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COMPARATIVE STUDY OF THE GAS–LIQUID CHROMATOGRAPHIC BEHAVIOUR OF THE PENTAFLUOROBENZYL ESTERS AND THE METHYL ESTERS OF TEN CHLOROPHENOXYALKYL ACIDS

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SUMMARY

The gas–liquid chromatographic (GLC) behaviour of the pentafluorobenzyl and methyl esters of ten structurally related chlorophenoxyalkyl acids was studied by comparing their retention indices on nine frequently used liquid phases with increasing McReynolds constants. The resolution of each liquid phase is different for the pentafluorobenzyl and the methyl ester derivatives. However, using an apolar and a polar phase, a graph of the retention index (I) on the apolar phase against the difference in retention indices (ΔI) between the polar and the non-polar phase, shows a good correlation between structure and retention in gas–liquid chromatography. The graphs constructed for the pentafluorobenzyl and for the methyl esters have the same structure–retention correlations.

INTRODUCTION

The separation and/or detection of chlorophenoxyalkyl acids, as the free acids or after derivatization under a variety of experimental conditions, has been achieved using spectrophotometry[1–4], UV spectrophotometry[5–7], paper- and thin-layer chromatography[8–14] and gas–liquid chromatography (GLC), combined with microcoulometric, flame-ionization or electron-capture detection, in herbicide formulations[15], water[16,17], plant tissues, crops and wheat[18–25], food[26–33], soil[16,21,25,34,35] and animal and human biological samples[36–38]. In most of the GLC methods, the chlorophenoxyalkyl acids are determined as their methyl esters after direct derivatization[39–41] or after transesterification[42,43]. Another derivatization reagent for carboxylic acids is pentafluorobenzyl bromide, which has been applied in chlorophenoxyalkyl acid analysis[44–46]. It is an interesting reagent because of the increased electron-capture sensitivity of the derivatives formed[47,48]. The fact that the pentafluorobenzyl ester derivatives of ten chlorophenoxyalkyl acids are completely separated by GLC on DC-200, unlike their methyl esters, stimulated us to make a comparative study of the GLC behaviour of both series of derivatives on different liquid phases with increasing McReynolds constants.

EXPERIMENTAL

Chlorophenoxyalkyl acids

The ten chlorophenoxyalkyl acids examined are shown in Fig. 1. They all are systemic herbicides, except *p*-chlorophenoxyisobutyric acid (CPIB) or clofibrinic acid, the active metabolite of clofibrate, a hypolipidemic drug. CPIB has the same UV spectrum as MCPP and for this reason it was included in this study.

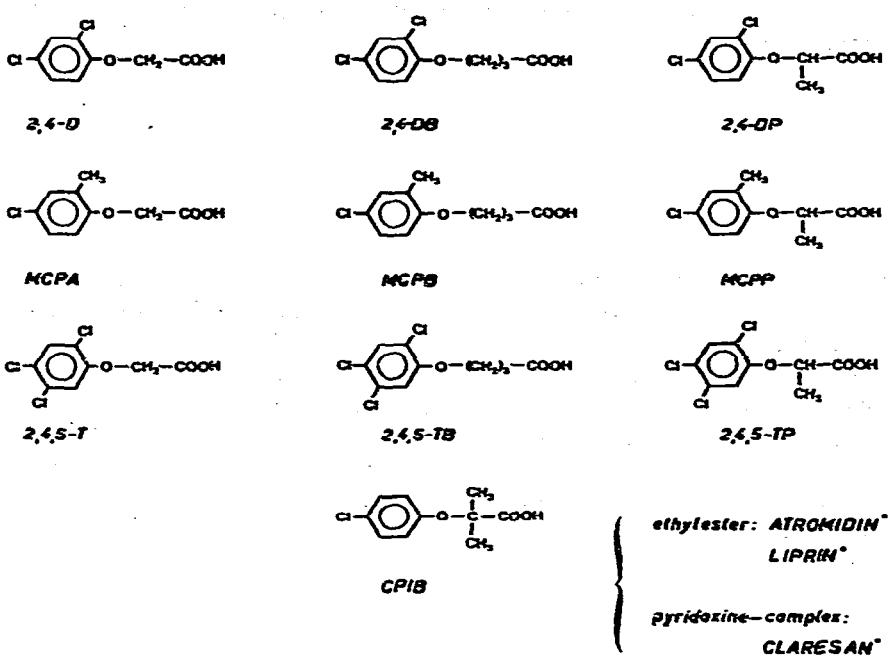


Fig. 1. The chlorophenoxyalkyl acids examined.

Reagents

Analytical-reagent grade chlorophenoxyalkyl acids (Riedel-de-Haën, Seelze-Hannover, G.F.R.) and pure *p*-chlorophenoxyisobutyric acid (Triosol, Laboratoires de Recherches Biologiques, Maisières, Belgium) were used as standards. The other reagents and solvents used for this study were: p.a. anhydrous potassium carbonate (J. T. Baker, Deventer, The Netherlands), 1% solution of p.a. pentafluorobenzyl bromide (PFB-Br, Pierce, Rockford, Ill., U.S.A.) in acetone, diazomethane solution in diethyl ether prepared from N,N'-dimethyl-N,N'-dinitrosoterephthalamide, 70% in mineral oil (Aidrich, Beerse, Belgium), p.a. ethyl acetate and p.a. *n*-hexane (Merck, Darmstadt, G.F.R.).

Standard solutions

All standard chlorophenoxyalkyl acid solutions were prepared at a concentration of 5 μg/μl in acetone.

n-Hydrocarbon solutions

For determinations of retention indices, 1 μg/μl *n*-hydrocarbon solutions in *n*-hexane were prepared.

Derivatization methods

With pentafluorobenzylbromide. Anhydrous potassium carbonate (10 mg) and 0.5 ml PFB-Br solution were added to 0.1 ml of a standard solution of chlorophenoxyalkyl acid in a glass-stoppered test-tube, which was heated for 90 min in a water-bath at 60°. The acetone was evaporated under a gentle stream of nitrogen; 1 ml of distilled water and 1 ml of ethyl acetate were added to the residue and the mixture was shaken for 1 min. The phases were allowed to separate and 0.5 μl of the ethyl acetate phase was injected into the chromatograph.

With diazomethane (CH_2N_2). A 0.1-ml volume of a standard chlorophenoxyalkyl acid solution was evaporated to dryness under nitrogen, and 0.5 ml of diazomethane solution in diethyl ether was added. The mixture was shaken for 2 min and the diethyl ether evaporated under nitrogen; 1 ml of ethyl acetate was added and 0.5 ml was injected into the chromatograph. After measurement of the retention time of each standard, a mixture of the ten standard chlorophenoxyalkyl acid derivatives was injected under the same GLC conditions.

Apparatus

A Varian 1800 gas chromatograph equipped with a flame-ionization detector was used. The chromatograms were recorded on a Varian Aerograph Model 20 1-mV recorder. The retention times used for retention index calculations were measured with an HP 3380 A electronic integrator.

GLC conditions

Silanized Pyrex glass columns of length 1.80 m, I.D. 2 mm and O.D. 1.8 in. were used.

The liquid phases examined were as follows:

(1) 5% DC-200 on Varaport 30 (100–120 mesh);
(2) 3% DC-11 on Chromosorb W AW DMCS (100–120 mesh);
(3) 3% OV-17 on Chromosorb W AW DMCS (100–120 mesh);
(4) 3% QF-1 on Varaport 30 (100–120 mesh);
(5) 3% OV-225 on Gas-Chrom Q (100–120 mesh);
(6) 3% XE-60 on Chromosorb W AW DMCS (100–120 mesh);
(7) 2.5% NPGA on Varaport 30 (100–120 mesh);
(8) 3% FFAP on Varaport 30 (100–120 mesh);
(9) 3% OV-275 on Chromosorb W (100–120 mesh).

The columns were conditioned for 24 h at 230° by passing a slow flow of nitrogen (10 ml/min) through them.

The conditions for the GLC of the PFB esters were: injector and detector temperature, 250°; column temperature, 210°. The conditions for the GLC of the methyl esters were: injector and detector temperature, 195°; column temperature, 165° for DC-200 and QF-1 and 175° for DC-11, OV-17, XE-60, OV-225, NPGA, FFAP and OV-275. The carrier gas was nitrogen at a flow-rate of 30–35 ml/min. The air flow-rate was 300 ml/min and the hydrogen flow-rate 30 ml/min.

Calculations

For calculating the retention indices, four or five *n*-hydrocarbons were chromatographed simultaneously with the derivatives on each column.

The retention indices of the PFB ester and the methyl ester derivatives were calculated both with the Kováts equation and by linear regression, plotting logarithm of the retention time on the ordinate and the carbon number of the *n*-hydrocarbons used $\times 100$ on the abscissa.

RESULTS AND DISCUSSION

The McReynolds constants of the liquid phases used are given in Table I[49]; they characterize the polarity of the liquid phases[50,51]. The retention times and the retention indices on the different liquid phases, calculated as mentioned above, are

TABLE I

GLC PHASES EXAMINED AND THEIR McREYNOLDS CONSTANTS

Liquid phase	*McReynolds constants*				
	X	*Y*	*Z*	*U*	*S*
DC-200	16	57	45	66	43
DC-11	17	86	48	69	56
OV-17	119	158	162	243	202
QF-1	144	233	355	463	305
OV-225	228	369	338	492	386
XE-60	204	381	340	493	367
NPGA	234	425	312	462	438
FFAP	340	580	397	602	627
OV-275	629	872	763	1106	849

TABLE II

RETENTION TIMES AND RETENTION INDICES OF PFB ESTERS, CALCULATED WITH LINEAR REGRESSION AND WITH KOVÁTS EQUATION ON THE NINE GLC–LIQUID PHASES EXAMINED

PFB ester	*DC-200*			*DC-11*			*OV-17*			*QF-1*		
	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}
CPIB	3′20″	1933	1934	2′32″	1951	1953	6′17″	2160	2161	3′01″	2571	2573
MCPP	3′46″	1974	1977	2′51″	1994	1997	7′46″	2225	2229	3′28″	2626	2634
MCPA	4′16″	2015	2020	3′10″	2035	2037	10′14″	2310	2315	4′22″	2721	2731
2,4-DP	4′34″	2038	2043	3′22″	2059	2060	10′14″	2310	2315	4′22″	2721	2731
2,4-D	5′14″	2083	2089	3′56″	2117	2118	13′46″	2402	2408	5′46″	2837	2847
2,4,5-TP	6′51″	2173	2179	4′47″	2192	2191	16′22″	2455	2459	6′15″	2870	2880
2,4,5-T	7′57″	2222	2228	5′25″	2239	2239	22′55″	2559	2560	8′34″	3001	3008
MCPB	8′50″	2257	2262	5′52″	2270	2271	22′55″	2559	2560	8′34″	3001	3008
2,4-DB	10′39″	2319	2323	6′51″	2328	2332	30′27″	2647	2646	10′49″	3098	3103
2,4,5-TB	17′18″	2481	2480	10′27″	2489	2492	53′21″	2819	2815	17′05″	3288	3290

* Calculated with linear regression.

** Calculated with Kováts equation.

tabulated for both series of derivatives in Tables II and III. The liquid phases DC-200 and DC-11 have McReynolds constants in the same range, and have identical separation patterns. This is also true for OV-225 and XE-60. However, we found for both the PFB ester and the methyl ester derivatives different orders of elution on liquid phases with different polarities. This is illustrated by the chromatograms in Figs. 2 and 3. From these chromatograms, it was concluded that both the PFB esters and the methyl esters of MCPA, 2,4-D and 2,4,5-T change positions with other compounds in the elution sequence. Tables IV and V give their elution positions on the different liquid phases used with respect to the other derivatives. Another important fact is that on all liquid phases, CPIB as either the PFB ester or the methyl ester is always the first eluting compound, completely separated from the herbicides.

The methyl esters and the PFB esters of the ten chlorophenoxyalkyl acids have been synthesized in our laboratory and their mass spectra recorded[52,53]. We were able to confirm by gas chromatography–mass spectrometry the structures of the methyl and PFB esters of the ten compounds.

A plot of retention indices against a specific phase polarity constant from the McReynolds system for a series of GLC phases gives complete information about the GLC behaviour of a series of compounds. Such graphs constructed for the PFB and methyl ester derivatives are given in Figs. 4 and 5, respectively. It should be noted that the GLC behaviour of both series of derivatives is not determined exclusively by the selected phase polarity constant, representing a specific type of solvent–solute interaction.

In both Figs. 4 and 5 the retention indices of the chlorophenoxyacetic acid derivatives increase faster on more polar phases in comparison with the other derivatives. This means that the chlorophenoxyacetic acid esters are more polar than their 2-propionic and butyric acid analogues. This also explains why changes in the elution order occur on some GLC phases, as summarized above.

XE-60			*OV-225*			*NPGA*			*FFAP*			*OV-275*		
R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}
3′48″	2544	2546	3′31″	2560	2563	3′00″	2554	2555	8′25″	2525	2525	2′48″	2739	2745
4′35″	2619	2626	4′26″	2642	2647	3′52″	2646	2651	11′21″	2620	2619	3′22″	2806	2818
6′21″	2748	2759	6′19″	2767	2771	6′09″	2814	2820	21′08″	2819	2820	5′36″	2991	3002
6′21″	2748	2759	6′19″	2767	2771	5′27″	2770	2776	17′24″	2757	2758	4′49″	2937	2948
9′22″	2903	2909	9′39″	2917	2919	9′10″	2959	2963	35′05″	2980	2980	9′10″	3170	3181
9′22″	2903	2909	9′39″	2917	2919	8′37″	2937	2942	27′26″	2902	2902	6′33″	3048	3059
14′36″	3079	3078	15′34″	3085	3085	15′24″	3147	3149	59′13″	3148	3147	12′58″	3296	3302
12′33″	3019	3021	13′28″	3034	3034	12′11″	3062	3065	43′03″	3046	3046	9′10″	3170	2181
16′55″	3138	3134	18′27″	3145	3144	16′57″	3181	3183	65′09″	3178	3177	12′58″	3296	3302
28′57″	3352	3347	32′24″	3345	3343	30′29″	3393	3391	117′29″	3366	3366	20′23″	3460	3459

TABLE III

RETENTION TIMES AND RETENTION INDICES OF METHYL ESTERS, CALCULATED WITH LINEAR REGRESSION AND WITH KOVÁTS EQUATION ON THE NINE GLC LIQUID PHASES EXAMINED

Methyl ester	*DC-200*			*DC-11*			*OV-17*			*QF-1*		
	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}
CPIB	2'55"	1474	1473	1'53"	1499	1498	5'30"	1708	1706	2'07"	1886	1886
MCPP	3'27"	1518	1519	2'15"	1544	1546	7'09"	1770	1769	2'29"	1937	1944
MCPA	3'30"	1522	1523	2'16"	1548	1549	8'31"	1812	1812	2'51"	1982	1993
2,4-DP	4'16"	1574	1576	2'30"	1595	1597	9'48"	1846	1846	3'13"	2022	2033
2,4-D	4'33"	1591	1593	2'37"	1613	1615	12'12"	1899	1899	3'57"	2089	2097
2,4,5-TP	7'13"	1712	1716	3'46"	1734	1738	17'36"	1986	1988	11'58"	2163	2169
2,4,5-T	7'52"	1736	1736	4'03"	1752	1753	22'48"	2047	2049	6'15"	2238	2241
MCPB	7'54"	1740	1740	4'05"	1756	1756	20'31"	2022	2024	6'06"	2231	2233
2,4-DB	9'55"	1795	1799	4'59"	1811	1813	29'01"	2105	2105	7'57"	2316	2316
2,4,5-TB	18'18"	1956	1955	8'41"	1964	1962	57'09"	2267	2266	13'34"	2491	2481

* Calculated with linear regression.
** Calculated with Kováts equation.

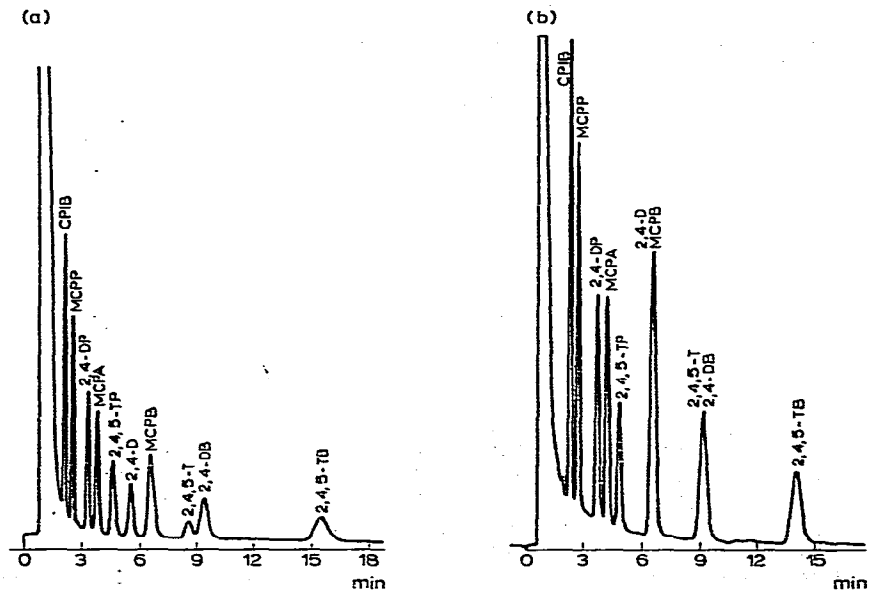


Fig. 2.

XE-60			*OV-225*			*NPGA*			*FFAP*			*OV-275*		
R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}	R_t	I^*	I^{**}
3'39"	1906	1903	3'10"	1953	1955	2'55"	1945	1948	7'52"	2026	2025	2'37"	2146	2152
4'31"	1975	1984	4'11"	2031	2035	4'00"	2031	2037	11'25"	2115	2115	3'18"	2213	2226
5'38"	2045	2057	5'21"	2108	2113	5'54"	2136	2143	19'25"	2241	2242	5'16"	2348	2360
6'10"	2074	2087	6'06"	2136	2141	5'54"	2136	2143	19'25"	2241	2242	5'00"	2332	2345
8'27"	2174	2189	8'43"	2236	2241	9'36"	2265	2270	37'07"	2396	2395	9'22"	2513	2520
9'50"	2222	2234	10'21"	2283	2287	10'37"	2295	2299	33'30"	2372	2371	7'09"	2435	2445
14'21"	2343	2348	15'44"	2400	2402	19'00"	2453	2453	71'13"	2552	2551	14'43"	2643	2643
11'41"	2277	2287	12'22"	2333	2336	12'56"	2349	2352	41'12"	2421	2420	9'00"	2501	2508
11'54"	2390	2393	18'17"	2442	2443	19'33"	2460	2460	87'18"	2552	2551	13'55"	2627	2628
30'31"	2580	2570	34'53"	2623	2620	40'34"	2668	2655	143'57"	2720	2720	23'25"	2776	2769

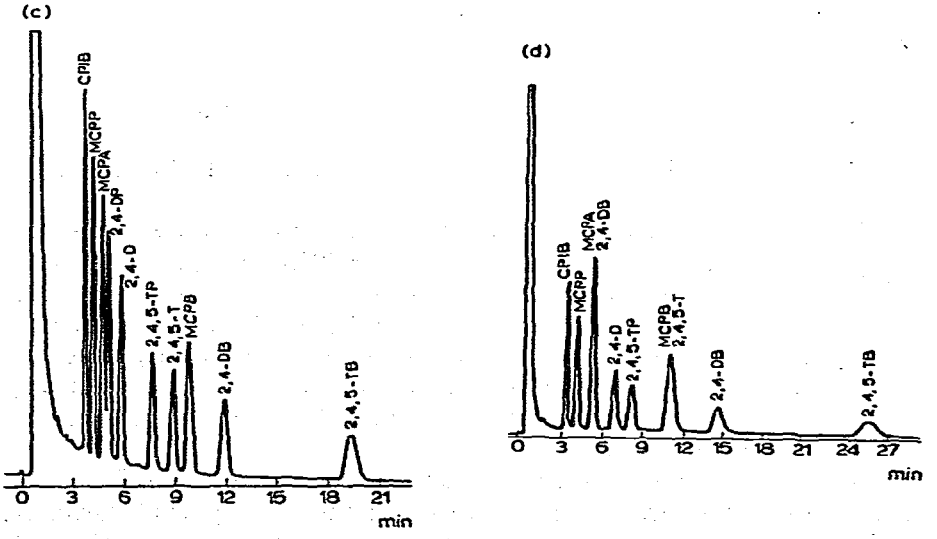


Fig. 2. Chromatograms of PFB esters. (a) 1% FFAP on Varaport 30 (100–120 mesh); (b) 3% OV-275 on Chromosorb W (100–120 mesh); (c) 5% DC-200 on Varaport 30 (100–120 mesh); (d) 3% OV-17 on Chromosorb W AW DMCS (100–120 mesh).

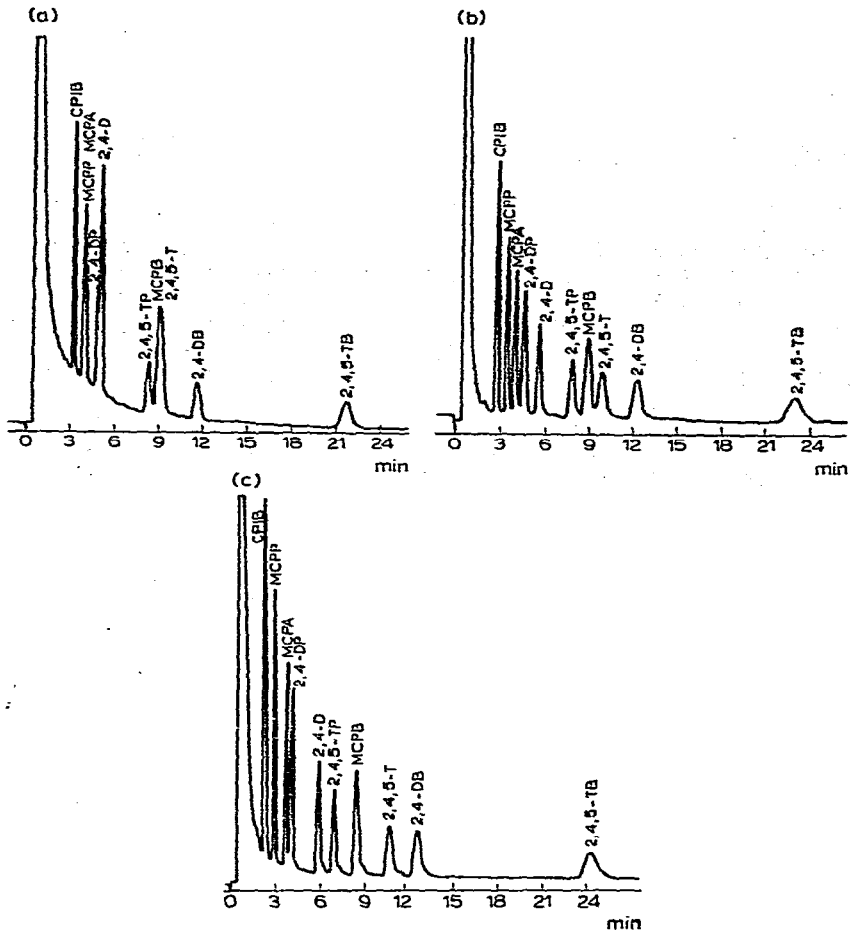


Fig. 3.

In some respects the PFB esters and the methyl esters have different GLC properties.

On all of the liquid phases examined, the MCPP and MCPA PFB esters were completely separated, unlike their methyl esters. The ten PFB ester derivatives were completely separated on the apolar phases DC-200 and DC-11, and on the polar phase FFAP with a different elution order. The methyl ester derivatives, however, were completely separated with the same elution order on the semi-polar phases OV-17, XE-60 and OV-225. On DC-200, DC-11 and FFAP they were not completely separated. All of these results contribute to the GLC identification of these ten structurally related chlorophenoxyalkyl acids.

In studies of correlations between structure and retention in GLC, the advantages of the retention index are accentuated by the fact that changes in logarithmic retention parameters may be regarded as proportional to the corresponding differences in the magnitude of the intermolecular forces between the solute and the stationary phase. Graphs with retention indices on two stationary phases along the

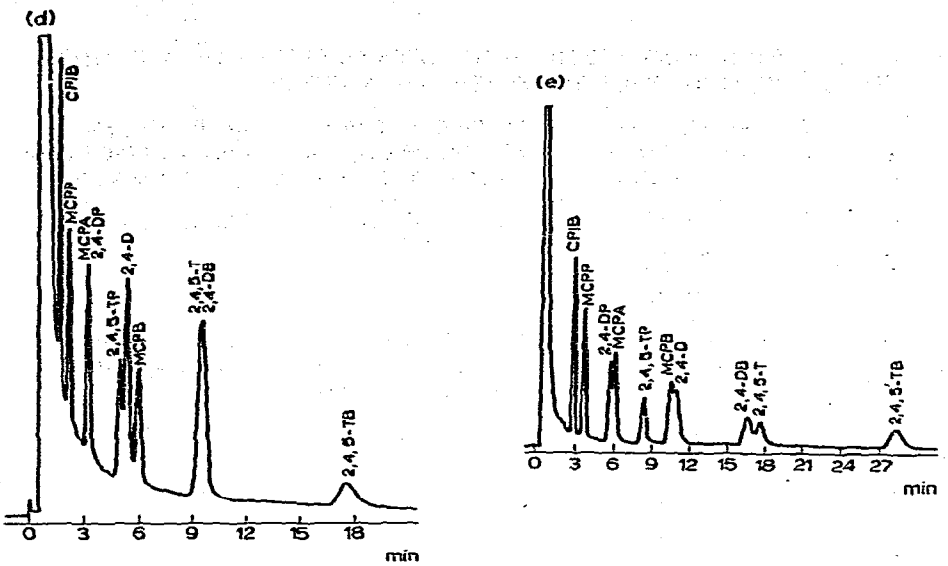


Fig. 3. Chromatograms of methyl esters. (a) 5% DC-200 on Diatoport S (100–120 mesh); (b) 3% OV-17 on Chromosorb W AW DMCS (100–120 mesh); (c) 3% XE-60 on Chromosorb W (100–120 mesh); (d) 1% FFAP on Varaport 30 (100–120 mesh); (e) 3% OV-275 on Chromosorb W (100–120 mesh).

TABLE IV

POSITIONS OF CHLOROPHENOXYACETIC ACID PFB ESTERS ON THE DIFFERENT LIQUID PHASES WITH RESPECT TO OTHER DERIVATIVES

MCPA-PFB eluting before 2,4-DP-PFB	*MCPA-PFB eluting together with 2,4-DP-PFB*	*MCPA-PFB eluting after 2,4-DP-PFB*
Phases: DC-200 DC-11	Phases: OV-17 QF-1 OV-225 XE-60	Phases: NPGA FFAP OV-275
2,4-D-PFB eluting before 2,4,5-TP-PFB	*2,4-D-PFB eluting together with 2,4,5-TP-PFB*	*2,4-D-PFB eluting after 2,4,5-TP-PFB*
Phases: DC-200 DC-11 OV-17 QF-1	Phases: OV-225 XE-60	Phases: NPGA FFAP OV-275
2,4,5-T-PFB eluting before MCPB-PFB	*2,4,5-T-PFB eluting together with MCPB-PFB*	*2,4,5-T-PFB eluting after MCPB-PFB*
Phases: DC-200 DC-11	Phases: OV-17 QF-1	Phases: OV-225 XE-60 NPGA FFAP OV-275
2,4,5-T-PFB eluting together with 2,4-DB-PFB	*2,4-D-PFB eluting together with MCPB-PFB*	
Phase: OV-275	Phase OV-275	

TABLE V

POSITIONS OF CHLOROPHENOXYACETIC ACID METHYL ESTERS ON THE DIFFERENT LIQUID PHASES WITH RESPECT TO OTHER DERIVATIVES

MCPA-CH_3 eluting together with MCPP-CH_3	*MCPA-CH_3 eluting after MCPP-CH_3 and before 2,4-DP-CH_3*	*MCPA-CH_3 eluting after MCPP-CH_3 and together with 2,4-DP-CH_3*	*MCPA-CH_3 eluting after MCPP-CH_3 and after 2,4-DP-CH_3*
Phases: DC-200 DC-11	Phases: OV-17 QF-1 XE-60 OV-225	Phases: NPGA FFAP	Phases: OV-275
2,4-D-CH_3 eluting together with 2,4-DP-CH_3	*2,4-D-CH_3 eluting after 2,4-DP-CH_3 and before 2,4,5-TP-CH_3*	*2,4-D-CH_3 eluting after 2,4-DP-CH_3 and togther with 2,4,5-TP-CH_3*	*2,4-D-CH_3 eluting after 2,4-DP-CH_3 and after 2,4,5-TP-CH_3*
Phases: DC-200 DC-11	Phases: OV-17 QF-1 XE-60 OV-225 NPGA	Phase: FFAP	Phase: OV-275
2,4,5-T-CH_3 eluting together with MCPA-CH_3 and before 2,4-DB-CH_3	*2,4,5-T-CH_3 eluting after MCPB-CH_3 and before 2,4-DB-CH_3*	*2,4,5-T-CH_3 eluting after MCPB-CH_3 and together with 2,4-DB-CH_3*	*2,4,5-T-CH_3 eluting after MCPB-CH_3 and after 2,4-DB-CH_3*
Phases: DC-200 DC-11 QF-1	Phases: OV-17 OV-225 XE-60 NPGA	Phase: FFAP	Phase: OV-275

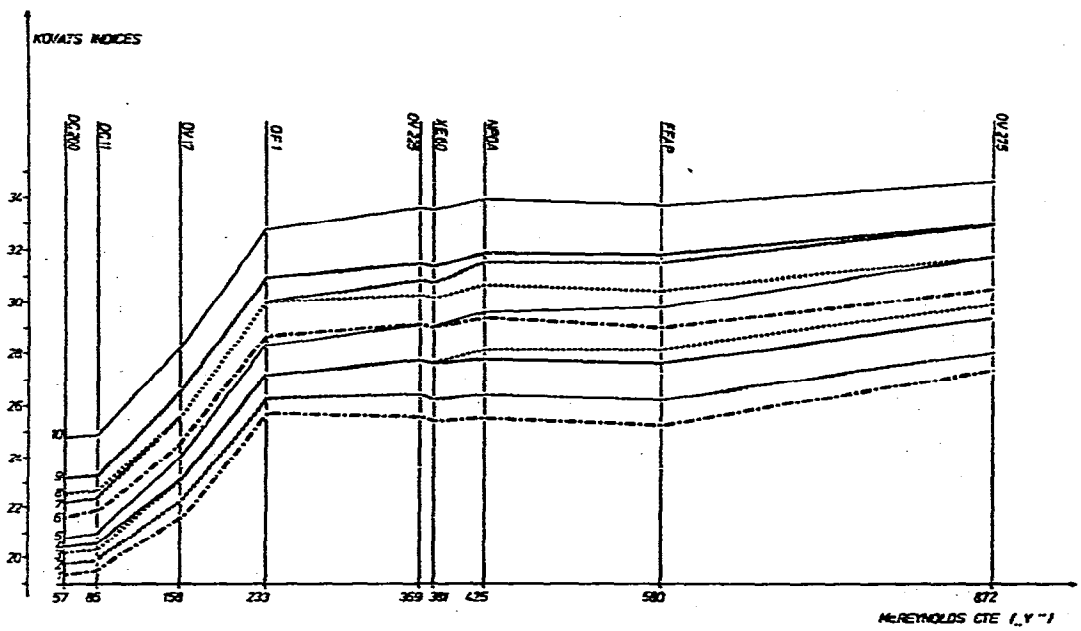


Fig. 4. Retention indices *versus* a McReynolds phase polarity constant of PFB esters for the nine liquid phases examined. 1 = CPIB; 2 = MCPP; 3 = MCPA; 4 = 2,4-DP; 5 = 2,4-D; 6 = 2,4,5-TP; 7 = 2,4,5-T; 8 = MCPB; 9 = 2,4-DB; 10 = 2,4,5-TB.

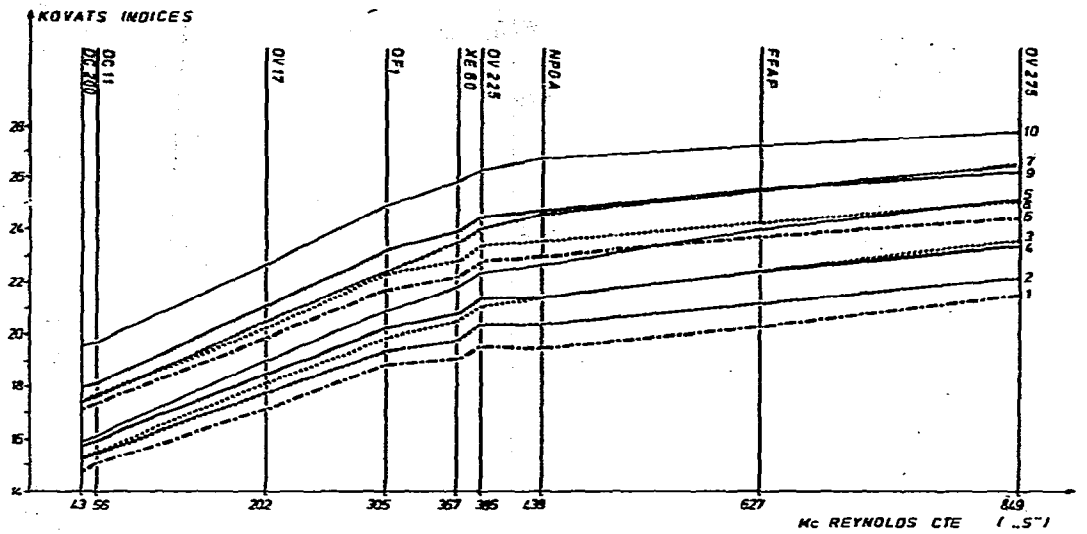
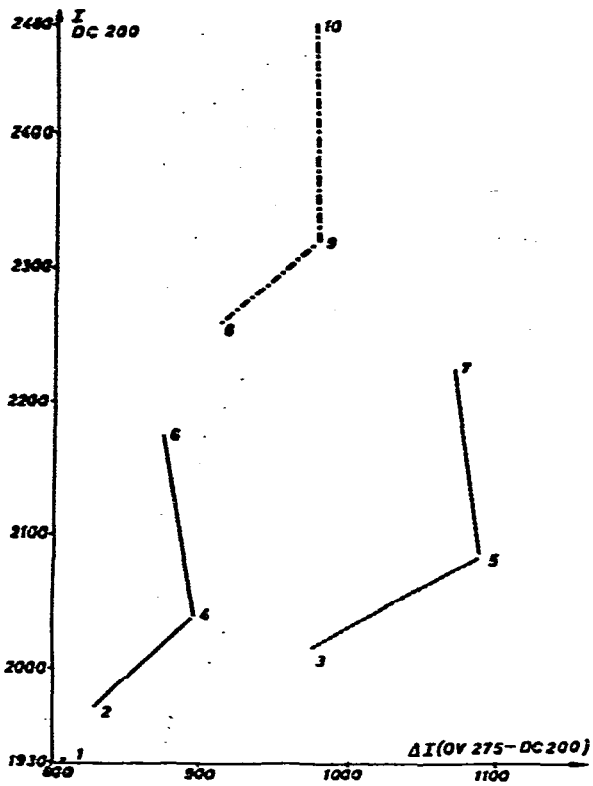


Fig. 5. Retention indices *versus* a McReynolds phase polarity constant of methyl esters for the nine liquid phases examined. 1 = CPIB; 2 = MCPP; 3 = MCPA; 4 = 2,4-DP; 5 = 2,4-D; 6 = 2,4,5-TP; 7 = 2,4,5-T; 8 = MCPB; 9 = 2,4-DB; 10 = 2,4,5-TB.

two axes are often recommended as a means for illustrating relationships between structure and retention and for extracting structural information from retention data[54]. The most fruitful results are normally obtained when one non-polar and one polar stationary phase are used. However, calculating the correlation coefficient between the retention indices on DC-200 and on OV-275, according to Moffat *et al.*[55], we obtain high values for both the PFB and the methyl esters. The reason is that the changes in the elution order of some derivatives after GLC on both stationary phases has no influence on the calculation of the correlation coefficient. More direct information is obtained when the retention index on the polar phase is replaced by the difference in retention indices, ΔI, between the polar and the non-polar phase. This concept, introduced by Kováts[56], represents the magnitude of polar and specific interactions, whereas the retention index on the non-polar phase represents the magnitude of non-polar and dispersion interactions between the compound and the stationary phase. As the integral retention index on the polar phase corresponds to the sum of polar and non-polar interactions, it can be argued that the *I versus* ΔI method gives the more direct characterization of a compound.

Figs. 6 and 7 show *I* (DC-200) *versus* ΔI (OV-275 — DC-200) graphs for the PFB and the methyl esters, respectively. The relative positions of the ten compounds in both figures are the same, independent of the derivatization method.

The basis of the retention index system is the constant increment in the retention index between members of a homologues series. The addition of structural units other than the methylene group may cause similar characteristic retention index increments[57]. Hence, some qualitative analytical information can be obtained from the retention data and *I versus* ΔI graphs. The position of an unknown compound on the *I versus* ΔI graph indicates the type of structure, and permits the exclusion of certain structural possibilities.



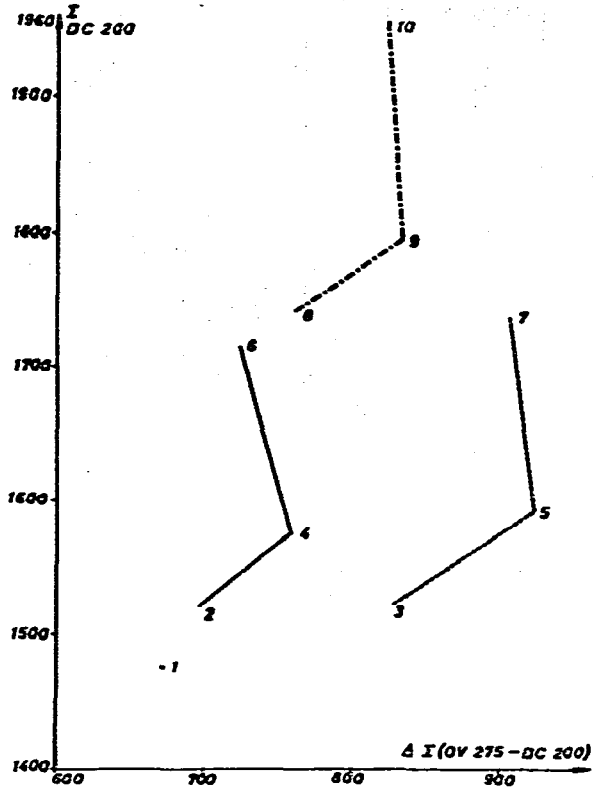


Fig. 6. *I versus ΔI* for PFB esters. 1 = CPIB; 2 = MCPP; 3 = MCPA; 4 = 2,4-DP; 5 = 2,4-D; 6 = 2,4,5-TP; 7 = 2,4,5-T; 8 = MCPB; 9 = 2,4-DB; 10 = 2,4,5-TB.

Fig. 7. *I versus ΔI* for methyl esters. 1 = CPIB; 2 = MCPP; 3 = MCPA; 4 = 2,4-DP; 5 = 2,4-D; 6 = 2,4,5-TP; 7 = 2,4,5-T; 8 = MCPB; 9 = 2,4-DB; 10 = 2,4,5-TB.

The approximate retention index data for a particular structurally related compound can be calculated. Structural units can be defined that correspond to characteristic changes in *I* and *ΔI*. Hence we find that the methylchloro-, dichloro- and trichloro-derivatives of the acetic, 2-propionic and butyric compounds have the same positions relative to each other in both of the *I versus ΔI* graphs. For both series of derivatives, the graphs were constructed using the apolar DC-200 phase and the polar OV-275 phase. On both phases the separation of the methyl ester derivatives is unsatisfactory, but on the *I versus ΔI* graph each methyl ester has a particular position and unambiguous identification is possible.

We conclude that using *I versus ΔI* graphs, a new derivatization technique will not contribute to the better identification of a series of structurally related compounds. However, the resolution for a series of compounds on some GLC phases can be increased so that a better separation pattern is obtained. A specific derivatization can also increase the sensitivity of the derivatives formed when a specific detector is used.

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