nate food sources of the boll weevil in a tropical environment. When components are found that may correlate with either the physiological state of the insect or its food source, efforts would be needed to make chemical identification of such markers.

Registry No. Triolein, 122-32-7; oleic acid, 112-80-1; cholesterol, 57-88-5; cholesterol oleate, 303-43-5.

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Behavior of Pyrethroid Insecticides under Liquid–Solid Chromatographic Conditions

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A series of pyrethroid insecticides and associated carbonyl compounds was chromatographed. A high-performance liquid chromatographic system equipped with an infrared detector was used with a 5-μm silica gel column that was eluted with either a ternary solvent mixture composed of acetonitrile, dichloromethane, and heptane or a binary mobile-phase system composed of 1-tetradecene in dichloromethane. The logarithm of the capacity factor (k') was found to be linearly correlated with the logarithm of the mole fraction (N_b) of acetonitrile or 1-tetradecene in the respective mobile phase. The slope and y-intercept values of the graphs obtained from log k' vs. log N_b were discussed in terms of the molecular structure and the biological activity of the investigated compounds.

Basically, two physical models have been proposed for the mechanism of retention in liquid–solid chromatography (LSC). They are the competitive displacement model (model I) formulated by Snyder (1968, 1974), Soczewinski (1969, 1977), and Soczewinski and Golkiewicz (1973) and the solvent interaction or sorption model (model II) proposed by Scott (1976) and Scott and Kucera (1975, 1978). Snyder (1974) and Snyder and Poppe (1980) compared the two models and provided a critical and comprehensive evaluation of their respective advantages and limitations.

Practical applications of these models in LSC are the planning of adequate separation procedures for the analysis of certain component mixtures, the prediction of retention data, and the formulation of quantitative structure–retention relationships that can be used in identifying the different components of the chromatographed samples. An attempt will be made in the present investigation to use the LSC structure–retention relationship data in structure–bioactivity relationship studies of a major class of synthetic insecticides, the pyrethroids. The pyrethroid insecticides are generally divided into two major categories, the "knockdown" and the "killing" agents. It has been reported (Briggs et al., 1974) that the important property that determines whether a particular pyrethroid will have

good knockdown or killing activity is the overall polarity of the pyrethroid molecule and that the optimum polarity for knockdown effect is greater than the polarity required for killing action. The explanation for the difference in polarity requirements between knockdown and killing activities was based on the assumption that the knockdown effect depends on relatively rapid penetration of the pyrethroid through the insect cuticle and into the hemolymph and hence faster arrival at the site of action, the central nervous system. It has also been suggested (Briggs et al., 1976) that both rate of penetration and susceptibility of the compound to detoxification depend upon the polarity of the pyrethroid molecule. However, no evidence was reported to show that knockdown agents penetrate faster or that they are detoxified faster. Partition coefficient values determined between nitromethane and petroleum ether for a series of pyrethroid compounds gave essentially no correlation to the knockdown index obtained with *Musca domestica* (Lee, 1976). Also, partition coefficient values of different pyrethroids estimated by using reversed-phase thin-layer chromatography showed no correlation with bioactivities, whereas the size, shape, and electronic effects of the pyrethroid molecules gave good correlations with bioactivities. From structure–activity relationship studies of two congeneric series of pyrethroids by using multiple regression analysis of bioactivity vs. substituent constants (Hansch's π values and Hammett's σ constants), different optimum π values were indicated for knockdown and killing toxicity (Ford, 1979). However, it was suggested that the difference in polarity require-

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ments between knockdown vs. killing agents is attributed to variations in the binding affinity of the pyrethroid molecules at the site of action. It was assumed that knockdown agents bind for a shorter time at the site of action compared to killing agents. If comparable complexes between pyrethroids–biological substrates and pyrethroids–stationary phase are assumed, then the derived chromatographic data under LSC could be indicative of the kind of interactions, the mechanism of adsorption, and the configurational arrangements of the pyrethroid molecules on the surface of a biological substrate.

EXPERIMENTAL SECTION

Materials. Analytical standards of d-trans-allethrin, cypermethrin, fenvalerate, cis- and trans-permethrin, trans-resmethrin, d-phenothrin, decamethrin, ethyl chrysanthemate, and cycloprate and technical-grade materials of tetramethrin and MGK-264 were donated by the manufacturing companies. Analytical standards of cis- and trans-cypermethrin and a sample of pyrethrum extract were provided by Dr. J. E. Casida of the University of California, Berkeley. Kadethrin and cismethrin were provided by Dr. G. Georghiou of the University of California, Riverside. Emulsifiable concentrate formulations of tralomethrin, AC-222,705 (Pay-Off), and fluvalinate were donated by colleagues at the University of California, Riverside.

Standards of pyrethrin I and II were obtained by fractionating a sample of pyrethrum extract by high-performance liquid chromatography (HPLC). The fractions corresponding to the two major peaks were collected and identified as pyrethrin I and pyrethrin II by proton magnetic resonance (¹H NMR) (Bramwell et al., 1969) and infrared (IR) (Chang, 1961; Elliott, 1961) spectroscopies. The cis and trans isomers of tetramethrin and d-phenothrin were also obtained by HPLC by fractionating the technical-grade materials. Fractions corresponding to the two major peaks given by both tetramethrin and d-phenothrin were collected and tentatively identified as the cis and trans isomers by examining their ¹H NMR spectra.

Solvents that were distilled in glass were purchased from Burdick and Jackson Laboratories, Inc. 1-Tetradecene was purchased from Aldrich Chemical Co., Inc.

Instrumentation. The liquid chromatographic system consisted of a single Waters Associates Model 6000A pump, a 25 cm × 4.6 mm i.d. Whatman column with 5-μm Partisil, a Rheodyne 7125 valve-type injector equipped with a 20-μL loop, and a Wilks/Foxboro Miran-1A variable-wavelength IR detector. The IR detector, which was operated at 5.75 μm, was equipped with a 4.5-μL barium fluoride cell and was connected to a Linear recorder operated at a chart speed of 1 cm/min.

Determination of p Values. Beroza's p values in the 1:1 hexane–acetonitrile, binary solvent system were determined according to the procedure described by Beroza and Bowman (1965). The equivolume hexane–acetonitrile mixture was shaken and allowed to stand overnight at ambient temperature. Approximately 20 mg of each compound was dissolved in 4 mL of the upper phase (hexane saturated with acetonitrile) to produce a solution A. Kadethrin was dissolved into 20 mL of the upper phase due to its low solubility. The fluvalinate formulation was diluted to 5% (v/v) with the upper phase. From each solution A, a 2-mL aliquot was transferred to a 10-mL glass-stoppered centrifuge tube containing 2 mL of the lower phase (acetonitrile saturated with hexane); the tubes were shaken for 1 min, and the upper phases were separated and transferred into other containers (solutions B). Samples of solutions A and B were analyzed by HPLC.

The mobile phase consisted of 1% acetonitrile, 49% dichloromethane, and 50% heptane (v/v/v). Tetramethrin, kadethrin, allethrin, and the pyrethrins were analyzed with a mobile phase that consisted of 5% acetonitrile, 45% dichloromethane, and 50% heptane (v/v/v). The p value for a particular compound is the ratio of the peak height (or area) obtained from the analysis of the solution B divided by the respective peak height (or area) given by solution A. The determination of p values was repeated twice.

Determination of Retention Volumes and Capacity Factors. Hexane solutions of the different pyrethroids and associated compounds at concentrations ranging from 1 to 2 mg/mL were used for the determination of retention volumes under LSC conditions by using a silica gel column eluted with acetonitrile–dichloromethane–heptane (A–D–H) and 1-tetradecene–dichloromethane (T–D) mobile phases. Fluvalinate and AC-222,705 formulations were diluted to 5% (v/v) with hexane, and the tralomethrin formulation was diluted to 10% (v/v) with hexane. Mobile-phase mixtures of A–D–H at seven different proportions, 0.5–49.5–50 (I), 1–49–50 (II), 1.5–48.5–50 (III), 2–48–50 (IV), 3–47–50 (V), 4–46–50 (VI), and 5–45–50 (VII) (v/v/v), and T–D mixtures at five different proportions, 1–99, 5–95, 10–90, 20–80, and 30–70 (v/v), were used.

The retention times were determined by injecting 20 μL of standard solutions or formulation dilutions onto the HPLC system. The capacity factors (k') were calculated by using the equation $k' = (V_r - V_m)/V_m$, where V_r (mL) is the measured retention volume [V_r = retention time (t_R) × flow rate (mL/min)] and V_m (mL) is the column void volume. The value of V_m was found to be in the range of 3.24–3.36 mL and was obtained by measuring the retention volume of hexane, a nonretained compound. The V_r of hexane was determined along with the V_r of each chromatographed compound to avoid errors associated with differential flow rates during long operations of the system. By use of the T–D mobile phase systems and a flow rate of 0.7 mL/min, all the compounds were eluted from the silica gel column except for tetramethrin, allethrin, kadethrin, pyrethrins, and MGK-264. Since the presence of a more polar modifier in the mobile phase was required for the elution of these compounds, they were omitted from this section of the study.

RESULTS AND DISCUSSION

Theoretical Considerations. Both model I and model II proposed for the mechanism of retention in LSC (Snyder, 1974) assume that the adsorbent surface is completely covered by adsorbed solute and/or solvent molecules. The displacement model (model I) assumes that there is a competition between the solute and solvent molecules in occupying the active sites on the surface of the adsorbent, and therefore, the adsorption of a solute results in the displacement of n molecules of adsorbed solvent. The following equation was derived by Snyder (1974) for binary mobile phases:

$$\log k'_2 = \log k'_1 - (A_s/n_b) \log N_b = \text{constant} - n \log N_b$$

A_s and n_b are the adjusted solute and stronger solvent molecular areas, respectively, k'_2 is the capacity factor of the solute eluted with the binary mobile phase, k'_1 is the capacity factor of the same solute eluted with just the stronger solvent, and N_b is the mole fraction of the stronger solvent in the binary mobile phase. Snyder (1968) proposed a flatwise adsorption for all molecules and that interactions involving solute–solvent molecules in the liquid phase are canceled by similar interactions in the adsorbed phase. Soczewinski (1969) reported that the

Table I. Chemical Names of the Investigated Compounds

compound	chemical name
	Non-Halogen-Containing Pyrethroids
d-trans-allethrin	(dl)-2-methyl-4-oxo-3-(2-propenyl)-2-cyclopent-1-yl d-trans-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
cismethrin	5-(phenylmethyl)-3-furyl (1R)-cis-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
kadethrin	5-benzyl-3-furylmethyl [1R,cis(E)]-2,2-dimethyl-3-[(2-oxo-3-thiocyclopentylidene)methyl]-1-cyclopropanecarboxylate
d-phenothrin	(3-phenoxyphenyl)methyl (1R)-2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
pyrethrin I	2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
pyrethrin II	2-methyl-4-oxo-3-(2,4-pentadienyl)-2-cyclopenten-1-yl 3-(3-methoxy-2-methyl-3-oxo-1-propenyl)-2,2-dimethylcyclopropanecarboxylate
resmethrin	5-(phenylmethyl)-3-furyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
tetramethrin	(1,3,4,5,6,7-hexahydro-1,3-dioxo-2H-isoindol-2-yl)methyl 2,2-dimethyl-3-(2-methyl-propenyl)cyclopropanecarboxylate
	Halogen-Containing Pyrethroids
cypermethrin	cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
decamethrin	[1R-[1(S*),3]]-cyano(3-phenoxyphenyl)methyl 3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate
fenvalerate	cyano(3-phenoxyphenyl)methyl 4-chloro-(1-methylethyl)benzeneacetate
fluvalinate	α-cyano(3-phenoxyphenyl)methyl 2-[2-chloro-4-(trifluoromethyl)anilino]-3-methylbutanoate
AC-222,705	(RS)-α-cyano(3-phenoxyphenyl)methyl (S)-2-[4-(difluoromethoxy)phenyl]-3-methylbutyrate
permethrin	(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate
tralomethrin	(S)-α-cyano-3-phenoxybenzyl cis-(1R,3R,1'R or S)-3-(1,2-dibromo-2,2-dibromoethyl)-2,2-dimethylcyclopropanecarboxylate
	Other Compounds
cycloprate	hexadecyl cyclopropanecarboxylate
ethyl chrysanthemate	ethyl 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxylate
MGK-264	N-(2-ethylbenzyl)bicyclo[2.2.1]-5-heptene-2,3-dicarboximide

slopes of log k' vs. log N_b plots will be equal to the number of strongly adsorbing substituent groups in the solute molecule. Thus, for small monofunctional solute molecules, unit slope values should be obtained; larger slope values might indicate multipoint adsorption of solutes or that the size and shape of the solute molecules require the displacement from the surface of the adsorbent of more than one solvent molecule or that solute molecules are solvated in the mobile phase (Soczewinski, 1977; Soczewinski and Golkiewicz, 1973).

In model II, the solvent interaction or sorption model, it is assumed that when the adsorbent surface is completely covered by the stronger solvent of a binary mobile phase (ca. $N_b > 0.02$), the retention is mainly determined by solute–solvent interactions in the mobile phase. Scott (1976) showed that at complete coverage of the surface of the adsorbent, a linear relationship exists between $1/V$ and the percentage of the stronger solvent component in the eluant. V is the solute-corrected retention volume. Soczewinski (1977) showed that model II is a special case of the more general relationship; linear relationships of $1/k'$ vs. concentration of the stronger solvent component of a binary mobile phase are observed for displacement from the adsorption sites in a 1:1 ratio or in cases that the solute and solvent molecules occupy equal areas on the adsorbent surface.

p Values. The chemical nomenclature of the compounds used in this study is given in Table I. The pyrethroid insecticides have been divided into two groups: (a) non-halogen-containing pyrethroids and (b) halogen-containing pyrethroids. All the investigated pyrethroids are esters of cyclopropanecarboxylic acid, except for fenvalerate, fluvalinate, and AC-222,705. The measured p values in the binary system of acetonitrile–hexane and a series of relative retention volumes are given in Table II.

Since extraction p values from the binary system hexane–acetonitrile denote the fraction of solutes partitioned into hexane, p values should be related to the lipophilicity of solutes. In Table II, the different compounds have been arranged in descending order of magnitude of p values.

Table II. Extraction p Values Determined by a Single Distribution in an Equal-Volume System of Acetonitrile–Hexane and a Series of HPLC Retention Volumes (V_r) of the Investigated Compounds

compound	p value	V_r^a
cycloprate	0.97	4.9
trans-ethyl chrysanthemate	0.66	5.4
cis-ethyl chrysanthemate	0.60	4.9
trans-phenothrin	0.52	4.8
cis-phenothrin	0.40	4.5
trans-resmethrin	0.40	5.2
cis-permethrin	0.39	4.1
d-trans-allethrin	0.31	57.6
MGK-264 I[b]	0.31	14.5
trans-permethrin	0.29	4.8
cis-resmethrin	0.28	4.8
MGK-264 II[b]	0.27	30.0
pyrethrin I	0.24	35.3
cis-cypermethrin	0.11	5.0
fenvalerate	0.11	5.5
decamethrin	0.10	5.1
fluvalinate	0.10	5.0
trans-tetramethrin	0.09	28.4
trans-cypermethrin	0.08	5.6
pyrethrin II	0.07	40.5[c]
cis-tetramethrin	0.06	24.2
kadethrin	<0.001	52.0

[a] The mobile phase was 1% acetonitrile, 49% dichloromethane, and 50% heptane (v/v/v). [b] MGK-264 I and MGK-264 II refer to endo and exo isomers of MGK-264. However, individual standards were unavailable for the assignment of the respective peaks. [c] Pyrethrin II was eluted with a 2% acetonitrile, 48% dichloromethane, and 50% heptane (v/v/v) mobile phase.

Judging from the recorded p values, for the non-halogen-containing pyrethroids, the trans isomer appears to be more lipophilic that its respective cis counterpart. This is expected from the fact that cis isomers have higher dipole moments and hence should be less lipophilic than their respective trans counterparts. However, for the halogen-containing pyrethroids (permethrin and cypermethrin), the cis isomer is more lipophilic that its respective trans counterpart. However, regardless of the

Table III. Experimentally Determined k' Values of Different Compounds Chromatographed on a 5-μm Silica Gel Column Eluted with Acetonitrile–Dichloromethane–Heptane Mobile Phases

mobile phase: N_b of acetonitrile:	I 0.0085	II 0.0170	III 0.0255	IV 0.0339	V 0.0507	VI 0.0674	VII 0.084
kadethrin		14.5	3.93	2.72	1.53	1.20	0.86
pyrethrin II			11.3	6.36	4.16	2.50	
d-trans-allethrin		16.1	6.04	4.15	2.41	1.75	1.14
trans-tetramethrin		7.44	2.96	2.09	1.15	0.87	0.55
cis-tetramethrin	13.3	6.19	2.39	1.70	0.94	0.72	0.42
pyrethrin I			5.52	3.23	2.05	1.45	0.96
trans-resmethrin	0.89	0.54	0.34	0.23	0.15	0.13	0.09
cismethrin	0.75	0.44	0.28	0.22	0.15	0.11	0.08
trans-phenothrin	0.75	0.42	0.25	0.19	0.15	0.11	0.09
cis-phenothrin	0.61	0.34		0.19	0.15	0.11	0.09
trans-cypermethrin	1.07	0.67	0.40	0.34	0.23	0.22	0.18
trans-permethrin	0.64	0.38	0.26	0.21	0.15	0.13	0.11
fenvalerate	1.04	0.63	0.38	0.32	0.23	0.21	0.18
cis-permethrin	0.36	0.22	0.15	0.11	0.09		0.07
AC-222,705 II[a]	1.46		0.57	0.47	0.34		0.29
AC-222,705 I[a]	1.53		0.57	0.47	0.34		0.29
tralomethrin II[a]	0.96		0.43	0.32	0.19		0.18
fluvalinate	0.89	0.54	0.38	0.31	0.23	0.21	0.16
decamethrin	0.82	0.54	0.32	0.30	0.22	0.20	0.18
cis-cypermethrin	0.75	0.50	0.32	0.26	0.21	0.20	0.18
tralomethrin I[a]	0.68		0.32	0.26	0.19		0.18
cis-ethyl chrysanthemate	0.79	0.46	0.31	0.23	0.15	0.14	0.14
trans-ethyl chrysanthemate	1.04	0.60	0.40	0.32	0.19	0.17	0.14
cycloprate	0.86	0.49	0.29	0.23	0.15	0.10	0.06
MGK-264 I[a]	0.86	0.49	0.29	0.23	0.15	0.10	0.06
MGK-264 II[a]			2.11	1.46	1.00	0.80	0.59

[a] I and II refer to the two diastereomers of AC-222,705 and tralomethrin and the exo and endo isomers of MGK-264. Isomer I is eluted before isomer II.

difference in lipophilicity between the cis and trans isomers of non-halogen- and halogen-containing pyrethroids, all the trans isomers of the examined pyrethroids are retained longer on the silica gel column that the respective cis counterpart. This is indicated by the retention volumes reported in Table II. There is no correlation between retention volumes and p values. The overall correlation coefficient from the linear regression analysis of p values vs. retention volumes was found to be –0.19. For the non-halogen- and halogen-containing pyrethroid subsets, the respective coefficients were –0.44 and –0.87.

Acetonitrile–Dichloromethane–Hexane Mobile-Phase Systems. The capacity factors of the investigated compounds eluted with the A–D–H systems are given in Table III. The slope, y-intercept, and linear correlation coefficient (r) values obtained by least-squares analysis of the log k' vs. log N_b plots are given in Table IV. N_b is the mole fraction of acetonitrile in 100 mL of the respective A–D–H mobile phase.

The different pyrethroid insecticides have been arranged in Table IV in ascending order of absolute slope values. The non-halogen-containing pyrethroids have absolute slope values ranging from 0.58 to 1.21. The halogen-containing pyrethroids have absolute slopes values ranging from 1.24 to 1.58. There is no clear demarcation in slope values between the two groups of pyrethroids. Kadethrin, pyrethrin II, d-trans-allethrin, trans- and cis-tetramethrin, and pyrethrin I have the smallest absolute slope values; they ranged from 0.58 to 0.71. As a consequence of model I, small slope values of solutes denote small surface areas of interaction with the adsorbent, and solutes probably take a vertical orientation on the silica gel surface. According to Soczewinski (1977), vertical orientation implies stronger interactions between solutes and the free silanol groups of the silica gel and the displacement of minimal number of solvent molecules from the adsorbent surface. The same conclusion with regard the strength of interaction of the different pyrethroids with the silica adsorbent will be made later by examining the magnitude of the

Table IV. Slope, y-Intercept, and Correlation Coefficient (r) Values of the Investigated Compounds from Plots of log k' vs. log N_b, where N_b is the Mole Fraction of Acetonitrile in Acetonitrile–Dichloromethane–Heptane Mobile Phases

compound	slope	y intercept	r
kadethrin	–0.58	–1.17	–0.972
pyrethrin II	–0.61	–0.82	–0.994
d-trans-allethrin	–0.63	–1.05	–0.991
trans-tetramethrin	–0.64	–1.25	–0.993
cis-tetramethrin	–0.66	–1.31	–0.995
pyrethrin I	–0.71	–1.08	–0.995
trans-resmethrin	–0.97	–2.07	–0.995
cismethrin	–1.01	–2.17	–0.991
trans-phenothrin	–1.07	–2.21	–0.997
cis-phenothrin	–1.21	–2.33	–0.999
trans-cypermethrin	–1.24	–2.03	–0.994
trans-permethrin	–1.27	–2.32	–0.997
fenvalerate	–1.27	–2.06	–0.993
cis-permethrin	–1.30	–2.66	–0.989
AC-222,705 II[a]	–1.30	–1.86	–0.989
AC-222,705 I[a]	–1.34	–1.88	–0.990
tralomethrin II[a]	–1.36	–2.10	–0.998
fluvalinate	–1.37	–2.15	–0.997
decamethrin	–1.43	–2.20	–0.988
cis-cypermethrin	–1.49	–2.27	–0.985
tralomethrin I[a]	–1.58	–2.36	–0.981
cis-ethyl chrysanthemate	–1.19	–2.19	–0.989
trans-ethyl chrysanthemate	–1.09	–2.03	–0.998
cycloprate	–0.88	–2.07	–0.991
MGK-264 I[a]	–0.97	–1.29	–0.997
MGK-264 II[a]	–0.91	–0.97	–0.994

[a] I and II refer to the two diastereomers of AC-222,705 and tralomethrin and the exo and endo isomers of MGK-264. Isomer I is eluted before isomer II.

y-intercept values given by the log k' vs. log N_b plots. The near-unity slope values of d-cis- and d-trans-phenothrin, cis- and trans-resmethrin, cis- and trans-ethyl chrysanthemate, cycloprate, and MGK-264 isomers suggest a single-point attachment with the silica stationary phase for these compounds and 1:1 solute–solvent displacement, while slope values of compounds being markedly higher

Table V. Experimentally Determined k' Values of Different Compounds on a 5-μm Silica Gel Column Eluted with 1-Tetradecene–Dichloromethane Mobile Phases

mobile phase: N_b of 1-tetradecene:	I 0.0025	II 0.0131	III 0.0273	IV 0.0594	V 0.0976
cis-phenothrin	0.53	0.58	0.61	0.82	1.06
trans-phenothrin	0.67	0.73	0.79	1.03	1.33
cismethrin	0.61	0.64	0.67	0.97	1.18
trans-resmethrin	0.76	0.79	0.88	1.09	1.49
tralomethrin I[a]	0.23	0.30	0.36	0.52	0.73
cis-cypermethrin	0.37	0.42	0.49	0.70	0.97
decamethrin	0.36	0.39	0.52	0.70	1.00
cis-permethrin	0.20	0.21	0.30	0.36	0.49
tralomethrin II[a]	0.34	0.42	0.55	0.73	1.12
trans-permethrin	0.38	0.42	0.49	0.64	0.85
trans-cypermethrin	0.54	0.61	0.70	1.00	1.42
fluvalinate	0.33	0.36	0.46	0.61	0.88
AC-222,705	0.59	0.70	0.85	1.21	1.79
fenvalerate	0.50	0.55	0.67	0.91	1.33
cis-ethyl chrysanthemate	0.94	0.94	1.06	1.18	1.42
trans-ethyl chrysanthemate	1.24	1.24	1.40	1.55	1.88
cycloprate	1.06	1.06	1.18	1.30	1.55

[a] Tralomethrins I and II refer to the two diastereomers of tralomethrin. Isomer I is eluted before isomer II.

than unity (halogen-containing pyrethroids) suggest larger surface areas of interaction of solutes with the stationary phase (flat orientation) or multipoint attachment of solutes with the stationary phase (Soczewinski, 1977; Soczewinski and Golkiewicz, 1973).

From the y-intercept values presented in Table IV, the following observations can be made: (1) The first six pyrethroids on the list have the highest y-intercept values. The strength of interaction of these compounds with the silica ranges from 25 to 75 times higher compared to cis-permethrin. These compounds (kadethrin, pyrethrin II, d-trans-allethrin, trans- and cis-tetramethrin, and pyrethrin I) are also the ones that have the smallest values of adjusted surface of interaction with the silica. This suggests that multiple hydrogen bonding is occurring with the free silanol groups of the silica, and the solute molecules take the vertical orientation on the silica surface. These same compounds, however, are also the well-known knockdown agents among the established pyrethroid insecticides. According to the information provided in Table IV, knockdown agents interact stronger but occupy smaller surface areas of the adsorbent, while the pyrethroids with killing activity (the remaining pyrethroid compounds listed in Table IV) form weaker complexes with the adsorbent but occupy larger areas on the adsorbent surface. (2) The y-intercept values of trans isomers are higher than the respective values of cis isomers. Cis isomers have higher dipole moments and therefore are more hydrophilic than the respective trans counterparts, and one would expect to find cis isomers interacting more strongly with other polar groups than their respective trans counterparts. Probably, steric hindrance forces from the cis substituents of the cyclopropane ring weaken the strength of interaction with the adsorbent of the carbonyl group of the pyrethroid ester. (3) With the exception of the first six pyrethroids, all the other compounds have y-intercept values ranging from −1.86 to −2.66.

1-Tetradecene–Dichloromethane Mobile-Phase Systems. The chromatographed compounds with the T–D mobile phases and their respective capacity factors are given in Table V. The slope, y-intercept, and linear correlation coefficient values (r) obtained from the least-square analysis of plots of log k' vs. log N_b are given in Table VI. N_b is the mole fraction of 1-tetradecene in the respective mobile phases. The slope values reported in Table VI are exceptionally high for all the investigated compounds. Compounds with the smallest molecular weights, e.g., ethyl chrysanthemate isomers and cycloprate,

Table VI. Slope, y-Intercept, and Correlation Coefficient (r) Values from Plots of log k' vs. log N_b, where N_b is the Mole Fraction of 1-Tetradecene in 1-Tetradecene–Dichloromethane Mobile Phases

compound	slope	y intercept	r
cismethrin	4.16	−1.22	0.857
cis-phenothrin	4.35	−0.97	0.897
trans-resmethrin	4.45	−1.58	0.863
trans-phenothrin	4.51	−1.41	0.883
tralomethrin II[a]	2.90	−0.97	0.936
AC-222,705	2.96	−1.58	0.921
tralomethrin I[a]	3.03	−0.43	0.955
decamethrin	3.12	−0.85	0.909
fenvalerate	3.20	−1.24	0.896
trans-cypermethrin	3.24	−1.34	0.895
fluvalinate	3.27	−0.65	0.904
cis-cypermethrin	3.32	−0.80	0.907
cis-permethrin	3.57	0.23	0.924
trans-permethrin	4.03	−0.55	0.909
cis-ethyl chrysanthemate	7.10	−1.94	0.865
trans-ethyl chrysanthemate	7.12	−2.79	0.866
cycloprate	7.86	−2.33	0.868

[a] Tralomethrins I and II refer to the two diastereomers of tralomethrin. Isomer I is eluted before isomer II.

have the highest slope and the smallest y-intercept values. One of the isomers of tralomethrin (tralomethrin II) has the smallest slope value. Tralomethrin has the highest molecular weight among all the investigated compounds. The correlation coefficient value from the linear regression analysis of molecular weights vs. slope values of the respective compounds was found to be −0.858, whereas the respective coefficient from the A–D–H system was −0.062. The y-intercept values increase as the molecular weights of the solutes increase, with the exception of cis-permethrin, which showed the highest y-intercept value. In general, non-pyrethroidal compounds have slope and y-intercept values that are much different from the respective values of pyrethroidal solutes. The absolute slope values of the non-pyrethroidal compounds examined are higher and 7.0, whereas all the pyrethroids have absolute slope values that ranged from 2.80 to 4.51. It appears that these is an optimum range of slope values for solutes with strong pyrethroid-type activity. Pyrethroids with strong killing activity have slope values ranging from 3.0 to 3.6. The slope values reported in Table VI were also correlated with the p values of the respective solutes; the correlation coefficient was 0.928.

The chromatographic data recorded from the T–D systems have been also applied to Scott-Kucera's model.

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Table VII. Slope, *y*-Intercept, and Correlation Coefficient (*r*) Values from Plots of 1/*V'* vs. *C*ₚ, Where *V'* Is the Relative Retention Volume and *C*ₚ Is the Percent (v/v) Concentration of 1-Tetradecene in 1-Tetradecene–Dichloromethane Mobile Phases

compound	slope	*y* intercept	*r*
cis-phenothrin	−109.6	61.27	−0.970
cismethrin	−115.8	59.88	−0.975
trans-resmethrin	−146.9	62.79	−0.982
trans-phenothrin	−148.2	63.80	−0.973
cis-permethrin	−32.78	47.07	−0.908
tralomethrin I[a]	−36.23	41.85	−0.920
fluvalinate	−52.96	46.69	−0.950
tralomethrin II[a]	−53.96	42.33	−0.937
decamethrin	−54.69	44.56	−0.937
cis-cypermethrin	−64.71	49.18	−0.960
trans-permethrin	−73.40	55.51	−0.963
fenvalerate	−82.17	47.70	−0.960
AC-222,705	−91.31	43.48	−0.945
trans-cypermethrin	−93.51	49.20	−0.964
cis-ethyl chrysanthemate	−281.8	90.57	−0.969
trans-ethyl chrysanthemate	−375.1	91.50	−0.975
cycloprate	−355.3	100.4	−0.961

[a] Tralomethrins I and II refer to the two diastereomers of tralomethrin. Isomer I is eluted before isomer II.

Table VII gives the slope, *y*-intercept, and linear correlation coefficient values obtained by least-squares analysis of the 1/*V*ᵣ vs. *C*ₚ plots, where *C*ₚ is the percent (v/v) concentration of 1-tetradecene in the respective mobile phases. In this system, the correlation coefficients are better than the respective coefficients reported in Table VI; however, the variation pattern of slope and *y*-intercept values is the same with the one given in Table VI. The correlation coefficient between molecular weights and the slope values of the respective solutes is 0.837. The correlation coefficient of *p* values vs. slope values is 0.672. Trans isomers have slope values larger than the respective cis counterparts. The slope and *y*-intercept values are generally larger for the smaller molecular weight compounds. Both slope and *y*-intercept values differentiate non-halogen- from halogen-containing pyrethroids and pyrethroid from nonpyrethroid compounds.

CONCLUSIONS

From the chromatographic behavior of some pyrethroid insecticides and other related compounds under liquid–solid chromatographic conditions eluted with acetonitrile–dichloromethane–heptane and 1-tetradecene–dichloromethane mobile phases, the following conclusions

were made: (1) The behavior of cis and trans isomers is markedly different by using both mobile-phase systems. The differences in the slope and *y*-intercept values derived from log *k'* vs. log *N*ᵦ plots for the two geometrical isomers might be used to differentiate between cis and trans isomers. (2) Slope and *y*-intercept values have differentiated the pyrethroids with knockdown activity from those having killing activity. Studies of this kind might provide information in structure bioactivity relationship evaluations. (3) The effect of the solute molecular size on the magnitude of the slope and *y*-intercept values derived from the 1-tetradecene–dichloromethane systems is very pronounced, and hence the LSC system described herein with the appropriate calibration can be used as a rapid procedure of molecular size estimations.

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