CHINESE JOURNAL OF ANALYTICAL CHEMISTRY
Volume 34, Issue 2, February 2006
Online English edition of the Chinese language journal

Cite this article as: Chin J Anal Chem, 2006, 34(2), 159−164.

RESEARCH PAPER

Enantioseparation of Four Aryloxyphenoxypropionic Acid Herbicides by HPLC on CDMPC and (*S*,*S*)-Whelk-O 1

Pan Chunxiu[1,2], Shen Baochun[1], Zhang Xuejun[1], Zhang Datong[1], Xu Xiuzhu[1,*]

[1]Department of Chemistry, Zhejiang University, Hangzhou 310027, China
[2]School of Chemistry & Chemical Engineering, Anhui University of Technology, Maanshan 243000, China

Abstract: This article reported the enantioseparation of diclofop, fluazifop, quizalofop-P and fenoxaprop using self-prepared cellulose derivative CDMPC and (*S*,*S*)-Whelk-O 1 columns. The influence of the mobile phase composition and solute structure on the chiral separation was studied. And their chiral recognition mechanism was discussed. The experiment results showed that fenoxaprop obtained the best resolution on (*S*,*S*)-Whelk-O 1, while the other three solutes obtained the best separation on CDMPC. It was concluded that the four aryloxyphenoxypropionic acid herbicides obtained excellent separation and the chiral recognition mechanisms of CDMPC and (*S*,*S*)-Whelk-O 1 are different from each other. And the structure of solutes and CSP play a key role in the chiral recognition.

Key Words: Enantioseparation; Aryloxyphenoxypropionic acid herbicides; cellulose tris (3,5-dimethylphenylcarbamate) (CDMPC); (*S*,*S*)-Whelk-O 1

1 Introduction

Aryloxyphenoxypropionic acid herbicides are usually utilized as esters which are rapidly hydrolyzed in soil or vegetable tissues to the corresponding acids which are biologically active agrochemicals. The two enantiomers of all studied compounds exhibit different herbicide activity (the *R*-enantiomer being the biologically active one). Therefore, enantioseparation of this kind of herbicides is of great interest. Desiderio[1] has reported the enantiomeric separation of acidic herbicides including diclofop, fluazifop, and fenoxaprop by capillary electrophoresis using vancomycin as chiral selector. Quizalofop has been resolved on amylase tris (3,5-dimethylphenylcarbamate)[2] and cellulose tris (4-methylphenylcarbamate) (CMPC)[3].

The majority of chiral separations were performed by high-performance liquid chromatography (HPLC), in which different chiral stationary phases (CSPs), including helical polymeric phases (cellulose and amylase derivative)[4], and Pirkle-type phases were widely used. And cellulose tris (3,5-dimethylphenylcarbamate) (CDMPC) is the most widely used CSP because of its versatility and capability[5]. It has proved to be a valuable chiral selector for discriminating many chiral drugs including amino acid, alcohol, ketone, etc[6–9]. Okamoto et al.[10,11] have reported that it is one of the most useful CSPs. However, the chiral recognition mechanism on these CSPs has not been adequately elucidated due to the presence of multiple chiral and achiral sites in or near the chiral cavity of these CSPs. (*S*,*S*)-Whelk-O 1 [12–14] belongs to donor-acceptor (Pirkle-type) CSP that acts through attractive interactions (π-π, dipole-dipole, and hydrogen bonding) between CSP and analyte. Its chiral recognition mechanism is relatively better understood, and it is possible in many cases to predict analytes which contain aryl group that can be resolved on this CSP[15, 16]. Besides the optical isomer separation of fluazifop reported on Whelk-O 1[17], there is no report in literatures about the chiral separation of other aryloxyphenoxypropionic acid herbicides by HPLC on CSPs. In this article, the enantioseparation of diclofop, fluazifop, quizalofop-P, and fenoxaprop using self-prepared

* Corresponding author. Email: xuxiuzhu@zju.edu.cn

cellulose derivative CDMPC and (*S*,*S*)-Whelk-O 1 columns were investigated. The influence of the mobile phase, including kind and concentration of polar alcoholic modifiers in hexane on the chiral separation was studied. The effects of the molecular formula of compounds on the enantioseparation were investigated. Separation experiments on CDMPC and (*S*,*S*)-Whelk-O 1 were compared, and the different chiral recognition mechanisms on the two different types of CPSs were discussed.

2 Experimental

2.1 Apparatus and chemicals

Chiral separations were performed using a Waters 2690 Separations Module equipped with a Waters 996 Photodiode Array Detector. The chromatographic data were acquired and processed by a Waters Millennium32 System (Waters Co., Milford, MA, USA).

Diclofop, fluazifop, quizalofop-P, and fenoxaprop (Fig. 1) were dissolved in ethanol and filtered through 0.2 m microfilm before injection. Hexane obtained from Hangzhou Refinery (China) was of analytical grade. The alcohols used in the experiment were of analytical grade. *Iso*-propanol was purchased from Ludu Reagent Factory of Shanghai (China). Ethanol and *n*-butanol were purchased from Hangzhou Changzheng Chemical Plant and Shuanglin Chemical Plant (China), respectively. All other reagents were analytical reagents produced in China.

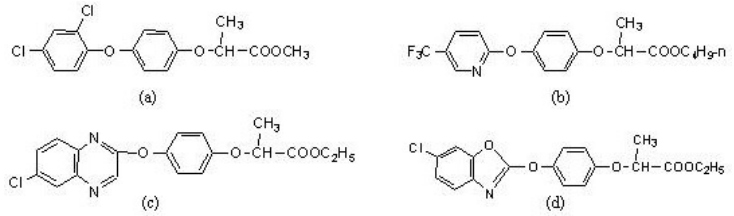

Fig. 1 Structure of diclofop (a), fluazifop (b), quizalofop-P (c), and fenoxaprop (d)

2.2 Chromatography

CDMPC chiral column (20 μm, 300 mm×4.0 mm i.d.) was self-prepared[18]. (*S*,*S*)-Whelk-O 1 chiral column (12 μm, 25×0.4 cm i.d.) was obtained as a gift from Prof. Dr. Kinkel. The structure of the CSPs is shown in Fig. 2. The mobile phase used in this study was hexane modified with alcohols, which were filtered through 0.45μm microfilm and degassed before use. The dead time (t_0) of the column was determined with 1,3,5-tri-*tert*-butylbenzene as a non-retained compound. The chromatographic parameters, retention factor (k'), separation factor (α), and resolution factor (Rs) were calculated automatically by Waters Millennium32 System.

All the experiments were carried out at 25℃. UV detection was performed at the maximum absorption wavelength (λ_{max}) of the solute.

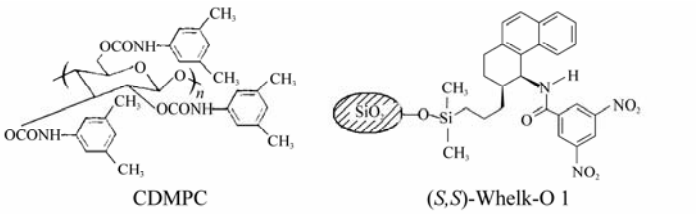

Fig. 2 The structure of chiral stationary phase

3 Results and discussion

3.1 Chiral separation of the solutes on cellulose derivative CDMPC

The enantioseparation of the four aryloxyphenoxypropionic acid herbicides was experimented on cellulose derivative CDMPC with ethanol, *n*-propanol, *iso*-propanol, and *n*-butanol as alcoholic modifier respectively. The influences of alcoholic modifier concentration in hexane are given in Tables 1–4.

Because of the different hydrogen bonding and dipole-dipole interactions of different magnitudes between the electronegative atoms and CSP, and the different π-π interaction between aromatic rings of each optical isomer and CSP, the chiral separation of the compounds occurred. From the data listed in the tables, it suggested that the size of alkoxy group far from the chiral carbon also has influence on