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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY OF ORGANOPHOSPHORUS INSECTICIDES

GÁBOR SZALONTAI

Analytical Department, Neviki, 8201 Veszprém Pf 39 (Hungary)

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SUMMARY

The high-performance liquid chromatographic behaviour of 23 organophosphorus insecticides has been studied on a stainless-steel column packed with silica gel. It has been stated that the usual classification of organophosphorus compounds into phosphonic, phosphoric, thiophosphoric and dithiophosphoric acid ester types gives some information about their adsorption properties. The chromatographic conditions of the analyses and a method for separation of the stereoisomers of tetra-chlorvinphos are presented.

INTRODUCTION

In recent years, high-performance liquid chromatography (HPLC) has become an important technique for the analysis of pesticides. Despite this, only a few authors¹⁻⁵ have reported the HPLC analysis of organophosphorus insecticides, and the aim of this work was to study the liquid-solid chromatographic (LSC) behaviour of such compounds.

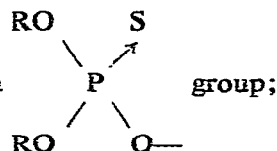
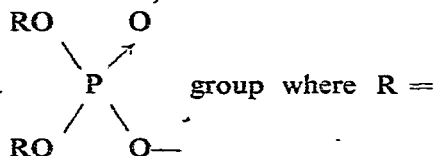
According to their chemical structures, organophosphorus acids and their derivatives can be divided into four types:

- (1) Phosphonic acid esters, which contain a P-C bond;

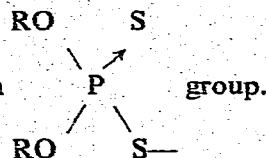
- (2) phosphoric acid esters, which contain a

alkyl (methyl or ethyl);

- (3) thiophosphoric acid esters, which contain a



(4) dithiophosphoric acid esters, which contain a



We used these types as a basis to establish whether the adsorption properties of the molecules also follow approximately such a classification.

EXPERIMENTAL AND RESULTS

Apparatus and materials

Standards were obtained from Polyscience Corp. (Evanston, Ill., U.S.A.) and from VNIISZZR, Moscow, U.S.S.R. The analyses were performed on a Pye Unicam Model LCM2 liquid chromatograph equipped with a transport wire flame-ionization detector. A 25 cm \times 2.2 mm stainless-steel column packed with silica gel (6–8 μ m) was used at room temperature. Commercially available analytical-grade solvents (Reanal, Budapest, Hungary) were dried and purified on an alumina column. The necessary solvent strengths and the relative retentions of the molecules to be separated were determined by thin-layer chromatography. In establishing the optimal solvent strength, in each case *n*-hexane was modified with *n*-propanol or ethanol.

Behaviour of different types of derivatives

Phosphonic acid esters. From this group, the behaviour of trichlorphon and

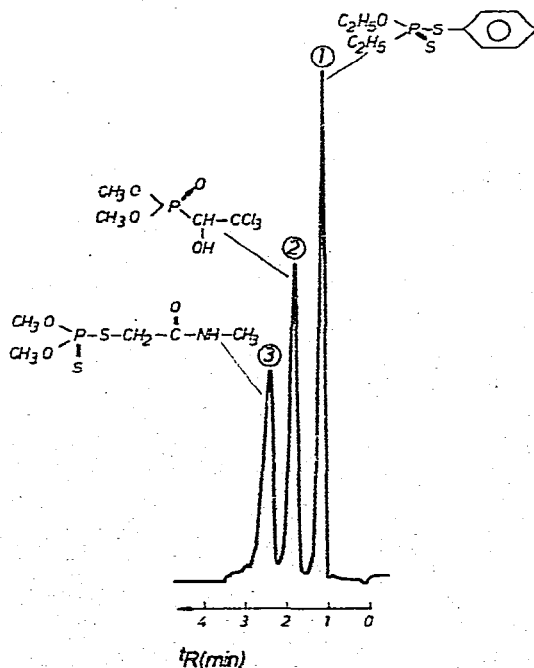


Fig. 1. Separation of (1) Dyfonate (fonofos), (2) Dipterex (trichlorphon) and (3) Dimethoat (dime-thoate). Eluent: 10% ethanol in *n*-hexane. Flow-rate: 0.85 ml/min. Pressure: 30 atm.

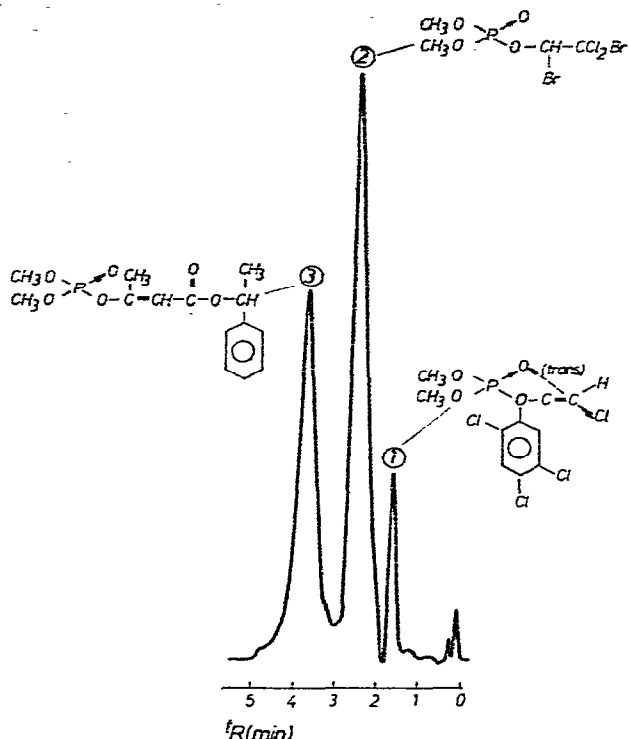


Fig. 2. Separation of (1) *trans*-Gardona (tetrachlorvinphos), (2) Naled (naled) and (3) Ciodrin (crotoxyphos). Eluent: 3% ethanol in *n*-hexane. Flow-rate: 0.55 ml/min. Pressure: 26 atm.

fonofos were studied (Fig. 1). The third peak on the chromatogram is dimethoate, which does not belong to this group (it is a dithiophosphoric acid), but its adsorption properties are more similar to those of the members of the phosphonic acid and phosphoric acid ester groups than to the members of the dithiophosphoric acid group.

Phosphoric acid esters. From this group, standards of dichlorvos, phospharidon, tetrachlorvinphos (both stereoisomers), dicrotophos, crotoxyphos, monocrotophos, mevinphos, naled and crufomate were available. With 3% ethanol in *n*-hexane as eluent, tetrachlorvinphos (α -isomer), naled and crotoxyphos were easily separable (Fig. 2).

The above molecules greatly differ in their structures. Crotoxyphos, eluted third, is similar to mevinphos, phosphamidon, monocrotophos and dicrotophos, but the latter compounds are adsorbed more strongly on the surface of silica and therefore for these compounds the optimal eluent contained 10% ethanol (Fig. 3).

A few members of this group (the vinyl phosphates) contain a carbon-carbon double bond, and they therefore have stereoisomers. These isomers may have greatly different toxicities, so that it is important to know their relative proportions. Previously gas chromatography (GC) has been used for measuring the exact amounts of isomers present, but the value of GC is questionable as the partition between the two energy states represented by the isomers depends on the temperature of the material. HPLC at room temperature seems to be more suitable for measuring the ratio of

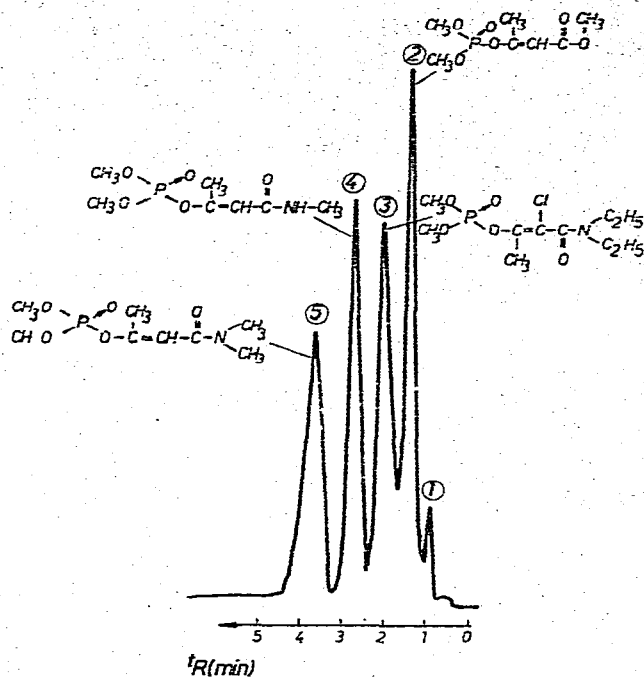


Fig. 3. Separation of (2) Phosdrin (mevinphos), (3) phosphamidon, (4) Azodrin (monocrotophos) and (5) Bidrin (dicrotophos). Peak 1: impurity. Eluent: 10% ethanol in *n*-hexane. Flow-rate: 1.16 ml/min. Pressure: 40 atm.

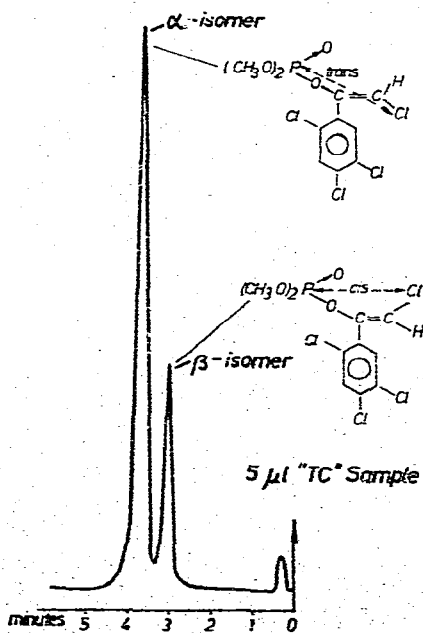


Fig. 4. Separation of the two stereoisomers of Gardona (tetrachlorvinphos). Eluent: 1.5% ethanol in *n*-hexane. Flow-rate: 0.5 ml/min. Pressure: 21 atm.

isomers in a mixture. We have developed an LSC method for separating the isomers of tetrachlorvinphos and the chromatogram obtained and the conditions used are illustrated in Fig. 4. The structures of the isomers were identified by proton magnetic resonance spectroscopy⁶.

Of the molecules tested, crufomate and dichlorvos show different adsorption properties compared with those of the above compounds. Even a few percent of *n*-propanol as polar modifier in the eluent was sufficient to bring their k' values (0.965 and 4.74, respectively) into the optimum range ($1 < k' < 10$).

For details, see Table I.

Thiophosphoric acid esters. The chromatographic behaviour of fenchlorphos, parathion-methyl and parathion was studied. These molecules proved to be more apolar than those in the groups considered above. In this case, the eluent contained only 1% *n*-propanol. As an example, the chromatogram of parathion-methyl is shown in Fig. 5.

TABLE I

RETENTION TIMES OF ORGANOPHOSPHORUS INSECTICIDES

Each experiment was performed on a 25 cm × 2.2 mm stainless-steel column packed with silica gel (6–8 μm).

Type	Common name (iso)	Eluent (% of alcohol in <i>n</i> -hexane)	Pressure drop (atm)	Flow-rate (ml/min)	t_R (sec)
Phosphonic acids	Trichlorphon	10% ethanol	30	0.85	114
	Fonofos	10% ethanol	30	0.85	72
Phosphoric acids	Monocrotophos	10% ethanol	40	1.16	162
	Dicrotophos	10% ethanol	40	1.16	222
	Crotoxyphos	3% ethanol	25	0.55	186
	Dichlorvos	0.5% propanol	33	1.05	265
	Tetrachlorvinphos	3% ethanol	25	0.55	96
	Naled	3% ethanol	25	0.55	144
	Mevinphos	10% ethanol	40	1.16	84
	Phosphamidon	10% ethanol	40	1.16	120
	Crufomate	5% <i>n</i> -propanol	23	0.83	115
Thiophosphoric acids	Parathion-methyl	1% <i>n</i> -propanol	50	1.75	42
	Parathion	1% <i>n</i> -propanol	50	1.75	42
	Fenchlorphos	1% <i>n</i> -propanol	50	1.75	45
Dithiophosphoric acids	Phenthoate	0.25% <i>n</i> -propanol	30	1.0	76
	Dimethoate	10% ethanol	30	0.85	144
	Azinphos-methyl	2% <i>n</i> -propanol	20	0.53	168
	Prolate	0.25% <i>n</i> -propanol	30	1.0	243
	Malathion	2% <i>n</i> -propanol	20	0.53	111
	Phosalon	0.25% <i>n</i> -propanol	30	1.0	99
	Phorate	2% <i>n</i> -propanol	20	0.53	90
	Carbophenthion	2% <i>n</i> -propanol	20	0.53	90
Gardona isomers	Tetrachlorvinphos, α-isomer	1.5% ethanol	21	0.5	222
	Tetrachlorvinphos, β-isomer	1.5% ethanol	21	0.5	183

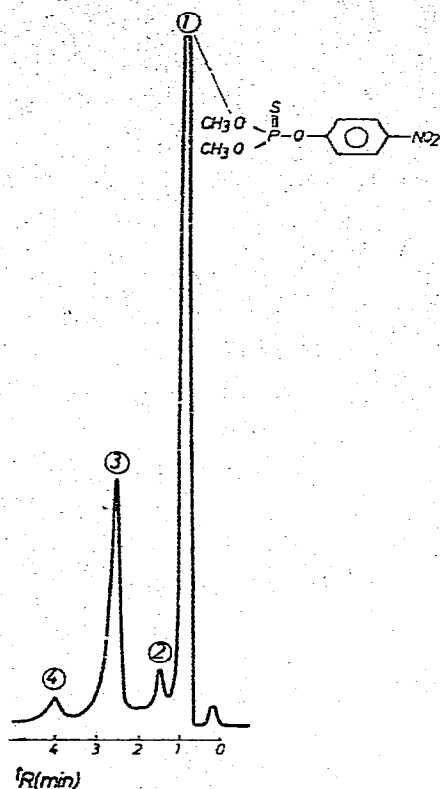


Fig. 5. Chromatogram of (1) Methyl-parathion (parathion-methyl). Peaks 2-4: unidentified. Eluent: 1% *n*-propanol in *n*-hexane. Flow-rate: 1.75 ml/min. Pressure: 50 atm.

The chromatographic conditions used in the analyses of fenchlorphos and parathion are given in Table I.

Dithiophosphoric acid esters. In this group, the following insecticides were available: prolate, phosalon, phenthoate, phorate, malathion, carbophenthion, azinphos-methyl and dimethoate. The adsorption properties of these molecules (except dimethoate) are similar to those of the thiophosphoric acid esters. Phenthoate, prolate and phosalon were separable with 0.25% *n*-propanol in *n*-hexane as the eluent (Fig. 6).

Phorate, malathion, azinphos-methyl and carbophenthion showed greater polarity, and in this case the optimal eluent contained 2% *n*-propanol. (Fig. 7)

Under the above conditions, carbophenthion and phorate eluted with the same k' value.

CONCLUSION

HPLC has been found to be a suitable method for separating and measuring the organophosphorus insecticides tested and, in the case of vinyl phosphate isomers, it offers certain advantages compared with GC.

It has been shown that the classification considered gives some information about the adsorption properties of the molecules. Eight of the ten phosphoric acid

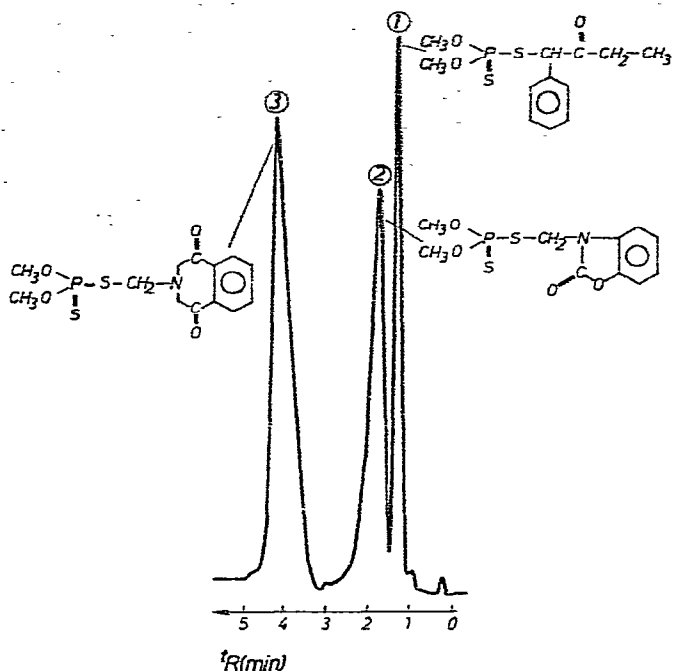


Fig. 6. Separation of (1) Cidial (phenthoate), (2) Phosalon (phosalon) and (3) Imidan (prolate). Eluent: 0.25% *n*-propanol in *n*-hexane. Flow-rate: 1 ml/min. Pressure: 30 atm.

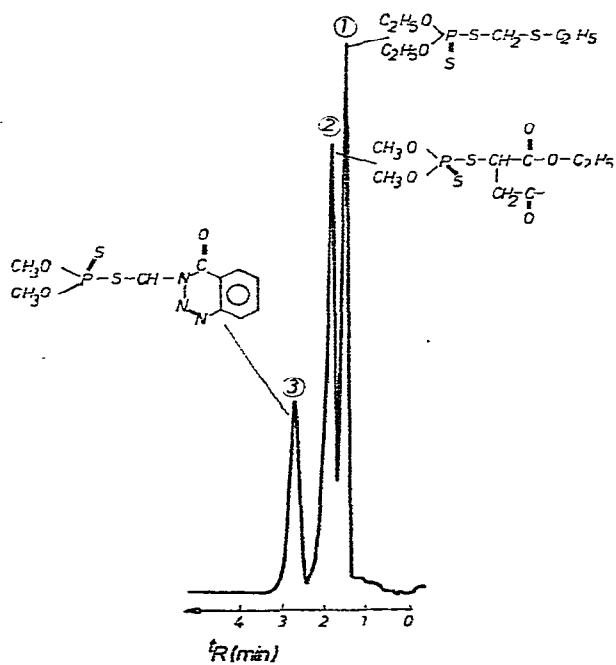


Fig. 7. Separation of (1) Thimet (phorate), (2) Malathion (malathion), and (3) Guthion (azinphos-methyl). Eluent: 2% *n*-propanol in *n*-hexane. Flow-rate: 0.53 ml/min. Pressure: 20 atm.

esters tested were successfully analyzed by varying the ethanol content of the eluent between 3 and 10% and the flow-rate from 0.55 to 1.16 ml/min. From this group, crufomate and dichlorphos show adsorption properties that are greatly different from those of the other compounds, presumably owing to the absence of a carbonyl group that is capable of forming hydrogen bonds. The thio- and dithiophosphoric acids tested have similar adsorption properties. With the exception of dimethoate they were successfully analyzed by varying the *n*-propanol content between 0.25 and 2% and the flow-rate from 0.53 to 1.75 ml/min. With dimethoate, the relatively strong adsorption of the molecule is caused by the $-\text{CO}-\text{NH}-$ functional group.

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