Chromatographic Resolution of Chiral Pesticides

Andy X. Wang, Heng L. Jin, Thomas E. Beesley
Advanced Separation Technologies Inc. (astec)
37 Leslie Court, P. O. Box 297
Whippany, NJ 07981 USA
Tel: (973) 428-9080 Fax: (973) 428-0152
E-mail: astecusa@aol.com

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Abstract

It is of increasing interest to monitor the chiral purity of pesticides and to study their metabolism. Though chromatographic methods have been successful in the enantioresolution of some chiral pesticides, to resolve many others still remains a challenge. Targeting these special groups of compounds, we have developed some effective chiral GC and HPLC methods. Low to moderate molecular weight pesticides can be resolved by GC with various derivatized cyclodextrin as chiral stationary phases. GC provides convenient and sensitive methods in the analysis of some standard materials and complicated samples, but has limitations for large molecules and large-scale preparation. HPLC is a complementary and often better approach. Some chiral pesticides are able to be resolved by HPLC using currently available macrocyclic glycopeptide (CHIROBIOTIC) or cyclodextrin (CYCLOBOND) chiral stationary phases. The separation conditions (GC & HPLC) will be described for dozens of resolved pesticides.

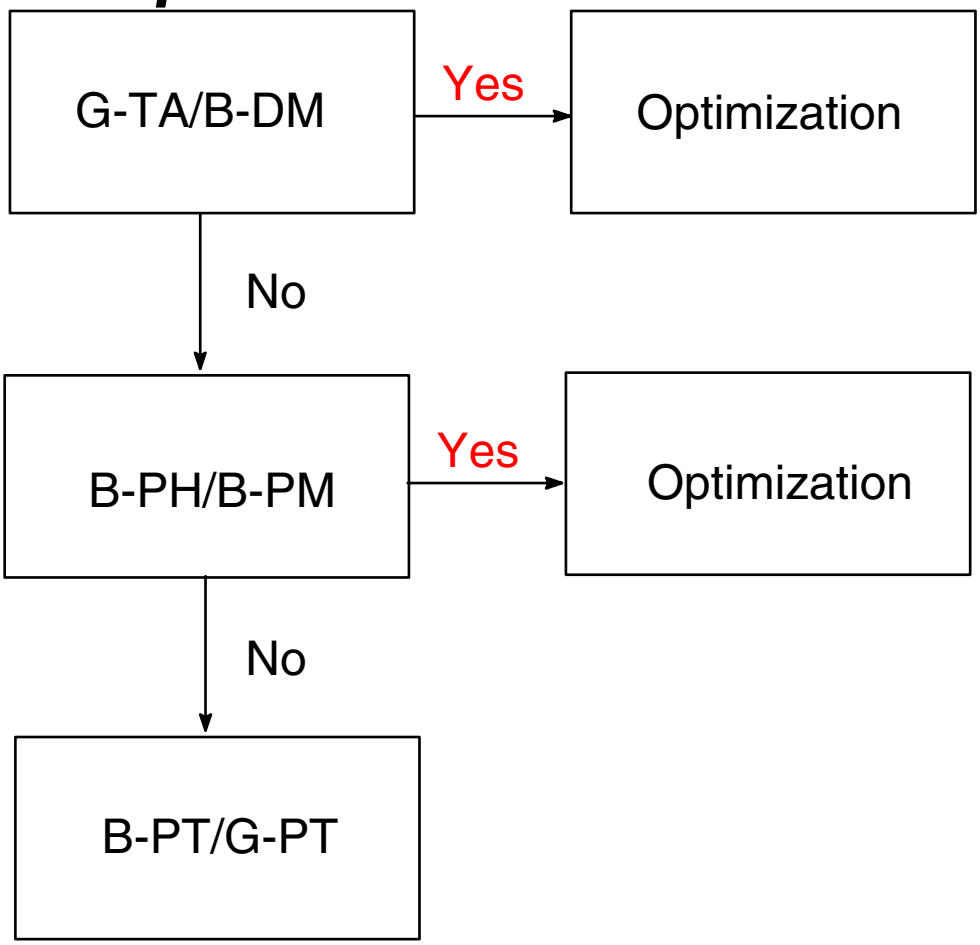
Introduction

Millions of pounds of pesticides are applied to the environment every year. Many of these pesticides are chiral entities. With the increasing awareness of different anti-pest potency, toxicological effects and biodegradation pattern of individual enantiomers, people are increasingly interested in the resolution of racemic pesticides. Chiral HPLC and GC are the dominant technologies to achieve this goal.

Among the chiral pesticides that are resolved by GC methods, over 90% of the separations are achieved on cyclodextrin-based chiral stationary phases. Examples will be given for the separation of pesticides on cyclodextrin derivatized G-TA, B-DM, B-PM, B-PH, B-PT and G-PT phases.

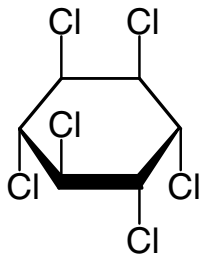
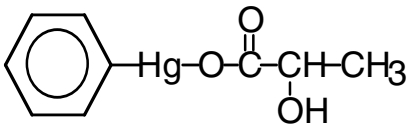
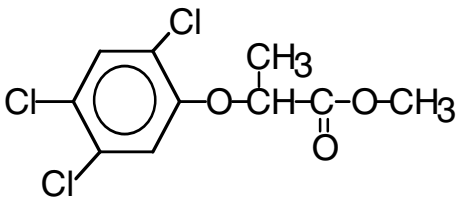
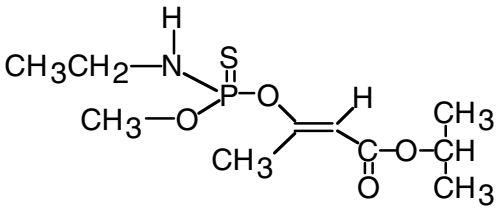
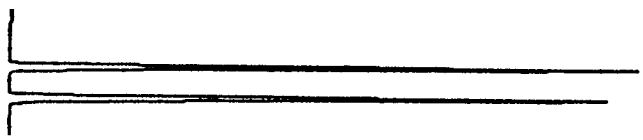
Cyclodextrin based HPLC chiral stationary phases such as CYCLOBOND I 2000 RN, SN, AC and DM can resolve pesticides in the reversed phase and polar organic mode. The more recently developed technique using macrocyclic glycopeptides as chiral stationary phases appears to be more powerful in resolving chiral pesticides. These CSPs such as CHIROBIOTIC V and T can be used in reversed phase and normal phase conditions. The combination of different HPLC methods often provides options in terms of accurate determination of trace amounts of enantiomeric impurity as well as large scale preparations.

GC Method Development Protocol for Pesticides

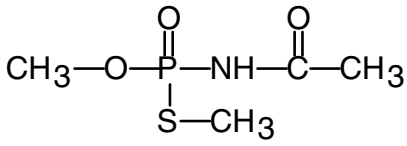
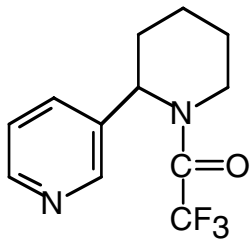
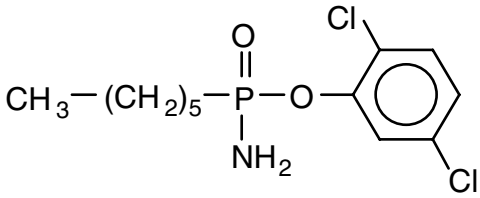
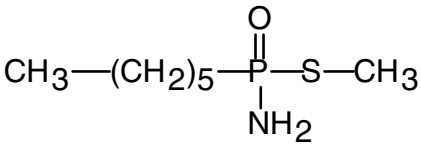


G-TA:	2,6-di-O-pentyl-3-trifluoroacetyl γ-cyclodextrin
B-DM:	di-O-methyl β-cyclodextrin
B-PH:	(S)-2-hydroxypropyl/methyl β-cyclodextrin
B-PM:	2,3,6-tri-O-methyl β-cyclodextrin
B-PT:	Trifluoroacetyl B-PH
G-PT:	Trifluoroacetyl G-PH

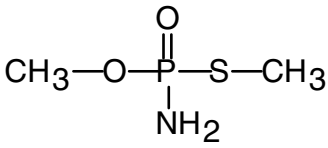
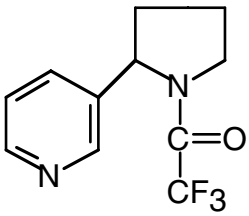
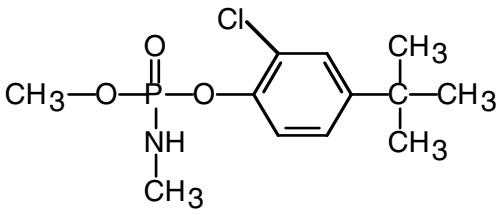
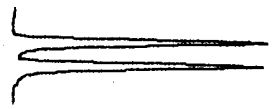
GC Separation of Pesticides on Chiraldex G-TA

Pesticide and Structure	Column Dimension and GC Conditions	Results (k_1, α)
α-HCH 	20m x 0.25mm 150°C	12.5, 1.08
Phenyl mercuric lactate 	20m x 0.25mm 50-90°C	12.4, 1.03
Silvex (methyl ester) 	20m x 0.25mm 145°C	20.1, 1.02
Propetamphos 	30m x 0.25mm 150°C 	24.5, 1.13

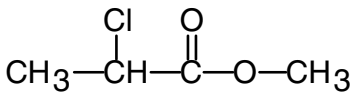
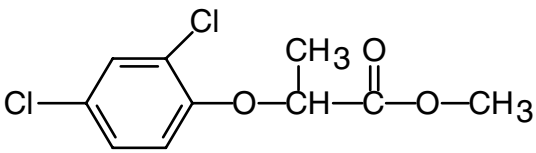
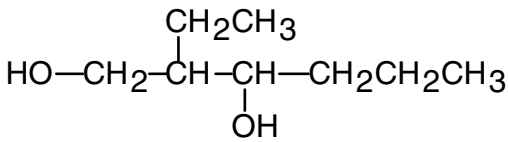
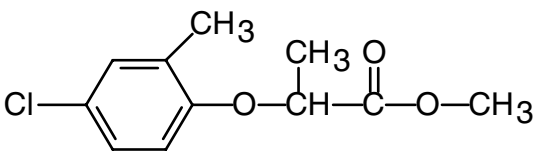
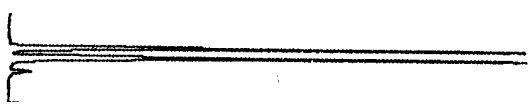
GC Separation of Pesticides on Chiraldex B-DM

Pesticide and Structure	Column Dimension and GC Conditions	Results (k_1, α)
Acephate 	20m x 0.25mm 140°C	22.8, 1.09
Anabasine-TFA 	30m x 0.25mm 50-90°C	19.4, 1.04
HDCP 	30m x 0.25mm 140°C	10.6, 1.09
HSP 	30m x 0.25mm 140°C	10.6, 1.09

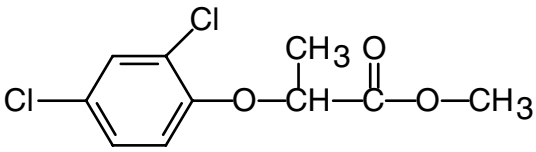
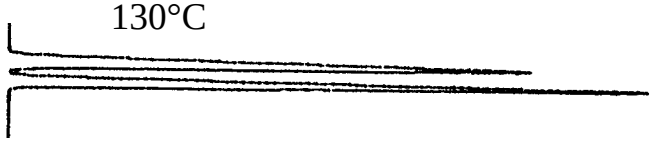
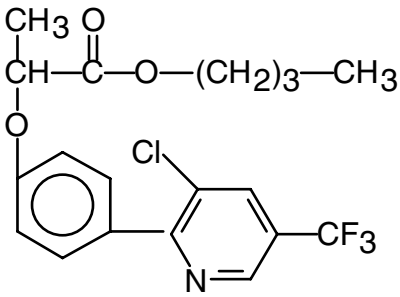
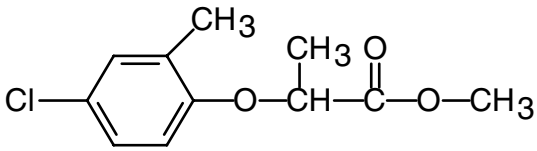
GC Separation of Pesticides on Chiraldex B-DM con't

Pesticide and Structure	Column Dimension and GC Conditions	Results (k_1, α)
Methamidophos 	20m x 0.25mm 140°C 	9.6, 1.08
Nornicotine-TFA 	30m x 0.25mm 145°C	17.6, 1.04
Ruelene 	20m x 0.25mm 160°C 	66.1, 1.05

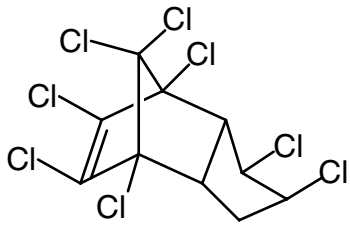
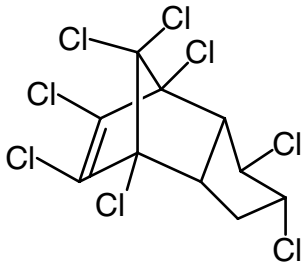
GC Separation of Pesticides on Chiraldex B-PH

Pesticide and Structure	Column Dimension and GC Conditions	Results (k_1, α)
2-Chloropropionic acid methyl ester 	20m x 0.25mm 42°C	6.0, 2.12
Dichlorprop-methyl 	20m x 0.25mm 125°C	21.4, 1.05
Ethohexadiol 	20m x 0.25mm 100-170°C	11.8, 1.02 12.6, 1.02
Mecoprop-methyl 	20m x 0.25mm 115°C 	19.4, 1.06

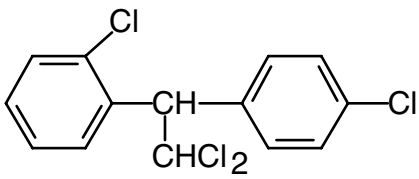
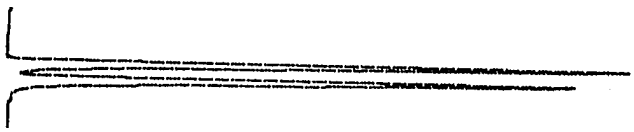
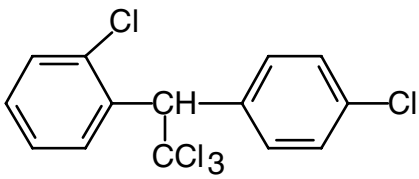
GC Separation of Pesticides on Chiraldex B-PM

Pesticide and Structure	Column Dimension and GC Conditions	Results (k_1, α)
Dichlorprop-methyl 	30m x 0.25mm 130°C 	34.9, 1.04
Fluazifop-butyl 	30m x 0.25mm 165°C	65.2, 1.02
Mecoprop-methyl 	30m x 0.25mm 130°C	22.8, 1.05

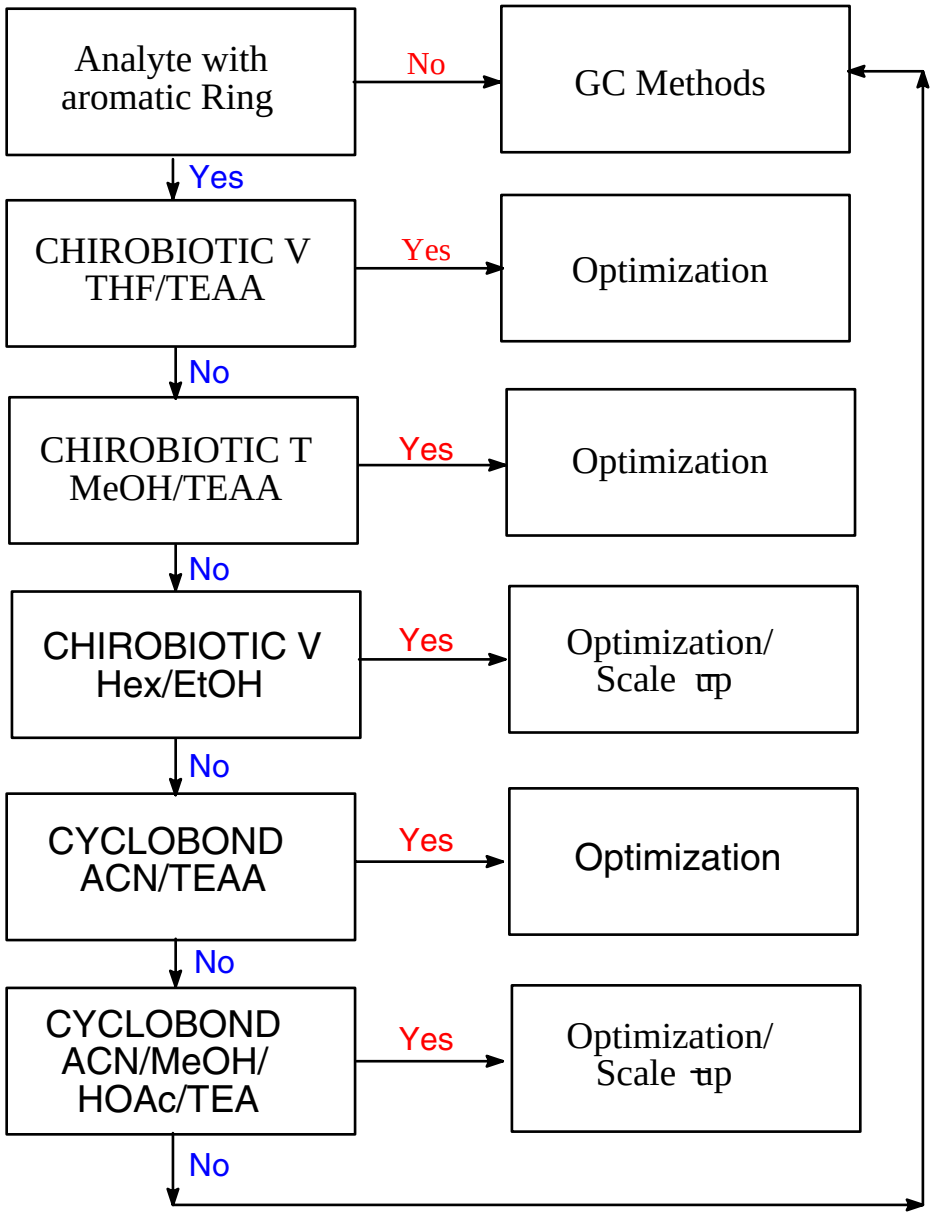
GC Separation of Pesticides on Chiraldex B-PT

Pesticide and Structure	Column Dimension and GC Conditions	Results (k_1, α)
cis-Chlordane 	15m x 0.25mm 165°C	34.6, 1.08
trans-Chlordane 	15m x 0.25mm 150°C	72.7, 1.03

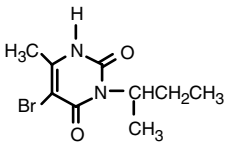
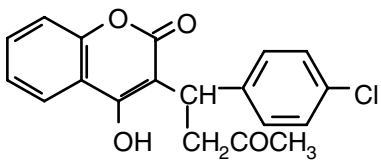
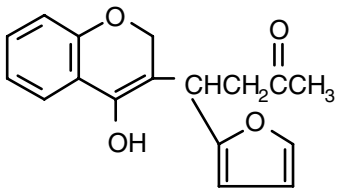
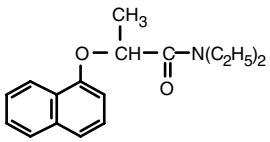
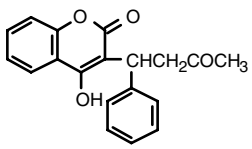
GC Separation of Pesticides on Chiraldex G-PT

Pesticide and Structure	Column Dimension and GC Conditions	Results (k_1, α)
O,P′–DDD 	12m x 0.25mm 165°C 	69.5, 1.07
O,P′–DDT 	12m x 0.25mm 165°C 	62.9, 1.04

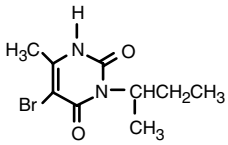
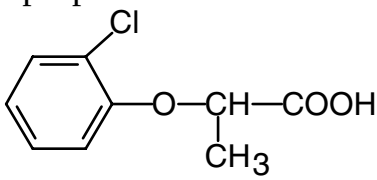
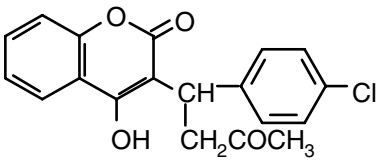
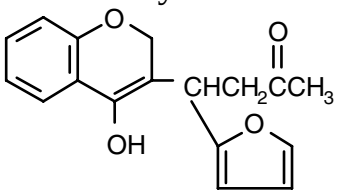
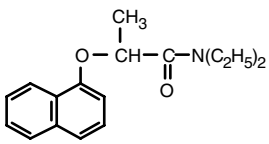
HPLC Method Development Protocol for Pesticides



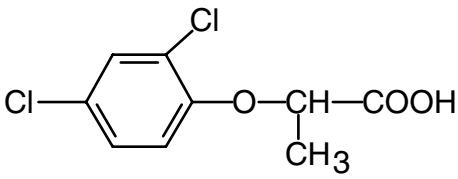
LC Separation of Pesticides on CHIROBIOTIC V in Reversed Phase

Pesticide and Structure	Mobile Phase	Results (k_1, α)
Bromacil 	10/90: THF/20mM NH_4NO_3 pH 5.5	2.44, 1.14
Coumachlor 	25/75: THF/20mM NH_4NO_3 pH 5.5	2.88, 1.21
Coumafuryl 	10/90: THF/20mM NH_4NO_3 pH 5.5	3.45, 1.39
Devrinol 	20/80: THF/0.1% TEAA pH 5.0	2.70, 1.24
Warfarin 	20/80: THF/0.1% TEAA pH 5.0	2.42, 1.30

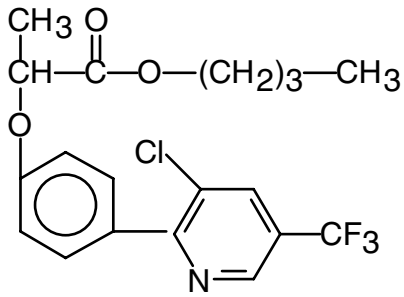
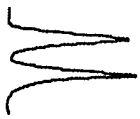
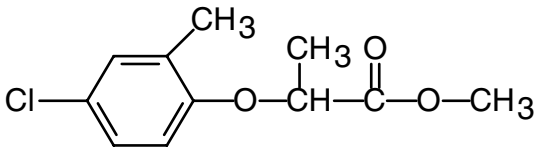
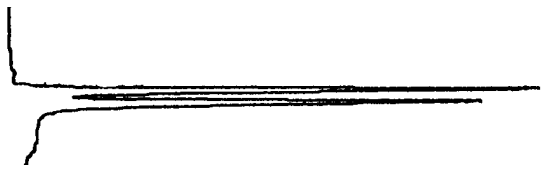
LC Separation of Pesticides on CHIROBIOTIC T in Reversed Phase

Pesticide and Structure	Mobile Phase	Results (k_1, α)
Bromacil 	30/70: EtOH/H_2O	1.29, 1.21
2-(2-Chlorophenoxy) propionic acid 	20/80: MeOH/1% TEAA pH 4.1	1.00, 1.50
Coumachlor 	20/80: MeOH/1% TEAA pH 4.1	7.75, 1.20
Coumafuryl 	20/80: MeOH/1% TEAA pH 4.1	3.02, 1.20
Devrinol 	20/80: MeOH/TEAA pH 4.1	3.34, 1.10

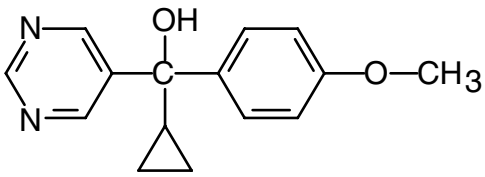
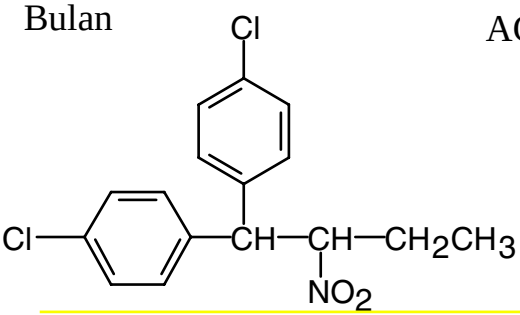
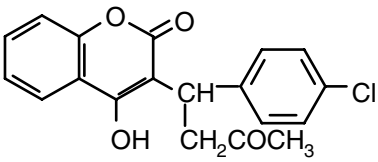
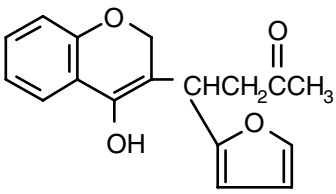
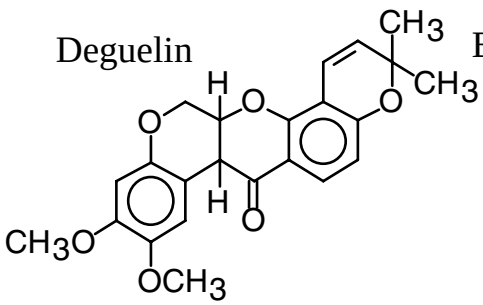
LC Separation of Pesticides on CHIROBIOTIC T in Reversed Phase con't

Pesticide and Structure	**Mobile Phase**	**Results (k_1, α)**
2-(2,4-Dichlorophenoxy) propionic acid 	5/95: MeOH/1% TEAA pH 4.1 	1.59,1.59

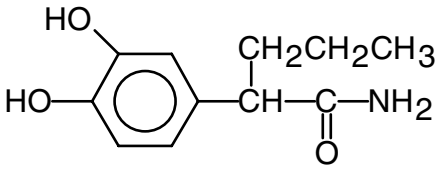
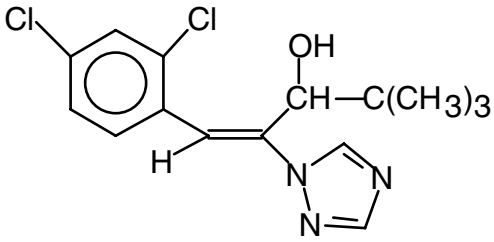
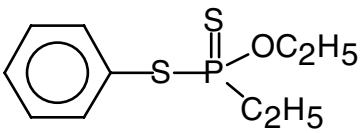
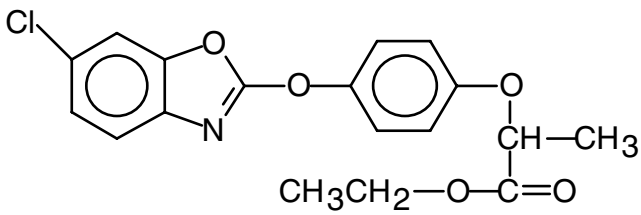
LC Normal Phase Separation of Fluazifop-butyl, Mecoprop-methyl on CHIROBIOTIC V

Pesticide and Structure	Mobile Phase	Results (k_1, α)
Fluazifop-butyl 	100/0.02: Hex/EtOH 	6.08, 1.08
Mecoprop-methyl 	100/0.02: Hex/EtOH 	23.94/1.12

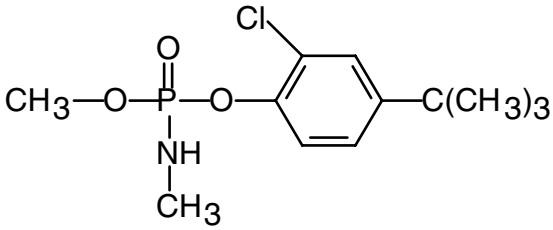
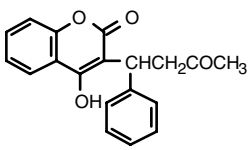
LC Separation of Pesticides on CYCLOBOND in Reversed Phase

Pesticide and Structure	Stationary Phase	Mobile Phase	Results (k_1, α)
Ancymidol 	SP	20/80: ACN/1% TEAA pH 7.1	2.9, 1.16
Bulan 	AC	30/70: ACN/10mM Na_3PO_4 pH 7.0	11.1, 1.09
Coumachlor 	DM	30/70: MeOH/1% TEAA pH 4.1	3.06, 1.37
Coumafuryl 	DM	20/80: MeOH/1% TEAA pH 4.1	3.08, 1.20
Deguelin 	Beta	50/50: MeOH/H_2O	2.39, 1.18

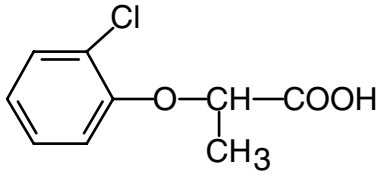
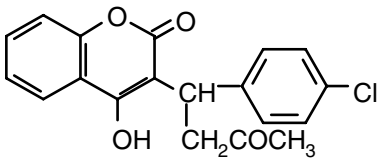
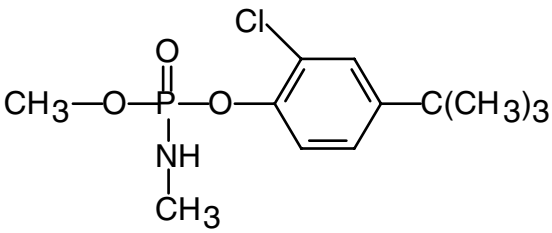
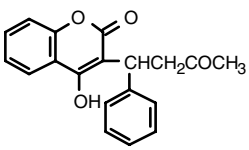
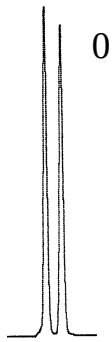
LC Separation of Pesticides on CYCLOBOND in Reversed Phase con't

Pesticide and Structure	Stationary Phase	Mobile Phase	Results (k_1, α)
3,4-Dihydroxyphenyl-α-propyl acetimide 	BetaX2	30/70: MeOH/1% TEAA pH 7.1	0.16, 1.31
Diniconazole 	Beta	80/20: ACN/H_2O	6.47, 1.19
Dyfonate 	RN	80/20: ACN/1% TEAA pH 4.5	12.0, 1.02
Fenoxaprop-ethyl 	DM	20/80: MeOH/1% TEAA pH 7.1	13.1, 1.13

LC Separation of Pesticides on CYCLOBOND in Reversed Phase con't

Pesticide and Structure	Stationary Phase	Mobile Phase	Results (k_1, α)
Ruelene 	RN	30/70: ACN/1% TEAA pH 4.5	7.3, 1.03
Warfarin 	DM	30/70: MeOH/1% TEAA pH 4.1	2.72, 1.58

LC Separation of Pesticides on CYCLOBOND in Polar Organic Mode

Pesticide and Structure	Stationary Phase	Mobile Phase	Results (k_1, α)
2-(2-Chlorophenoxy propionic acid 	RN	95/5/0.6/0.4: ACN/ MeOH/HOAc/TEA	1.00, 1.27
Coumachlor 	RN	98/2/0.8/0.6: ACN/ MeOH/HOAc/TEA	0.46, 1.25
Ruelene 	Beta	90/10/0.02/0.01: ACN/MeOH/HOAc/TEA	0.71, 1.18
Warfarin 	Beta	95/5/0.3/0.2: ACN/MeOH/HOAc/TEA 	0.79, 1.17

Summary

- Chiral GC and HPLC methods appear to be complementary in the resolution of chiral pesticides, though certain pesticides can be resolved by both techniques.
- It depends on the structure of the pesticide whether to choose HPLC or GC method. Considering the attachment such as an aromatic ring, carboxyl, amine, hydroxyl, amide, carbonyl, alkoxyl or alkyl as functional groups, LC methods tend to work well with molecules having three or more such functional groups, and GC methods word well for compounds having fewer functional groups.
- Cyclodextrin based GC chiral stationary phases such as G-TA, B-DM are the best choices for high to medium volatility pesticides. Macrocyclic antibiotics based HPLC CSPs such as CHIROBIOTIC V and T are the most powerful tool in resolving large variety of pesticides, in analytical scale and preparative scale alike. CYCLOBOND phases also provide broad options in the resolution of chiral pesticides.