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Simultaneous enantiomeric determinations of acid and ester imidazolinone herbicides in a soil sample by two-dimensional direct chiral liquid chromatography

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ABSTRACT

A two-dimensional HPLC method for the simultaneous direct chiral enantiomeric determination of acid and ester IMI herbicides has been described. Difficulties arising from differences in polarity were overcome. Firstly, the imazaphyr, imazethapyr and imazamethabenz methyl herbicides were separated in a C_{18} achiral column. Then, their respective enantiomers were separated using a protein chiral AGP™ column; a heart-cut mode was used. Mobile phases of the two systems were compatibilized, after optimizing by factorial design using multiple response analysis. The proposed method has been validated by recovery studies from an enriched soil sample. Important enantiomer parameters such as enantioresolution higher than 1.12, enantiomeric ratio (ER) close to 1 and enantiomeric fraction (EF) around 0.5 were obtained for standards, confirming that herbicides are present as racemates.

1. Introduction

At present, about 25% of pesticides are chiral; i.e., they exist as enantiomers. It is known that the chemical properties of enantiomers are alike but they often differ in their toxicity and biological activity [1]; the active enantiomer should have the desired effects on a target species, while the inactive one may have adverse effects on some non-target species. Imazapyr (IM), imazethapyr (IMP) and imazamethabenz-methyl (IMBM) herbicides are chiral members of the imidazolinone family (IMIs), which are used in modern agriculture and are applied both via foliage and through the soil. The imidazolinone structure shows a stereogenic center in the imidazolinone ring, which is a ramified chain amino acid inhibitor [2,3]. The inhibitor power of the R(−)-IMP enantiomer to acetohydroxy acid synthase was found to be 10-fold that of the S(+)-enantiomer [4–6] and their persistence in agricultural soil is high, affecting crop rotations [4,7–9]. Therefore, in order to reduce the amount of herbicides used and prevent unnecessary enantiomer waste, which has an adverse impact, several European countries have suggested that only the active enantiomer should be employed [10,11]; Sweden has implemented a tax on agrochemicals based on the weight of the active ingredient and Netherlands and Switzerland have revoked registration for racemic mixtures of chiral phenoxyalkanoic acids, while approving the registration of single-isomer products; however, few single-enantiomer pesticides are synthesized or produced [12].

Degradation of IMIs in soil depends on this pH; wet and alkaline media allow a significant biological breakdown of IMIs, while dry and acid ones bind them strongly to the soil, limiting their mobility and slowing down their biological degradation; for example, the p-IMBM enantiomers are more stable in the environment than the m-IMBMs and, therefore, they are present in greater proportion [8]. Consequently, there is an urgent need to develop analytical methods to determine the stereoselectivity, bioactivity and environmental behavior of these chiral pesticides [10].

HPLC is one of the most powerful techniques for enantiomer analysis; historically, it has been the standard technique and the first choice for chiral analysis because a wide variety of chiral stationary phases (CSPs) are available. The separation of enantiomers by HPLC using CSPs is based on the formation of transient diastereomeric complexes between the enantiomorphs of the solute and a chiral selector which is an integral part of the stationary phase. The difference in stability between these complexes leads to a difference in retention time; the enantiomer that forms the less stable complex will be eluted first. These

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Table 1
Direct chiral IMI HPLC.

Imidazolinone	Sample	Sample treatment		HPLC system			Observation	Reference
		Extraction	Clean-up	Stationary phase	Mobile phase	Detector		
IMP; IM; IMQ; IMM; IMO	Soil	NaOH 0.5 M two times	Extract at pH 2.8. Eluted: 3 × 60 mL DCM	Chiralcel OJ column (250 × 4.6 mm^2), 10 μm	Hexane (0.1% TFA)-2-PrOH (75:25)	UV–vis λ=254 nm	Enantiomers of IMI methyl derivatives were also resolved on Chiralcel OJ	[6]
IMP; IM; IMQ				Chiralcel OD-R column (250 × 4.6 mm^2), 10 μm	ACN: (50 mM phosphate buffer), 80:20			
IM; IMM; IMP; IMO; IMQ	Standards			Chiralcel OJ column (250 × 4.6 mm^2), 10 μm	Hexane/2-PrOH (85:15, 80:20, 75:25, 70:30, 60:40)	DAD	Satisfactory results at 15–50 °C; below 15 °C should be avoided	[14]
IMP; IM; IMQ	Standards			Chiralpak AS and AD, Chiralcel OD and OJ columns (250 × 4.6 mm^2), 5 μm	Hexane:EtOH/HAc (77:23:0.1)	DAD, CD, LC–MS	The Chiralcel OJ column was found to give the best enantioselectivity for the three IMIs	[15]
IMQ	Water	pH ~2 with HCl 6 M	PPL Sorbents.Eluted: 2 × DCM	Chiralcel OJ column (250 × 4.6 mm^2), 10 μm	n-hexane:2-PrOH:TFA (65:35:0.1)	UV–vis λ=254 nm	LD=0.5 μg/mL Both enantiomers degraded at a similar rate. Enantioselectivity	[16]
IMP	Rice	Phosphate buffer 20 mM, pH 7.4 in ice bath		Chiral OJ column (250 × 4.6 mm^2)	Hexane:EtOH:HAc (75:25:0.5)	CD λ=250 nm	Using R(−)IMP alone would reduce the total IMP usage and relieve the environment	[17]
IMP	Maize			Chiral OJ column (250 × 4.6 mm^2)	Hexane:EtOH:HAc (75:25:0.5)	CD λ=250 nm	R(−)IMP affected the root growth of maize seedlings more severely than S(+)IMP	[18]
IMQ	Soil	NaOH 0.5 M (pH 2.8 with HCl 6 M)	NH_2 + PPL C18 +-SCX sorbents	Chiralcel OJ column (250 × 4.6 mm^2), 10 μm	n-hexane:2-PrOH:TFA (65:35:0.1)	UV–vis λ=240 nm	LD=0.5 μg/mL	[19]
IMP; IM; IMQ	Soil	NaOH 0.5 M (pH ~ 2 with HCl 6 M)	C_{18} +-SCX sorbents. Extract :3 × DCM	Chiracel OJ column	ACN:1% HAc (55:45)	UV–vis λ=254 nm	LD=0.5 μg/mL RL, 0.5–10 μg/mL	[20]
IMBM	Assert 30 formulation	ACN		Protein chiral AGP™ column (100 × 4 mm^2, 5 μm)	ACN:NH_4Ac-HAc 60 mM (3:97) at pH 4.00	UV–vis λ=247 nm	LD < 0.43 μg/mL LQ < 2.17 μg/mL *R* > 93%	[21]
IM; IMP IMQ; IMM IMO	Standards			Chiralcel OJ column (250 × 4.6 mm^2), 10 μm	Hexane/2-PrOH (85:15, 80:20, 75:25, 70:30, 60:40)	UV–vis λ=254 nm	LR between ΔH and ΔS for 15–50 °C	[22]

IM, Imazapyr; IMM, Imazapic; IMP, Imazethapyr; IMO, Imazamox; IMQ, Imazaquin; IMBM, Imazamethabenz-methyl DCM, dichloromethane; PPL, modified styrene divinyl benzene copolymer sorbent; SCX, Benzene sulfonic acid bonded silica sorbent; 2-PrOH, 2-propanol; TFA, trifluoroacetic acid; EtOH, ethanol; DAD, diode array detector; CD, circular dichroism; LC–MS, liquid chromatography-mass spectrometry; LD, detection limit; LQ, quantification limit; R,recovery; LR, linear regression