Journal of Chromatography, 321 (1985) 115–125
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 17,388

GAS–LIQUID CHROMATOGRAPHIC ANALYSES

XXXII*. INCREMENTAL EFFECTS OF HYDROXY, METHOXY AND ACETOXY GROUPS INTRODUCED INTO ISOMERIC CHLOROBENZENES

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(Received October 13th, 1984)

SUMMARY

Incremental effects of the additional hydroxy, methoxy and acetoxy groups introduced into various non-chlorinated and chlorinated positions of isomeric chlorobenzenes have been investigated on low-polarity and polar capillary columns isothermally at 160°C. On low-polarity columns the retention increments for chlorophenols varied from −59 to 359 index units (i.u.), being in the ranges −30–260 i.u. with chloroanisoles and 68–363 i.u. with chlorophenyl acetates. On polar columns the retentions were markedly enhanced, *viz.*, up to 352–1293 i.u. for phenols, −3–471 i.u. for anisoles and 223–600 i.u. for phenyl acetates. The *m*- and *p*-hydroxy substitutions maximized the retention enhancements, which were markedly reduced with the *o*-hydroxy substitution. The effects of the other substituents are not so significant.

INTRODUCTION

Recently, a series of gas chromatographic (GC) studies aimed a maximizing the separation of complex mixtures of various chlorinated aromatics have been carried out, using temperature programming and low-polarity and polar capillary columns[1]. The retention indices and the retention index increments for each position of substitution, together with the effect of increasing temperature on the values, have been discussed for seven groups of chlorinated aromatics, *viz.*, benzenes[2], phenols[3], anisoles[4], phenyl acetates[5], veratroles[6], 2-hydroxybenzaldehydes[1] and 4-hydroxybenzaldehydes[7].

This paper extends the earlier studies[2–5] by showing the retention increments of the OH, CH_3O and CH_3COO groups introduced into various non-chlorinated and chlorinated positions of isomeric chlorobenzenes. The effects of each of the three substituents on both low-polarity and polar capillary columns based on the retention index data reported previously[2–5] are discussed.

* For Part XXXI, see ref. 3.

0021-9673/85/$03.30

EXPERIMENTAL

Materials

Chlorobenzenes and chlorophenols were commercial products (Fluka, Buchs, Switzerland). Chlorophenols were converted into chloroanisoles[4] and chlorophenyl acetates[5] by using the known methylation and acetylation methods. Commercial mixtures of *n*-alkanes were obtained from different sources.

Methods

GC analyses were carried out on a Varian Model 2400 gas chromatograph or on a Perkin-Elmer Sigma 3 instrument under the operating conditions reported earlier[2–5]. Different glass or quartz capillary columns with low-polarity (SE-30) and polar (Carbowax 20M, OV-351 or FFAP) stationary phases were used. All data presented were recorded isothermally at 160°C and the retention indices were determined as described previously[2–5].

RESULTS AND DISCUSSION

Additional group introduced into non-chlorinated positions of isomeric chlorobenzenes

Incremental effects due to an additional hydroxy, methoxy and acetoxy group introduced into different non-chlorinated positions of isomeric chlorobenzenes, *i.e.*, $\Delta I = I_{nCl}$ (isomer formed) $- I_{nCl}$ (benzene), obtained on low-polarity and polar capillary columns are presented in Table I and Figs. 1 and 2. A summary of the increments is shown in Table II and the differences in the values between the three groups are given in Table III.

With the monochloro isomers the greatest retention enhancements are shown by most bulky phenyl acetates, those of the 3- and 4-chloro isomers being about 360 retention index units (i.u.), reducing to *ca.* 330 i.u. with the 2-chloro isomer. Owing to the smaller size of the methoxy substituent, the increments with chloroanisoles fall from 74 to 113 i.u., the 2-chloro isomer showing the highest increase[4]. The differences between the increments for isomeric monochlorinated phenyl acetates and anisoles are small, in contrast to those of chlorophenols. Owing to the *ortho*-effect, only an enhancement of 151 i.u. for 2-chlorophenol is observed, the retention increasing up to 317 i.u. with the 3-(*m*-) and 4-(*p*-)chlorophenols. The values of the latter are 72 and 63 i.u. higher, respectively, than those of the corresponding more bulky anisoles, owing to the increased polarity of phenols, giving rise to enhanced retention also on the low-polarity columns.

With higher chlorinated isomers the increments generally fall, the trends being almost the same as with the monochloro isomers. The hydroxy and acetoxy groups introduced into isolated positions, *i.e.*, positions without adjecent chlorine atoms of the 1,2- and 1,3-di- and 1,2,3-trichlorobenzenes, show the highest increments, the values for the 3,4- and 3,5-di- and 3,4,5-trichlorophenols being higher than those of the corresponding phenyl acetates and even higher than those for 3- and 4-chlorophenols (Table I, Fig. 1). With chlorinated anisoles, however, the greatest enhancements are shown by the vicinally substituted 2,3-di-, 2,3,4-tri- and 2,3,4,5-tetrachloro isomers owing to the steric effect reported earlier[4]. Anisoles and phenyl acetates with two adjacent chlorine atoms, *i.e.*, the 2,6-di-, 2,3,6- and 2,4,6-tri-, 2,3,4,6- and

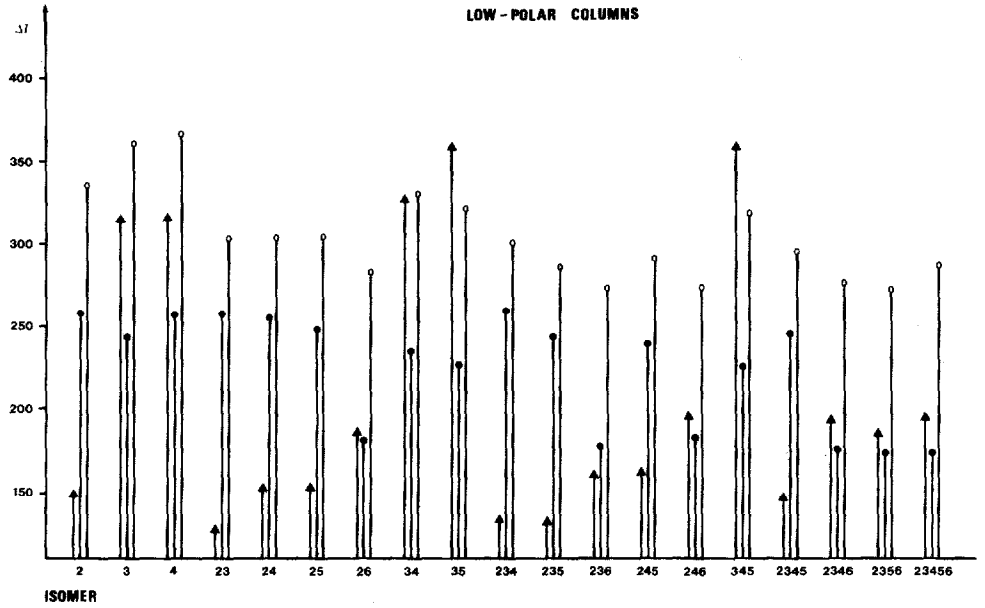

Fig. 1. Incremental effects due to additional hydroxy, methoxy and acetoxy groups introduced into various non-chlorinated positions of isomeric chlorobenzenes, obtained on low-polarity capillary columns at 160°C (Table I). (▲) Phenol; (●) anisole; (○) phenyl acetate. The numbers indicate the positions of chlorination.

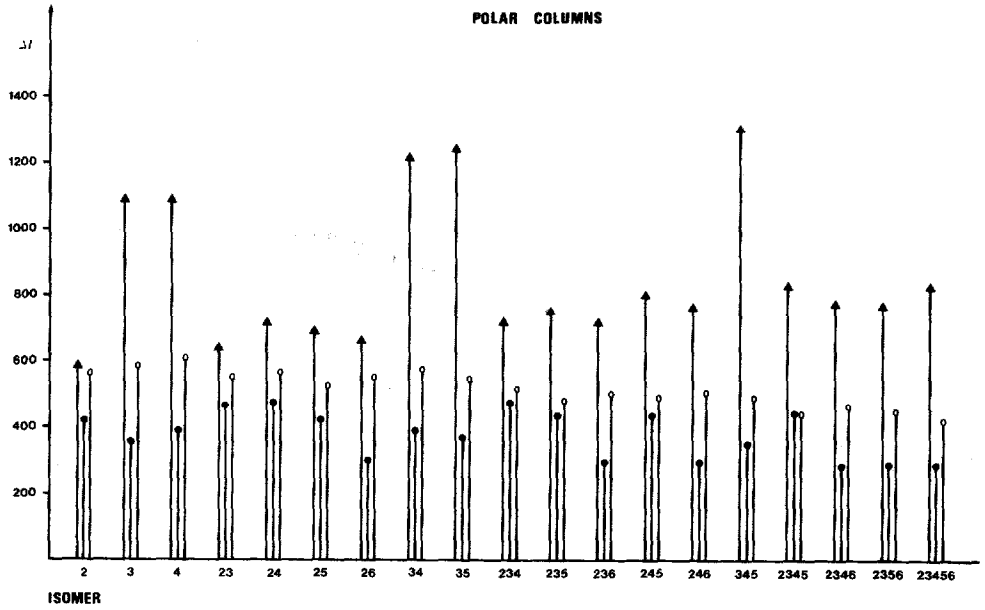

Fig. 2. Effects as in Fig. 1, obtained on polar capillary columns at 160°C (Table I).

TABLE I

INCREMENTAL EFFECTS DUE TO THE ADDITIONAL HYDROXY, METHOXY AND ACETOXY GROUPS INTRODUCED INTO ISOMERIC CHLOROBENZENES, OBTAINED ON LOW-POLARITY AND POLAR CAPILLARY COLUMNS AT 160°C

Chlorobenzene isomer with (in parentheses) positions of additional groups*		*Chloro isomer formed*	*Column*								
			Low-polarity			*Polar*			*Difference: polar – low-polarity*		
			*Phenol**: ΔI_{OH}§§*	*Anisole***: ΔI_{OCH_3}§§*	*Phenyl acetate§: ΔI_{OCOCH_3}§§*	*Phenol**: ΔI_{OH}§§*	*Anisole***: ΔI_{OCH_3}§§*	*Phenyl acetate§: ΔI_{OCOCH_3}§§*	*ΔI_{OH}§§*	*ΔI_{OCH_3}§§*	*ΔI_{OCOCH_3}§§*
1-	(2,6)	2-	151	259	333	596	420	559	445	161	226
1-	(3,5)	3-	317	245	358	1101	358	578	784	113	220
1-	(4)	4-	317	254	363	1101	386	600	784	132	237
1,2-	(3,6)	2,3-	130	259	300	646	463	538	516	204	238
1,3-	(4,6)	2,4-	154	256	301	717	471	552	563	215	251
1,4-	(2,3,5,6)	-2,5-	154	248	301	689	421	515	535	173	214
1,3-	(2)	2,6-	184	182	280	663	298	537	479	116	257
1,2-	(4,5)	3,4-	328	235	327	1217	385	558	889	150	231
1,3-	(5)	3,5-	359	227	318	1241	366	530	882	139	212
1,2,3-	(4,6)	2,3,4-	135	260	297	718	469	498	583	209	201
1,2,4-	(6)	2,3,5-	134	244	283	750	432	464	616	188	181
1,2,4-	(3)	2,3,6-	161	178	270	715	290	486	554	112	216
1,2,4-	(5)	2,4,5-	163	240	288	800	427	480	637	187	192
1,3,5-	(2,4,6)	2,4,6-	196	183	270	756	292	490	560	109	220
1,2,3-	(5)	3,4,5-	359	226	315	1293	345	480	934	119	165
1,2,3,4-	(5,6)	2,3,4,5-	148	245	291	822	432	425	674	187	134
1,2,3,5-	(4,6)	2,3,4,6-	194	176	273	768	285	450	574	109	177
1,2,4,5-	(3,6)	2,3,5,6-	186	174	268	760	278	432	574	104	164
1,2,3,4,5-	(6)	2,3,4,5,6-	195	174	283	822	280	402	627	106	119

* For the retention indices of chlorobenzenes, see ref. 2.
** For the retention indices of chlorophenols, see ref. 3.
*** For the retention indices of chloroanisoles, see ref. 4.
§ For the retention indices of chlorophenyl acetates, see ref. 5.
§§ $\Delta I = I_{(n-1)Cl}$ (isomer formed) $- I_{nCl}$ (benzene).

TABLE II

SUMMARY OF THE INCREMENTAL EFFECTS PRESENTED IN TABLE I

Isomer formed	*Column*								
	Low-polarity			*Polar*			*Polar – low-polarity*		
	ΔI_{OH}	ΔI_{OCH_3}	ΔI_{OCOCH_3}	ΔI_{OH}	ΔI_{OCH_3}	ΔI_{OCOCH_3}	ΔI_{OH}	ΔI_{OCH_3}	ΔI_{OCOCH_3}
o-	130–163	240–260	283–333	596–822	420–471	425–559	445–674	161–215	134–251
o,o'-	161–196	174–183	268–283	663–822	278–298	402–537	479–627	104–116	119–257
m-, p-	317–359	226–254	315–363	1101–1293	345–385	480–600	784–934	113–150	165–237

TABLE III

DIFFERENCES IN THE RETENTION INCREMENTS BETWEEN CHLORINATED PHENOLS, ANISOLES AND PHENYL ACETATES, OBTAINED ON LOW-POLARITY AND POLAR CAPILLARY COLUMNS AT 160°C

Isomer	*Column*					
	Low-polarity			*Polar*		
	$\Delta I_{OH} - \Delta I_{OCH_3}$*	$\Delta I_{OH} - \Delta I_{OCOCH_3}$*	$\Delta I_{OCOCH_3} - \Delta I_{OCH_3}$*	$\Delta I_{OH} - \Delta I_{OCH_3}$*	$\Delta I_{OH} - \Delta I_{OCOCH_3}$*	$\Delta I_{OCOCH_3} - \Delta I_{OCH_3}$*
Parent-	49	− 79	128	627	367	260
2-	−108	−182	74	176	37	139
3-	72	− 41	113	743	523	220
4-	63	− 46	109	715	501	214
2,3-	−129	−170	41	183	108	75
2,4-	−102	−147	45	246	165	81
2,5-	− 94	−147	53	268	174	94
2,6-	2	− 96	98	365	126	239
3,4-	93	1	92	832	659	173
3,5-	132	41	91	875	711	164
2,3,4-	−125	−162	37	249	220	29
2,3,5-	−110	−149	39	318	286	32
2,3,6-	− 17	−109	92	425	229	196
2,4,5-	− 77	−125	48	373	320	53
2,4,6-	13	− 74	87	464	266	198
3,4,5-	133	44	89	948	813	135
2,3,4,5-	− 97	−143	46	390	397	−7
2,3,4,6-	18	− 79	97	483	318	165
2,3,5,6-	12	− 82	94	482	328	154
2,3,4,5,6-	21	− 88	109	542	420	122

* For the retention increments of the components, see Tables I and IV.

2,3,5,6-tetra- and pentachloro isomers, show the smallest enhancements. Owing to the competing chlorine atoms, the steric effect in anisoles is prevented and the *ortho*-effect in *o,o'*-chlorophenols is not as pronounced as with the *o*-isomers, the latter always giving smaller retention enhancements (Tables I and II).

As a summary of the data presented in Table III, it can be seen that on low-polarity columns the differences between the increments for phenols and anisoles varied from −129 (2,3-isomer) to 133 i.u. (3,4,5-isomer) for phenols and phenyl acetates from −182 (2-isomer) to 44 i.u. (3,4,5-isomer) and for phenyl acetates and anisoles from 37 (2,3,4-isomer) to 113 i.u. (3-isomer).

With the polar columns the retention increments are markedly increased, particularly in the case of chlorophenols (Tables I–III and Figs. 2 and 3). The effects indicated above are generally observed, the variation shown being more pronounced owing to the polar components on more polar stationary phases.

Chlorophenols always show the highest increments, the differences between chlorophenyl acetates varying from 37 (2-isomer) up to 813 i.u. (3,4,5-isomer) (Table III). The differences between phenols and anisoles are from −7 to 239 i.u. higher, being in the range 176 (2-isomer) –948 i.u. (3,4,5-isomer). In contrast to the low-polarity columns, 2,3,4,5-tetrachloroanisole shows a 7 i.u. higher enhancement than the corresponding phenyl acetate. This phenomenon supports the assumption of a steric effect in *o*-chloroanisoles[4], this effect not occurring or having a negligible influence in *o,o'*-chloroanisoles and *o*- and *o,o'*-chlorophenyl acetates. This can also be seen from the relatively smaller differences between the increments for the 2,3-, 2,4- and 2,5-di- and 2,3,4-, 2,3,5- and 2,4,5-trichloro isomers in these two series, compared with the other isomers, the differences being much more pronounced on the polar columns[4], as expected (Table III and Fig. 3).

The enhanced retention increments of the various isomers are shown in Table I and Fig. 3, falling into two general groups with chlorophenols (*o*-isomers and *m*- and *p*-isomers) and chloroanisoles (*o*-isomers and the other isomers) (Table II). Chlorophenyl acetates, however, show variable values.

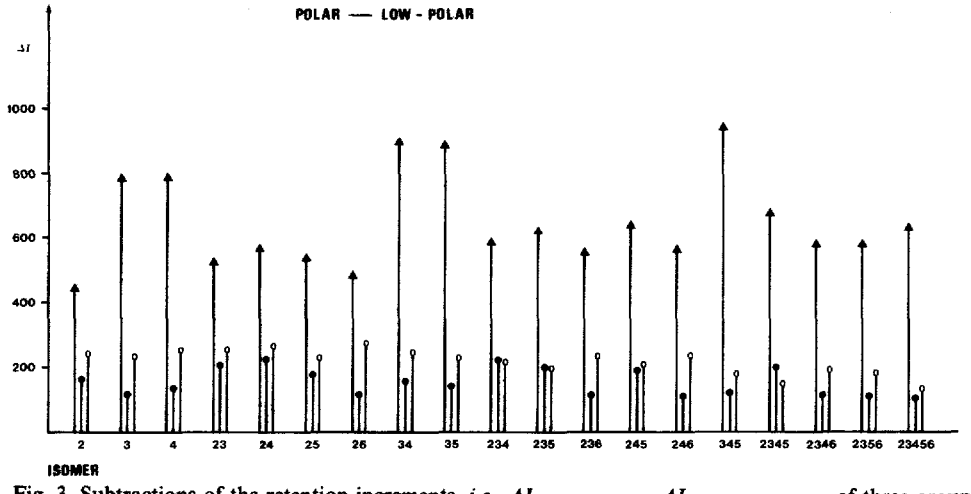

Fig. 3. Subtractions of the retention increments, *i.e.*, $\Delta I_{\text{polar columns}} - \Delta I_{\text{low-polarity columns}}$, of three groups of chlorinated aromatics (Table I). (▲) Phenol; (●) anisole; (○) phenyl acetate. The numbers indicate the positions of chlorination.

TABLE IV

INCREMENTAL EFFECTS DUE TO SUBSTITUTION OF ONE CHLORINE ATOM IN CHLOROBENZENES WITH HYDROXY, METHOXY AND ACETOXY GROUPS, OBTAINED ON LOW-POLARITY AND POLAR CAPILLARY COLUMNS AT 160°C

Chlorobenzene isomer with (in parentheses) positions of substituted group		*Chloro isomer formed*	*Column*								
			Low-polarity			*Polar*			*Difference: polar − low-polarity*		
			*Phenol***: ΔI_{OH}§§	*Anisole****: ΔI_{OCH_3}§§	*Phenyl acetate*§: ΔI_{OCOCH_3}§§	*Phenol***: ΔI_{OH}§§	*Anisole****: ΔI_{OCH_3}§§	*Phenyl acetate*§: ΔI_{OCOCH_3}§§	ΔI_{OH}§§	ΔI_{OCH_3}§§	ΔI_{OCOCH_3}§§
1-	(1)	Parent-	89	40	168	730	103	363	641	63	195
1,2-	(1,2)	2-	−59	49	123	352	176	315	411	127	192
1,3-	(1,3)	3-	141	69	182	937	194	414	796	125	232
1,4-	(1,4)	4-	141	78	187	900	185	399	759	107	212
1,2,3-	(1,3)	2,3-	−48	81	122	425	242	317	473	161	195
1,2,4-	(1)	2,4-	−23	79	124	498	252	333	521	173	209
1,2,4-	(2)	2,5-	−23	71	124	507	239	333	530	168	209
1,2,3-	(2)	2,6-	−28	−30	68	362	−3	236	390	27	168
1,2,4-	(4)	3,4-	185	92	184	1078	246	419	893	154	235
1,3,5-	(all)	3,5-	225	93	184	1130	255	419	905	162	235
1,2,3,4-	(1,4)	2,3,4-	−25	100	137	545	296	325	570	196	188
1,2,3,5-	(1,3)	2,3,5-	−17	93	132	617	299	331	634	206	199
1,2,3,4-	(2,3)	2,3,6-	−34	−17	75	460	35	231	494	52	156
1,2,4,5-	(all)	2,4,5-	12	89	137	660	287	340	648	198	203
1,2,3,5-	(2)	2,4,6-	2	−11	76	515	51	249	513	62	173
1,2,3,5-	(5)	3,4,5-	243	110	199	1242	294	429	999	184	230
1,2,3,4,5-	(1,5)	2,3,4,5-	11	108	154	731	341	334	720	233	180
1,2,3,4,5-	(2,4)	2,3,4,6-	13	−5	92	555	72	237	542	77	145
1,2,3,4,5-	(3)	2,3,5,6-	5	−7	87	554	72	226	549	79	139
1,2,3,4,5,6-	(all)	2,3,4,5,6-	25	4	113	643	101	223	618	97	110

* For the retention indices of chlorobenzenes, see ref. 2.
** For the retention indices of chlorophenols, see ref. 3.
*** For the retention indices of chloroanisoles, see ref. 4.
§ For the retention indices of chlorophenyl acetates, see ref. 5.
§§ $\Delta I = I_{(n-1)Cl}$ (isomer formed) − I_{nCl} (benzene).

TABLE V

SUMMARY OF THE INCREMENTAL EFFECTS PRESENTED IN TABLE IV

Isomer formed	*Column*								
	Low-polarity			*Polar*			*Polar – low-polarity*		
	ΔI_{OH}	ΔI_{OCH_3}	ΔI_{OCOCH_3}	ΔI_{OH}	ΔI_{OCH_3}	ΔI_{OCOCH_3}	ΔI_{OH}	ΔI_{OCH_3}	ΔI_{OCOCH_3}
Parent-	89	40	168	730	103	363	641	63	195
o-	−59–12	49–108	122–154	352–731	176–341	315–340	411–720	127–233	180–209
o,o'-	−34–25	−30–4	68–113	362–643	−3–101	223–249	390–618	27–97	110–173
m-, p-	141–243	69–110	182–199	900–1242	185–294	399–429	759–999	107–184	212–235

Substitution of one chlorine atom in chlorobenzenes with an additional group

Table IV and Figs. 4 and 5 show the incremental effects due to the substitution of one chlorine atom in chlorobenzenes with hydroxy, methoxy or acetoxy groups, obtained on low-polarity and polar capillary columns. A summary of the values is presented in Table V.

The effects observed are almost the same as presented above, the enhancements being lower as a consequence of the substitution, *i.e.*, $\Delta I = I_{(n-1)Cl}$ (isomer formed) $- I_{nCl}$ (benzene).

Anisole, phenol and phenyl acetate on low-polarity columns show enhancements of 40, 89 and 168 i.u. relative to chlorobenzene, the values increasing on polar columns to 103, 730 and 363 i.u., respectively.

The replacement of an *o*-chlorine atom with a hydroxy group generally gives rise to a reduction in the retention on the low-polarity columns, as shown in Table IV and Fig. 4. The increments for *o*-chlorophenols lie in the range −59–12 (352–731) i.u., for the *o,o'*-isomers −34–25 (362–643) i.u. and for the *m*- and *p*-isomers 141–243 (900–1242) i.u., the values on polar columns, given in parentheses, being markedly higher (Tables IV and V).

With methoxy substitution the smallest retention enhancements are shown by the *o,o'*-isomers, the increments on low-polarity and polar columns lying in the ranges −30–4 and −3–101 i.u., respectively. With the other isomers enhanced retentions of 49–110 i.u. on low-polarity and 176–341 i.u. on polar columns are observed.

Increased retention always occurred on acetoxy substitution and it is apparent that the increments fall into three groups, particularly on polar columns, *viz.*, 122–

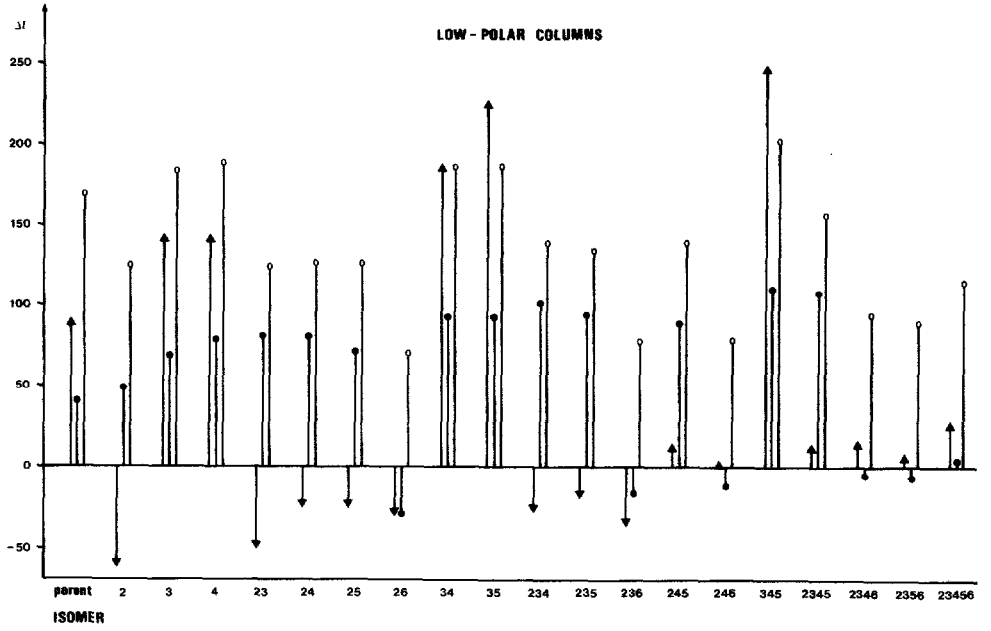

Fig. 4. Incremental effects due to the replacement of one chlorine atom in chlorobenzenes with hydroxy, methoxy and acetoxy groups, obtained on low-polarity capillary columns at 160°C (Table IV). (▲) Phenol; (●) anisole; (○) phenyl acetate. The numbers indicate the positions of chlorination.

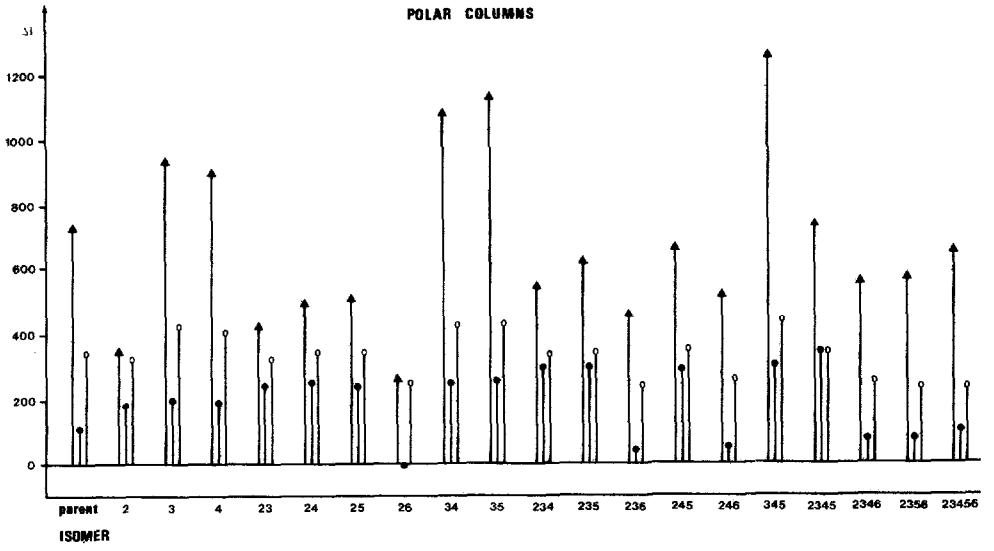

Fig. 5. Effects as in Fig. 4, obtained on polar capillary columns at 160°C (Table IV).

154 (315–340) i.u. for the *o*-isomers, 68–113 (223–249) i.u. for the *o,o'*-isomers and 182–199 (399–429) i.u. for the *m*- and *p*-isomers on low-polarity and (in parentheses) polar columns, as shown in Table V.

Subtraction of the non-polar contributions given in Table IV and particularly the summary of the values presented in Table V show the relatively lower values for *o,o'*-chloroanisoles and -chlorophenyl acetates and also for some *o,o'*-chlorophenols compared with the other isomers, or with the data presented in Tables I and II. This is due to the facts that (i) vicinally substituted chlorobenzenes have higher retention times than the other homologues, particularly on the polar column[2], and (ii) an additional group substituted into vicinal 1,2,3-tri-, 1,2,3,4-tetra-, 1,2,3,5-tetra-, penta- and hexachlorobenzenes prevents the interaction of the chlorine atoms, giving rise to smaller retention increments than the substitution producing the other isomers.

ACKNOWLEDGEMENTS

Financial support for this work from the Kalle and Dagmar Välimaa Foundation (Cultural Foundation of Finland), the Medica Corporation Research Foundation, the Alfred Kordelin Foundation and the Academy of Finland is gratefully acknowledged.

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