of one compound was achieved. When adding organic modifier some changes in separations occurred. For three compounds that were only partially separated with pure CO_2 on Sino-Chiral OJ column, the addition of organic modifier completed the separation. On Chiralpak AD-H column four more compounds could be separated than before. The capacity factors of ten substances on four chiral columns became shorter. Besides the separated compounds resolutions did not demonstrate regular changes and different modifiers have different effects on resolution.

The best column for separating these ten herbicides was the Sino-Chiral OJ, which resolved six herbicides in baseline separation. Only one analyte was separated completely by using Chiralpak IB column, which had lower chiral recognition ability than coated CSPs. Cyhalofop-butyl could only be separated by the ADMPC. Separation of clodinafop-propargyl and haloxyfop-methyl were not obtained. Chiral recognition of propaquizafop and quizalofop-ethyl by the CDMPC-CSP showed that CDMPC was suitable for separating chiral compounds that contain dinitrogen heterocyclic ring structure.

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